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Electronic structure of F, F^+-center in MgO

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Abstract. The embedded-cluster numerical variational method has been developed to calculate the electronic structure of perfect MgO, F and F^+-centers in MgO. The energy band, bulk density of states has been calculated by cluster $Mg_{14}O_{13}$, $Mg_{14}O_{12}F^+$ and $Mg_{14}O_{12}F$. The calculated absorption energy for F^+ and F centers is in good agreement with experimental data. In our calculated defect energy levels, that the first excited state of F^+-center is at CB-3.46 eV, indicates the necessity of a large photoelectron yielding energy. We also calculate the radius of color center electron, and plot the map of charge-density distribution of valence electrons in which the structure of the color center is shown directly.

PACS. 71.20.-b Electron density of states and band structure of crystalline solids – 71.55.-i Impurity and defect levels – 78.40.-q Absorption and reflection spectra: visible and ultraviolet

1 Introduction

MgO is a prototype for simple oxides, is also an important material with many applications. Color centers in MgO has been receiving attention from both experimentalists and theorists for many years. When there is a lattice defect in MgO, it will give rise to a variety of optical, catalytic, and electrical conductivity phenomena [1–4]. As we know, MgO is of the rocksalt structure with each Mg and O atom sixfold coordinated. The experimentally determined forbidden gap of MgO is 7.8 eV [5]. A strong absorption band centered at 5 eV has been assigned to contributions from F and F^+-centers, which are experimentally observed in the γ-ray irradiation [6] and the additive colored MgO crystals when they are produced in a vapor of metals other than magnesium [7].

In an effort to characterize the properties of the color center in crystal matter and to explain the optical experiments on MgO, it is necessary to obtain systematic information on the electronic structure of crystalline MgO with color centers. Up to now, there have already been a considerable number of theoretical works on this aspect [4,8,9]. In 1994, Gibson calculated the energetic and electronic structure of defects in MgO [8] by using a stationary total-energy functional. In 1995, Kantorovich *et al.* [10] obtained the electronic structure of color center in MgO. Yet, the viewpoints on the energy level structure and optic transition model can not keep identity. This represses the further application of crystal MgO.

The purpose of this paper is to calculate the electronic structure of color center in MgO crystal, by using a self-consistent charge-discrete variation-embedded cluster model (SCC-DV-ECM) containing a H-like wave function of the F-center. We studied the electronic structure of sapphire [11] in 1986 and the doped TiO_2 crystal [12] in 1994 by this method. The results both are very excellent. Recently, the embedded-molecular-cluster model has been extensively used to study the properties of defects in crystals [13,14]. In this paper, we take the H-like HFS wave function as the primary basis function of F and F^+-center and construct a embedded-cluster. As a result, we get the energy levels of color center and discuss the optic transition model. The present study clarifies the properties of F^+ and F center and gives a useful clue to understanding the color center founding processes in this material.

This paper is organized as follows. In Section 2, we simplify method of SCC-DV-SEM. In Section 3, the cluster is specified and method of numerical compute is discussed. The results of the calculations are discussed in detail in Section 4 and a brief conclusion is given in Section 5.

2 Theory and numerical method

As to the theory of the embedded cluster model, a detailed description has been involved in previous work [15].

Energy levels and the density of state are calculated by the Hatree-Fock-slate (HFS) local-density one-electron model. The HFS equation is

$$\left(-\frac{1}{2}\nabla^2 + V_c^{\text{tot}} + V_{\text{xc}}\right)\Psi = E\Psi \tag{1}$$

where the Hamiltonian consists of the sum of a kinetic energy operator, nuclear and electron coulomb potentials

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and an exchange potential. The exchange potential is given by

$$V_{\mathrm{xc}} = -3\alpha \left(\frac{3}{8\pi}\rho_{(r)}\right)^{\frac{1}{3}}. \tag{2}$$

The coulomb potential is given by:

$$V_{\mathrm{c}}^{\mathrm{tot}} = V_{\mathrm{c}}^{\mathrm{clust}} + V_{\mathrm{c}}^{\mathrm{emb}} \tag{3}$$

where $V_{\mathrm{c}}^{\mathrm{emb}}$ is the coulomb potential contributed by the assumed charge distribution of embedding lattice. $V_{\mathrm{c}}^{\mathrm{emb}}$ is calculated by Ewald summation.

