Study of electronic structures and absorption bands of $BaMgF_4$ crystal with F colour centre*

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The electronic structures of $BaMgF_4$ crystals containing an F colour centre are studied within the framework 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 the F colour centre are located in the forbidden band. The optical transition energy from the ground state to the excited state for the F colour centre is about 5.12 eV, which corresponds to the 242-nm absorption band. These calculated results can explain the origin of the absorption bands.

Keywords: electronic structures, F-type colour centre, DV-Xα (numerically discrete variational method), $BaMgF_4$ crystal

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1. Introduction

$BaMgF_4$ crystal is known as the wide-gap fluorides with ultrafast (∼1 ns) core valence emission in the 190 nm–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 metals 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 previous articles, the radiating sensitivity of $BaMgF_4$ crystals from the point of view of the structural defect presence has 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 correspond to the F-centre in different positions due to the low symmetry of this crystal structure.[5] Due to a lack of direct experimental evidence or theoretical calculations, the origins of 236-, 257- and 274-nm absorption bands have not been clear up to now.

In order to elucidate the absorption in the crystal produced by the F-centre, in the present paper, the discrete variational (DV-Xα) method based on density functional theory (DFT) has been used to study the electronic structures in the crystal. So far, DFT is used in different methods to modify the crystal field.[6,7] DV-Xα has been successfully applied to confirm the absorption bands of the colour centre.[8−11] However, the 2p state (excited state of the F colour centre) has not been considered in calculations. So the optical transition from the ground state to the excited state for the F-type colour centre always treats the transition from the ground state to the conduction band. These calculated results are physical irrationality and should be checked again. In this paper, the 2p state is firstly incorporated into calculations for colour centres to ensure that the results are reasonable.

2. Calculation method and 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}

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(No. 36) ($Cmc21$) with four molecules per unit cell. The unit cell is shown in Fig. 1. The structure includes octahedrons. Each octahedron consists of a central Mg and six nearest-neighbour 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 neighbours. 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 Å to 3.00 Å (Ba–F) and from 1.93 Å to 2.07 Å (Mg–F). The shortest F–F distance is 2.58 Å (1 Å = 0.1 nm).

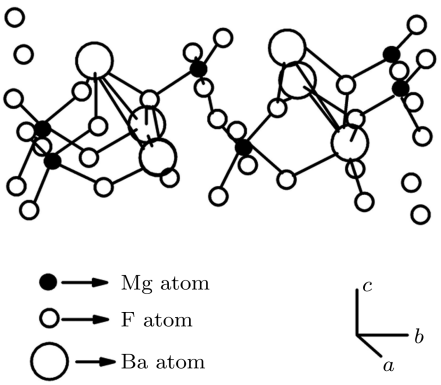


Fig. 1. The structure of the $BaMgF_4$ crystal, projected approximately along the a axis.

In this work, we chose the model from Ref. [12]. The parameters are listed in Table 1.

Table 1. Atomic coordinates (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 shown in Fig. 1, we chose the F atom in the middle of two Mg–F octahedrons as the centre of the cluster. The structure of the selected cluster consists of 6 Ba, 6 Mg and 33 F centred at F^-, having the chemical formula $(Ba_6Mg_6F_{33})^{9-}$. The "embedding cluster scheme" describes the boundary condition for the cluster.[13] 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'.[14]

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

Table 2. 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

2.2. Calculation method

The molecular–cluster model in 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 the $BaMgF_4$ crystal. The method has high calculation precision with a relatively small workload and fits the calculations for big molecules.

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

$$\begin{aligned} & h_{\mathrm{ks}}\varphi_i(r) \\ &= \left[-\frac{\nabla^2}{2} - \sum_q \frac{Z_q}{|r-R_q|} + \int \frac{\rho(r)}{|r-r'|}\,\mathrm{d}r' + V_{\mathrm{xc}}\right] \\ &\quad \times\varphi_i\,(r) \\ &= \varepsilon_i\varphi_i\,(r)\,, \end{aligned} \tag{1}$$

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

$$\rho\,(r) = \sum_i n_i\,|\varphi_i\,(r)|^2\,. \tag{2}$$

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 chosen for the calculations are listed in Table 2. The formula of the funnel potential well is

$$V = \begin{cases} V_0, & r \le R_1, \\ V_0 \dfrac{2(R_2 - r)^2 \times (r - (3R_1 - R_2/2))}{(R_2 - R_1)^3}, & R_1 < r < R_2, \\ 0, & r \ge R_2, \end{cases} \tag{3}$$

where V_0 denotes the depth of the atom potential well, and R_1 and R_2 are 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 disperse smaller, and it also makes calculation converge more easily.

