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Short Communication

Calculation of the Quasiparticle Energies of Electrons and the Exciton Spectrum in the Region of the Fundamental Absorption Edge in a Perovskite Crystal $KMgF_3$

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In this paper, the electronic and optical properties of the most effective $KMgF_3$ material are studied, thin films of which are used as a solid-state vacuum ultraviolet phosphor. At the first stage, we obtained wave functions in the framework of the electron density functional GGA. In the second stage, we calculated the improved value of the band gap using the Green's function (approximation GW), constructed on the wave functions calculated in the GGA approximation. We found that the band gap evaluated within the GGA method is about 4.73 eV less than the experimental value. At the third stage the absorption spectrum of the material was calculated on the basis of data obtained in the previous steps. For the first time, quasiparticle electron energies and the absorption spectrum on their basis are found.

Keywords: Fluoroperovskite, GGA approach, Quasiparticles, Exciton energy, Absorption spectrum.

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1. INTRODUCTION

Fluoro-perovskite crystal $KMgF_3$ exhibits attractive properties such as high thermal stability, high optical transparency and low melting point. $KMgF_3$ has been extensively studied as promising material for radiation dosimetry when it was doped with rare earth ions [1]. Due to its short emission spectrum $KMgF_3$ has been identified as possible material for scintillators [2]. Doped $KMgF_3$ crystals are expected to be photocatalysts under visible light [3]. Recently, the study of vacuum-ultraviolet fluorescence from $KMgF_3$ and $BaLiF_3$ crystals has been reported. These perovskite fluoride materials can be useful for developing light emitting diodes in the vacuum ultraviolet region [4]. The reflectivity of $KMgF_3$ has been investigated over a wide energy range as well as XPS spectra. The dominant excitonic structure has been predicted in 10-12 eV region [5].

Theoretical investigations of $KMgF_3$ have also been performed. Structural, electronic and optical properties of $KMgF_3$ have been calculated within local density approximation (LDA) using FP-LAPW method [6]. Dependence of the electronic structure, elastic properties and related parameters, mechanical stability, dielectric functions on hydrostatic pressure was presented for $KMgF_3$ crystal. The calculations were performed using general gradient approximation functionals (GGA-PBE, GGA-PBE-sol) by means of FP-(L)APW+lo framework [7]. Structural, electronic, elastic and dielectric properties of $KMgF_3$ have been studied using GGA as exchange-corelation functional within PAW method. The phonon dispersions in $KMgF_3$ crystal have been calculated [8]. Earlier, the electronic structure and density of states of $KMgF_3$ were performed within the local density approximation (LDA) as implemented in the VASP package and with the ultrasoft pseudopotentials provided with the VASP. The calculated indirect band gap is 7.27 eV which is lower then the experimental value of 10.8 eV [9]. Recently it was successfully demonstrated a VUV emitting lamp by employing a $KMgF_3$ thin film as a phosphor [10]. The thin film was grown in vacuum atmosphere by applying pulsed laser deposition. The fluorescence performance of the thin film was nearly equal to that of a single crystal. The quasiparticle electron energy bands and excitonic properties of the $KMgF_3$ until now have not yet been studied. So, the following paragraphs of this work are devoted to solving this problem.

2. CALCULATION

At the first stage the electron energy spectrum $\varepsilon_{n\mathbf{k}}$ and eigenfunction $\varphi_{n\mathbf{k}}$ are searched in the local electron density approximation (LDA, GGA) from the Schrödinger equation (1) [11, 12]:

$$(-\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}))\varphi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}}\varphi_{n\mathbf{k}}(\mathbf{r}), \quad (1)$$

where $-\nabla^2$ is the kinetic energy operator, V_{ext} denotes the ionic pseudopotential, V_H and V_{xc} are the Hartree and exchange-correlation potential, respectively. Here n and $\mathbf{k}$ denote a band index and a wave vector in the Brillouin zone, respectively. The quasiparticle energies $E_{n\mathbf{k}}$ and eigenfunctions $\psi_{n\mathbf{k}}$ can be obtained from the quasiparticle equation (2) [13, 14]:

$$(-\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}))\psi_{n\mathbf{k}}(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}', E_{n\mathbf{k}})\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}' = E_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r}), \quad (2)$$

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where Σ is the non-local self-energy operator. The wave functions can be expanded as follows:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{n'} a_{nn'} \varphi_{n'\mathbf{k}}(\mathbf{r}). \quad (3)$$

From Eqs. (1) – (3) the perturbative quasiparticle Hamiltonian is obtained in the form

$$H_{nn'}(E) = \varepsilon_{n\mathbf{k}} \delta_{nn'} + < \varphi_{n\mathbf{k}} \mid \Sigma(E) - V_{xc} \mid \varphi_{n'\mathbf{k}} >, \quad (4)$$

where the second term in Eq. (4) represents a perturbation.

