Study on the Electronic Structures and Absorption Bands of BaMgF$_4$ Crystal with F Color Centre*

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Abstract：The electronic structures of BaMgF$_4$ crystal containing F color center are studied within the frame work of the fully relativistic self-consistent Direc-Slater theory, using a numerically discrete variational (DV-Xα) method. It is concluded from the calculated results that the energy levels of F color center locate in the forbidden band. The optical transition energy from the ground state to excited state for F color center is about 5.12eV, which corresponds to the 242nm absorption band. These calculated results are well explaining the origin of the absorption bands.

Key words: Electronic Structures; F TypeColor Center; DV-X α (Numerically Discrete Variational Method); BaMgF$_4$ Crystal

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1. Introduction

BaMgF$_4$ crystal is known as the wide-gap fluorides with the ultrafast (~1ns) core

valence emission in the 190-220 nm region [1]. A fast Ce^{3+}-associated photo- and X-ray luminescence was found in Ce: $BaMgF_4$ [2,3]. This material is a very suitable host for transition metal and rare earth ion impurities and has promising properties for solid state laser applications. The crystal is of interest for the development of radiation detectors. Scintillation availability is substantially determined by the transparency losses due to the radiation coloration. From this point of view, the problem of the radiation resistance of the crystals is relevant. In the previous articles, the radiating sensitivity of $BaMgF_4$ crystals from the point of view of the structural defect presence had been mentioned, and the transition energy was calculated by a semi-empirical Mollwo-Ivey equation [4]. The absorption band triplet with maxima at 236, 257 and 274 nm should be corresponding to the F-centre in different positions due to a low symmetry of this crystal structure [5]. Due to lack of direct experimental evidence or theoretical calculations, the origins of 236, 257 and 274 nm absorption bands are not clearly up to now.

In order to elucidate the absorption in the crystal produced by F-center, in the present paper, the discrete variational (DV-Xα) method has been used to study the electronic structures in the crystal. This technique has been successfully applied to confirm the absorption bands of the color center [6-9]. However, the 2p state (excited state of the F color center) has not been taken into calculation. So the optical transition from the ground state to excited state for F-type color center always treats as the transition from the ground state to conduction band. These calculated results are physical irrationality and should be checked again. In this paper, the 2p state is firstly taken into calculation for color centers to ensure the results reasonably.

2. Calculation method and the cluster models

2.1 The cluster models

The $BaMgF_4$ crystal has the same structure with the orthorhombic $BaZnF_4$. Its space group is C_{2v}^{12} (No.36) (Cmc21) with four molecules per unit cell. The unit cell is shown in Fig.1. The structure includes octahedrons. Each octahedron is consists of

a central Mg and six nearest-neighbor F-ligand ions, which are linked via cis vertices to zigzag chains parallel to the c axis. Along the axis, these chains are connected via trans vertices to slabs parallel to the ac plane. The Ba^{2+} ions occupy the cavities between these slabs; they have nine fluorine neighbors. The coordination polyhedron of Ba derives from a trigonal prism by capping one face with one and a second face with two fluorine ligands. The metal-fluorine distances range from 2.60-3.00 Å (Ba-F) and from 1.93-2.07 Å (Mg-F). The shortest F-F distance is 2.58 Å.

In this work, we chose the model from F. Gingl's work [10]. The parameters are listed as in the Table 1:

Table 1. Atomic coordinates parameters (Å) for $BaMgF_4$

atom	x/Å	y/Å	z/Å
Ba	0.00000	0.32729	0.34622
Mg	0.00000	0.06085	0.31110
F1	0.00000	0.00000	0.00000
F2	0.00000	0.14223	0.57700
F3	0.00000	0.17181	0.11340
F4	0.00000	0.55419	0.30280