In the present study, the electronic initial wave function containing an F centre is substituted approximately by the wave functions of the hydrogen atom.[15] In this paper, the F centre is a fluorine ion vacancy V_F^+ trapping one electron. In the calculation of the electronic structures of F centres, a hydrogen atom with the nuclear frozen substitutes for the F centre on the fluorine vacancy in the centre of the crystal.

For considering the relaxation effect produced by the electronic transition in the crystal, the transition state method[16] is used to calculate the transition energy. The ionization energy $E_{\rm ion}$ is the negative value of the orbit energy that is achieved by taking out half an electron from its primary orbit

$$\begin{aligned} E_{\rm ion} &= E(n_i - 1) - E(n_i) \\ &\cong -\frac{\partial E}{\partial n_i}\bigg|_{n_i - 1/2} \\ &= -\varepsilon_i T. \end{aligned} \tag{4}$$

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

$$E_{i\to j} = E(n_i - 1, n_j + 1) - E(n_i, n_j) = \varepsilon_j T - \varepsilon_i T. \tag{5}$$

3. Results and discussion

The total density of states (TDOS) and partial density of states (PDOS) for the perfect $BaMgF_4$ crystal are calculated, as shown in Fig. 2. By comparing the TDOS with the PDOS, it can be seen that the top of the valence band is mainly composed of the Ba 5p states while the bottom of the conduction band is mainly composed of the Mg 3s states and the F 3s states. However, the valence band also contains the F 2p states in the deep band and the Mg 2p states located far away from the valence band. So the Mg 2p states have no effect on the optical properties of the crystal. The calculated band gap is about 10.333 eV, which is close to the intrinsic absorption edge value.[17] 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.

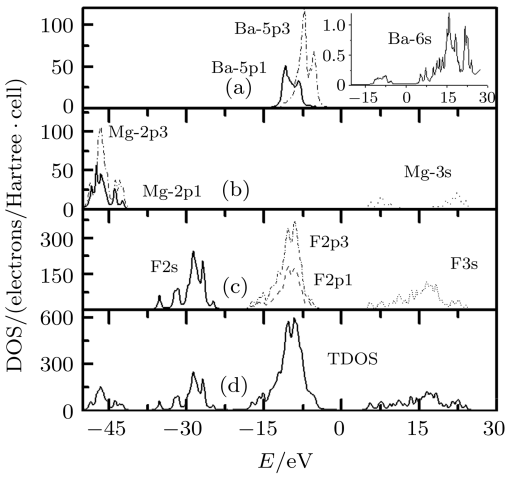


Fig. 2. Total DOS and partial DOS for the perfect $BaMgF_4$ crystal.

For colour centres, we dig out the fluorine ion in the centre of the crystal model, and put an electron at that position. We use the H-like wave function to simulate the colour centre'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 appear in the forbidden band in the $BaMgF_4$ crystal containing an F colour centre, as shown in Fig. 3, so we think the new energy levels occurring in the forbidden band are directly related to the colour centre.

By analysing the results, we find that the peak nearly above the valance band and below the Fermi level is occupied by the 1s state of the colour centre, and the level below the conductive band is occupied by the 2p state of the colour centre. As indicated by the transition rule, $L = \Delta \pm 1$, the transition form of the 1s state to 2p state is allowed. The

calculated transition energy between the two levels using the transition state method is 5.12 eV, which corresponds to the 242-nm absorption band, and is close to the experimental results (236 nm–274 nm).

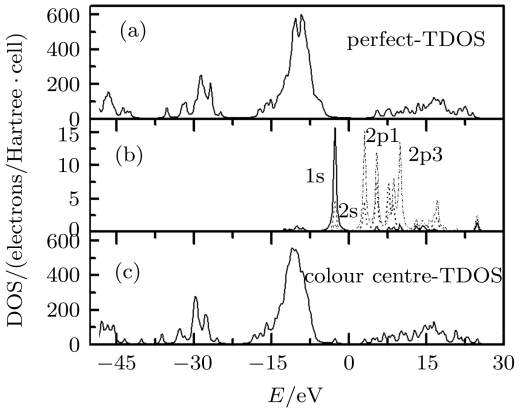


Fig. 3. Total DOS of the perfect $BaMgF_4$ crystal and the crystal with an F colour centre and partial DOS of the crystal containing the F colour centre.

For its low lattice symmetry of the crystal, the different symmetry positions of the F colour centre location may cause some small different absorption bands. So we predicate that the 236 nm–274 nm absorption bands may originate from F colour centres in different positions. The position for the absorption band for the crystal is near the rare earth intrinsic absorption edge.

4. Conclusion

The electronic structures of $BaMgF_4$ containing an F-colour centre are studied by using an H-like wave function. The results predict that the 236 nm–274 nm absorption bands may originate from the F colour centres in the $BaMgF_4$ crystal. It can be concluded that adding a 2p state in the program should be trustworthy for reasonable results.

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