3. RESULTS AND DISCUSSION

The results obtained on the basis of equation (1) are shown in Figs. 1, 2. As can be seen from Fig. 1, the upper part of the valence band is built of p-electrons of fluorine. Deeper states in the valence band are populated with p-electrons of potassium and s- electrons of fluorine, respectively.

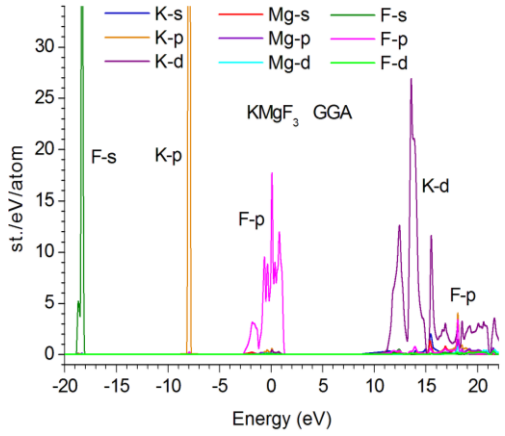

Fig. 1 – Partial densities of the electronic states in the crystal $KMgF_3$ obtained within the GGA approach

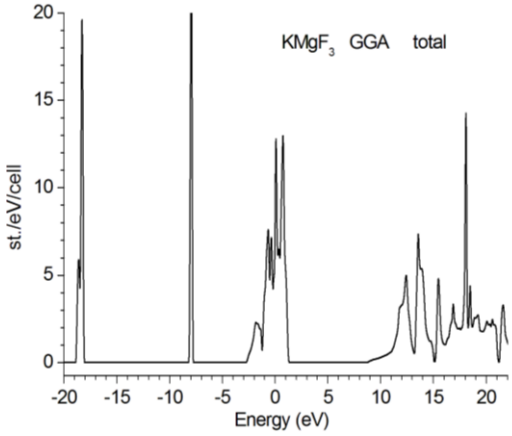

Fig. 2 – Total density of the electronic states in the crystal $KMgF_3$ obtained within the GGA approach

In Fig. 3 is presented the total density of electronic states, calculated in the quasiparticle GW approach using equation (3). It is obvious that the densities of the electronic states, depicted in Fig. 2, 3, differ in quantitative and qualitative characteristics. So far, in the ABINIT program, the energy eigenvalues within the GW formalism can not be evaluated at an arbitrary point in the Brillouin zone. Therefore, it is not possible to calculate the density of electronic states within the GW approximation. Nevertheless, we calculated the full density of states, depicted in Fig. 3, by means of broadening of the energy levels obtained in the GW approach [15]. The difference between the energies corresponding to the top of the valence band ε_v, and the bottom of the conduction band ε_c, is determined on the basis of the data found within the GW (Fig. 3) and GGA (Fig. 2) approaches, by the following equations: $\varepsilon_v(GW) - \varepsilon_v(GGA) \approx -4.0$ eV, $\varepsilon_c(GW) - \varepsilon_c(GGA) \approx 1.7$ eV.

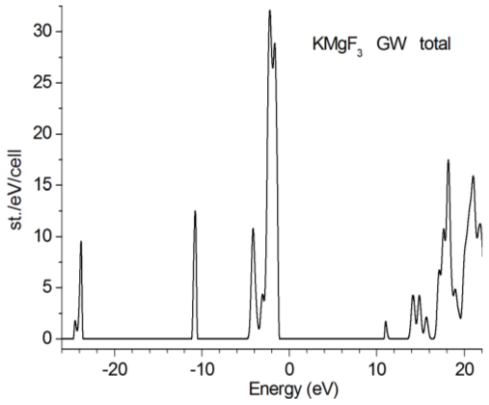

Fig. 3 – Total density of the electronic states in the crystal $KMgF_3$ obtained within the GW approach