It is important to choose an appropriate cluster to calculate the crystal electronic structures using the cluster-embedding calculation method. As showing in Fig.1, we choose the F atom in the middle of the two Mg-F octahedrons as the center of the cluster. The structure of the selected cluster consisting of 6 Ba, 6 Mg and 33 F centered at F^- having the chemical formula of $(Ba_6Mg_6F_{33})^{9-}$. The "embedding cluster scheme" describes the boundary condition for the cluster [11]. The potentials of the crystal ions around the cluster are simulated by Madelung potentials. Pseudo-potentials are used for the cluster ions to avoid false charge transfer from the clusters to the external 'host' [12].
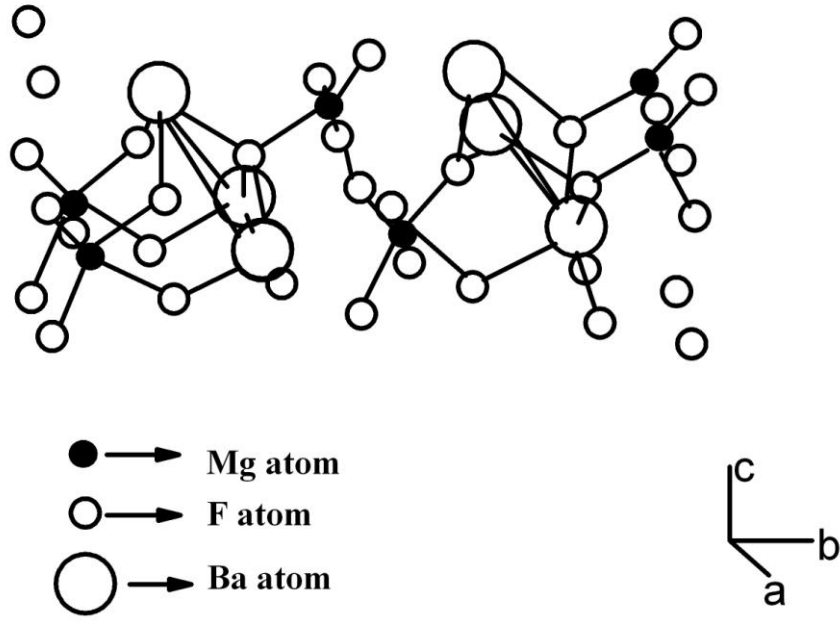
Fig.1 The structure of BaMgF$_4$ crystal, projected approximately along the a axis.

The original basis sets are composed of free ionic and atomic orbits, and these basis sets are optimized in iterative process according to the occupation of molecule orbits. The simulation parameters are listed in Table 2.

2.2 Calculation method

The molecular-cluster model with the framework of the fully relativistic self-consistent Direc-Slater theory, using a numerically discrete variational (DV-Xα) method, is adopted to study the electronic structures for BaMgF$_4$ crystal. The method has a high calculation precision with a relatively less workload and fits the calculations for big molecules.

In embedding cluster scheme method, one suitable ionic cluster is chosen. The eigen-function can be obtained by solving the Kohn-Sham equations:

$$h_{ks}\varphi_i(r) = \left[-\frac{\nabla^2}{2} - \sum_q \frac{Z_q}{|r-R_q|} + \int \frac{\rho(r)}{|r-r'|}dr' + Vxc \right] \times \varphi_i(r) = \varepsilon_i\varphi_i(r)$$

(1)

Where the first term is the kinetic energy, the second term is the attraction coulomb potential between nuclei in all molecules and electrons and the third part is coulomb

potential of electrons. V_{xc} is the exchange-correlation potential and $\rho(r)$ is the density of charge. The state intensity being given by

$$\rho(r)=\sum_{i}n_{i}\left|\varphi_{i}(r)\right|^{2},$$ (2)

Here $\varphi_{i}(r)$ is the single electron wave function of the atom or molecule cluster and n_{i} is the occupied number. The original basis sets and the funnel potential well chose for the calculations are listed in Table 2. The formula of the funnel potential well is

$$V=\begin{cases}V_{0}, & r\leq R_{1}\\ V_{0}\dfrac{2(R_{2}-r)^{2}\times(r-(3R_{1}-R_{2}/2))}{(R_{2}-R_{1})^{3}}, & R_{1}<r<R_{2}\\ 0, & r\geq R_{2}\end{cases}$$ (3)

Where V_{0} denotes the depth of the atom potential well, R_{1} and R_{2} show the bottom radius of atoms and the cutoff radius, respectively. These parameters will be used in the calculation of atomic orbits. The funnel potential makes atomic wave functions dispersion smaller, and it also makes calculation convergence more easily.