The discrete variational method(DVM) is now applied to solve the HFS equation. $\Psi_i(r)$ is a linear combination of atomic orbitals (LCAO) $\phi_k(r)$.

$$\Psi_i(r) = \sum_{k=1}^{n} \mathcal{C}_{ki}\,\phi_k(r). \tag{4}$$

The expansion coefficients are obtained as usual by solving the matrix secular equation

$$\sum_{l}(H_{kl} - E\,s_{kl})c_{li} = 0. \tag{5}$$

The whole process of the calculation is self-consistent. It is implemented by estimating the initial charge density, and by solving the HFS equation for eigenvalues, which is then employed to calculate the new charge density to begin the next iteration. The process repeats until convergence is achieved. This method is relatively efficient in computer time and providing reasonably accurate electronic states.

3 Numerical calculation

MgO is in NaCl structure. The unit cell contains four Mg atoms and four O atoms. Each Mg atom has six O neighbours at a distance $d_1 = 3.96$ Å, as does each O atom. The point group of the MgO structure is C_{4v} [16].

The cluster model on which the calculation of prefect crystal is based is shown in Figure 1. This cluster includes 14 O atoms, 13 Mg atoms. The center site in the cluster is one O atom. The Z-axis is along the (100) direction. We call this cluster $Mg_{14}O_{13}$. This cluster has C_{4v} point group symmetry and the central O atom has all its nearest- and nearer-neighboring atoms. This cluster is big enough to represent the relation between lattice atoms clearly. We sum over 224 atoms that are close to the initial cluster to represent the crystalline environmental field. This is big enough to satisfy a MgO crystal. In other words, the initial cluster is embedded in a microcrystal that contains 224 atoms for numerical computation.

The atomic wave functions needed in the molecular orbital expansion are obtained by solving the self-consistent free atom problem in the HFS scheme. Spherical wells of variable depths and radial extent are added to atomic potentials to include additional bound-state orbital wave function. In our calculation, for O, the well depth is 3.5 eV, and well begins at a radius of 2 a.u, for Mg, is 4 eV and 2 a.u, respectively. For O and Mg, the basis set consists of 1s, 2s, 2p, 3s orbital. However, the lower- energy orbitals (1s for O, 1s, and 2s for Mg) are treated as frozen cores. The Hamiltonian and overlap matrices are calculated using a Diophantine grid of 3600 integration points weighted by Fermi distribution.

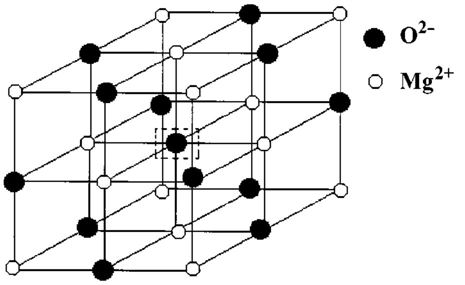

Fig. 1. The embedded-cluster $Mg_{14}O_{13}$, the framed lattice is the O^{2-} displaced site by F and F^+- center.

We know the electrons of the F- and F^+-center can be explained by the H-like atom model. For describing the wave function of the color center, Ferrari *et al.* [17] uses the O atomic wave function for F-center to calculate the defect in MgO. In this work, the H-like and H–like atomic HFS wave function, which include 1s, 2s, 2p states, are employed as basis wave function of F^+ and F-center. It can be explained, in the color center lattice position, that there is one H- or H^--like wave function without nuclear charge. The H(1s) represents the ground-state of the F-center, H(2p) represents the excited state of the F-center. The reasonableness of the calculation shows that the choice of color center wave function is successful. In the process of calculating the color center, all parameters are the same as for the perfect crystal. The precision of calculation is $< 10^{-4}$.