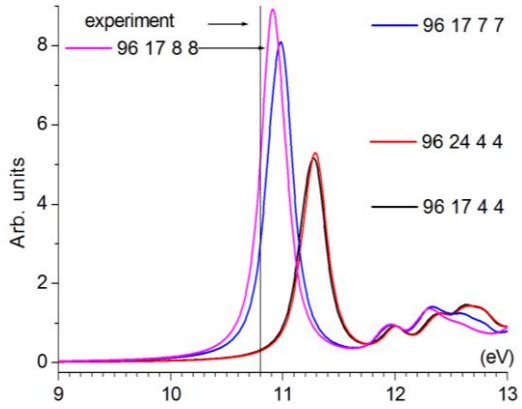

Fig. 4 – The imaginary part of the dielectric constant evaluated from the Bethe-Salpeter equation

The dielectric constant $\varepsilon_2(E)$ shown in Fig. 4 has been evaluated from the Bethe-Salpeter equation, as implemented in the ABINIT code [16]. The label {96 17 4 4} means that the self-consistent calculation is made with 96 bands, and a cutoff energy defining the plane waves basis equals 17 Ha (34 Ry). The transition space includes 4 valence and 4 conduction band states.

As can be seen from the comparison of black and red curves in Fig. 4, they are almost identical, although they are obtained with values of the cutoff energies of 34 and 48 Ry, respectively. We also see that the energy of the first excitonic peak of these curves is much higher than the experimental energy of fundamental absorption.

Now consider the curve, evaluated with electron-hole transition space composed of 7 valence and 7 conduction band states. Consequently, the expansion of the space of the electron-hole transitions from {4, 4} to {7, 7} led to the energy of the first excitonic peak, which is quite close to the experimental value. Taking into account the space of states used to construct the transition space {8, 8} reveals a better comparison of the energy of the first exciton maximum with the experiment (see Fig. 4).

4. CONCLUSIONS

The quasiparticle energies of the material $KMgF_3$, which is intensively used in science and industry, have been calculated here for the first time. For the first time, the the absorption spectrum in the region of the fundamental absorption edge has been evaluated. The theoretical results show a good comparison with the experimental data.

Расчет квазичастичных энергий электронов и спектра экситонов в области края фундаментального поглощения в кристалле перовскита $KMgF_3$

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В настоящей работе изучаются электронные и оптические свойства наиболее эффективного в настоящее время материала $KMgF_3$, тонкие пленки которого используются в качестве твердотельного вакуумного ультрафиолетового люминофора. На первом этапе мы получили волновые функции в рамках функционала плотности электронов GGA. На втором этапе мы рассчитали улучшенное значение ширины запрещенной зоны с использованием функции Грина (приближение GW), построенной на волновых функциях, вычисленных в приближении GGA. Мы обнаружили, что найденная в методе GGA ширина запрещенной зоны на 4,73 эВ меньше экспериментального значения. Третий этап был посвящен вычислению спектра поглощения материала на основе данных, полученных на предыдущих этапах. Впервые найдены квазичастичные энергии электронов и спектр поглощения на их основе.

Ключевые слова: Фтороперовскит, Метод GGA, Квазичастицы, Энергия экситона, Спектр поглощения.

Розрахунок квазічастинкових енергій електронів і спектра екситонів в області краю фундаментального поглинання в кристалі перовскиту $KMgF_3$

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У даній праці вивчаються електронні та оптичні властивості найбільш ефективного в даний час матеріалу KMgF3, тонкі плівки якого використовуються в якості твердотільного вакуумного ультрафіолетового люмінофора. На першому етапі ми отримали хвильові функції в рамках функціонала щільності електронів GGA. На другому етапі ми розрахували точніше значення ширини забороненої зони з використанням функції Гріна (наближення GW), побудованої на хвильових функціях, обчислених в наближенні GGA. Ми виявили, що знайдена в методі GGA ширина забороненої зони на 4,73 еВ менша за експериментальне значення. Третій етап був присвячений обчисленню спектра поглинання матеріалу на основі даних, отриманих на попередніх етапах. Вперше знайдені квазічастинкові енергії електронів і спектр поглинання на їх основі.

Ключові слова: Флуороперовскит, Метод GGA, Квазічастинки, Енергія екситона, Спектр поглинання.

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