Table2. The initial basis sets and the FPWPs

Ions	Frozen core	Orbits for basis functions	FPWP (arb. units)		
			V_0	R_1	R_2
Ba^{++}	1s—5s	5p,6s	-3.55	2.0	2.58
Mg^{++}	1s—2s	2p,3s	-2.492	1.5	2.0
F^-	1s	2s,2p,3s	-3.55	2.5	3.0
H		1s,2s,2p	-3.5	2.15	4.5

In the present study, the electronic initial wave function containing F centre is substituted approximately by the wave functions of the hydrogen atom [13]. In this

paper, the F center is a fluorine ion vacancy V_F^+ trapping one electron. In the calculation of the electronic structures of F centers, a hydrogen atom with the nuclear frozen substitutes the F center on the fluorine vacancy in the center of the crystal.

For considering the relaxation effect produced by the electronic transition in the crystal, the transition state method [14] is used to calculate the transition energy. Ionization energy E_{ion} is the negative value of the orbit energy that is achieved by taking out half an electron from its primary orbit

$$E_{ion} = E(n_i - 1) - E(n_i) \cong -\left. \frac{\partial E}{\partial n_i} \right|_{n_i - \frac{1}{2}} = -\varepsilon_i T . \tag{1}$$

Similarly, excitation is also achieved by talking out half an electron from the ith orbit while putting half an election into the jth orbit, thus the excitation energy can be expressed as the energy difference between orbits i and j,

$$E_{i \to j} = E(n_i - 1, n_j + 1) - E(n_i, n_j) = \varepsilon_j T - \varepsilon_i T . \tag{2}$$

3. Results and discussion

Total density of states (TDOS) and partial density of states (PDOS) for the perfect BaMgF$_4$ crystal are calculated, as shown in Fig.2. Compared the TDOS with PDOS, it can be seen that the top of the valence band is mainly composed by the Ba 5p states while the bottom of the conduction band is mainly composed by the Mg 3s states and the F 3s states. However, the valance band also contains the F 2p states in the deep band and the Mg 2p states locate far away from the valance band. So the Mg 2p states have no effect for the optical properties in the crystal. The calculated band gap is about 10.333eV, which is close to the intrinsic absorption edge value [15]. Also we can confirm that the BaMgF$_4$ crystal is absolutely an ionic bond-type insulator. So the physical property of the crystal is stable.
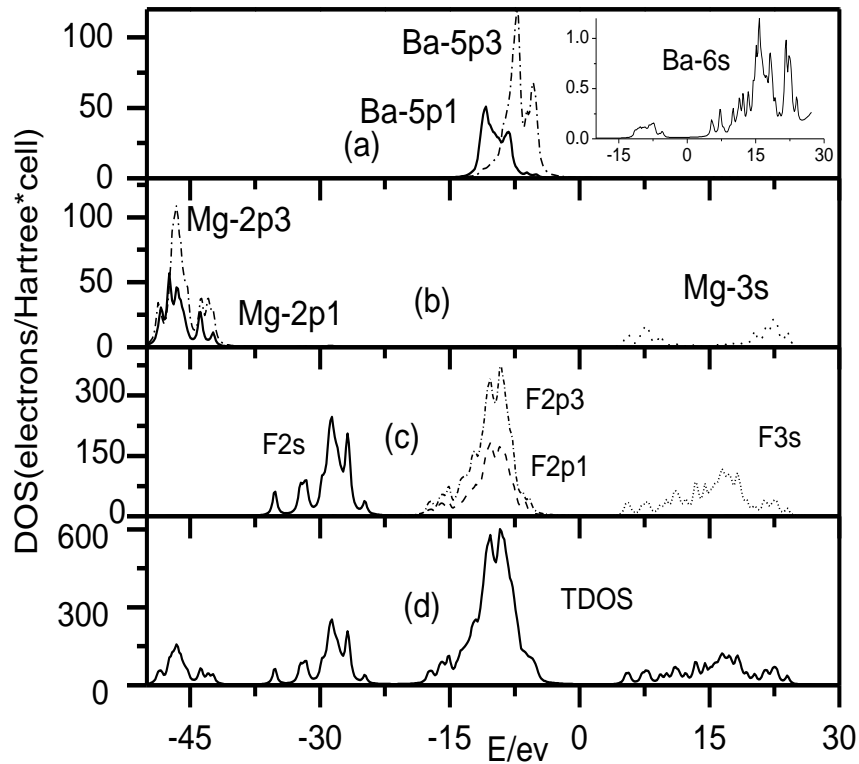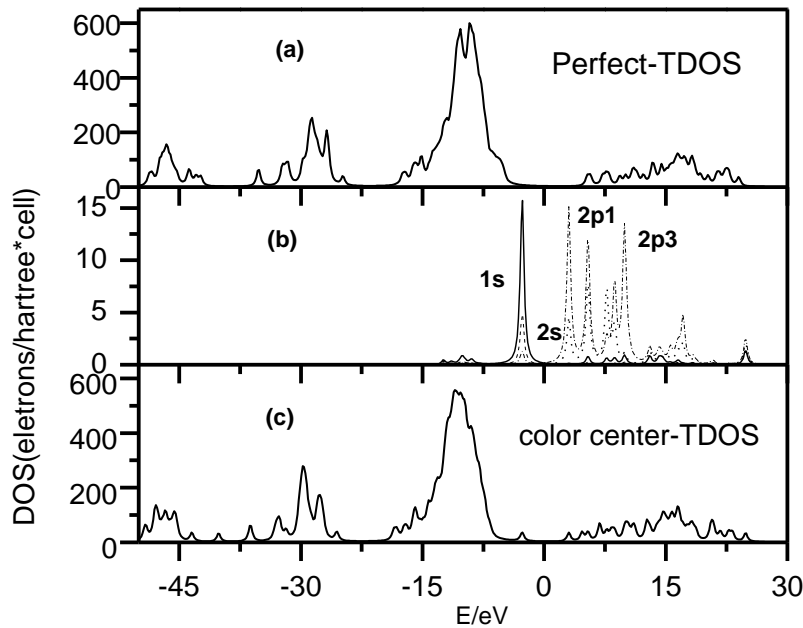
Fig.2 Total DOS and partial DOS for the perfect BaMgF$_4$ crystal.

For color centers, we dig out the fluorin ion in the center of the crystal model, and put an electronic at that position. Using the H-like wave function simulates the color center's wave function to achieve reasonable results.

In the total density of states for the perfect BaMgF$_4$ crystal, there is no state occurring in the forbidden band; however, two new energy levels appears in the forbidden band in the BaMgF$_4$ crystal containing a F color centre, as shown in Fig.3, so we think the new energy levels occurring in the forbidden band are directly related to the color centre.

By analyzing the results, we know that the peak nearly above the valance band and below the Fermi level is occupied by the 1s state of the color center, and the level

below the conductive band is occupied by the 2p state of the color center. As the transition rule, $\triangle L=\pm 1$, the transition form the 1s state to 2p state is allowed. The calculated transition energy between the two levels using the transition state method is 5.12eV, which corresponds to the 242nm absorption band, which is close to the experimental results (236-274 nm). For its low lattice symmetry of the crystal, the different symmetry positions of the F color center locating may cause some small different absorption bands. So we predicate that the 236-274 nm absorption bands may originate from F color centers in different positions. The position for the absorption band for the crystal is near to the rare earth intrinsic absorption edge.

Fig.3 Total DOS of the perfect $BaMgF_4$ crystal and the crystal with F corler center and partial DOS of the crystal containing the F color center.

4. Conclusion

The electronic structures of $BaMgF_4$ containing F-color center are studied by using H-like wave function. The results predict that the 236-274 nm absorption bands are originated from the F color centers in the $BaMgF_4$ crystal. It can be concluded that adding 2p state in the program should be trustworthy for the reasonable results.

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