When calculating the electronic structure of F^+-center, one F^+-center displaces the center lattice O atom, see Figure 1. This cluster is called $Mg_{14}O_{12}F^+$. In the calculation, the H-like HFS wave function without nuclear charge is placed on the color center site. This is in agreement with the experimentally observed site of F^+ centers in MgO. Around the central F^+-center, there are six nearest-neighbor Mg atoms and twenty nearer-neighboring O and Mg atoms. In this cluster, the relation between surrounding atoms and color center is considered enough. For calculation of F-center, a similar cluster model as F^+-center is constructed in which one F-center displaces the center lattice O atom in cluster $Mg_{14}O_{13}$, called $Mg_{14}O_{12}F$.

4 Result and discussion

4.1 MgO crystal

We calculate the bulk total density of states and band energy of perfect crystalline MgO. The bulk total density

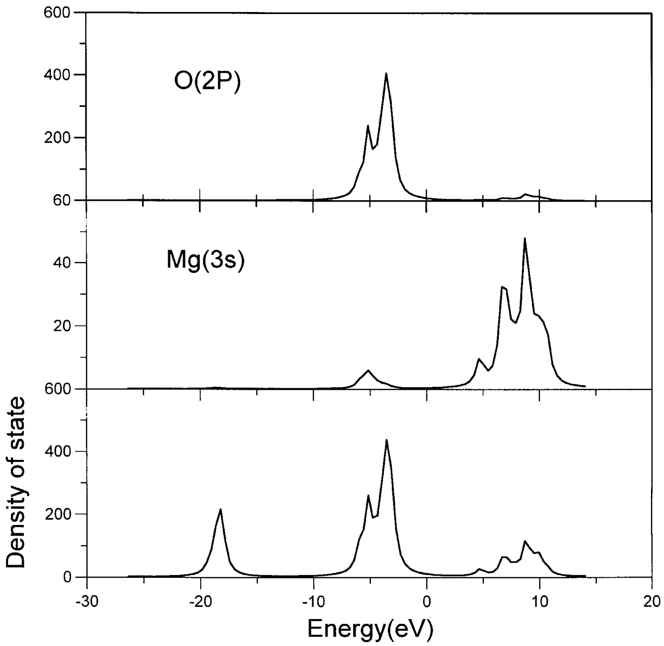

Fig. 2. The total density of states and partial density of states of MgO.

of states (DOS) and partial density of states (POS) are shown in Figure 2. The conduction-band (CB) peak is at 4.75 eV, and the valence-band (VB) peak is at −3.07 eV. From the DOS and POS, the main component of the valence band is O(2p) orbital with a width of 4.5 eV. There exist two peaks in the VB that has the separation energy of 1.6 eV. The O(2s) orbital forms the lower valence-band (LVB), which lies 15 eV lower than the VB with width of 6.2 eV. The main contribution to the conduction band comes from Mg(3s) orbital. We find that the forbidden gap is $E_g = 7.82$ eV, which agrees perfectly with the experimental optical forbidden gap $E_g = 7.83$ eV [5]. So far, the best obtained result is $E_g = 7.7$ eV and 7.76 eV using first the principle method and Tight-binding method [18,19], respectively.

Our calculated result can be in good agreement with the experimental XPS spectrum [6]. The experimentally measured valence-band width for MgO is 5–6 eV and the valence band shows two peaks separated by 2.5 eV. The position of the top of the low-lying oxygen 2s band in the XPS spectrum is between 18–21 eV. As can be seen in Figure 2, all their features are present in our theoretical DOS result. Quantitative comparison is given in Table 1 in which results from the first principle calculation [18] are also listed.

As can be seen from the partial density of states in Figure 2, there is a significant hybridization between Mg(3s) and O(2p) in both the valence and conduction bands. Although the valence band is predominantly O(2p) in character and the conduction band is predominantly Mg(3s), it is found that the VB contains a small contribution from Mg(3s) and the CB contains a small contribution from O(2p). This phenomenon reflects a strong interaction between Mg and O atoms.

Table 1. The results of calculated density states of MgO crystal (unit: eV).

Method	E_g	valence band width	ΔVB*	O(2s)
XPS	7.82	5 – 6	2.5	18 – 21
First principles	7.7	4.9		15.5
Present work	7.83	4.5	1.6	18.07

∗ Separation between valence band.

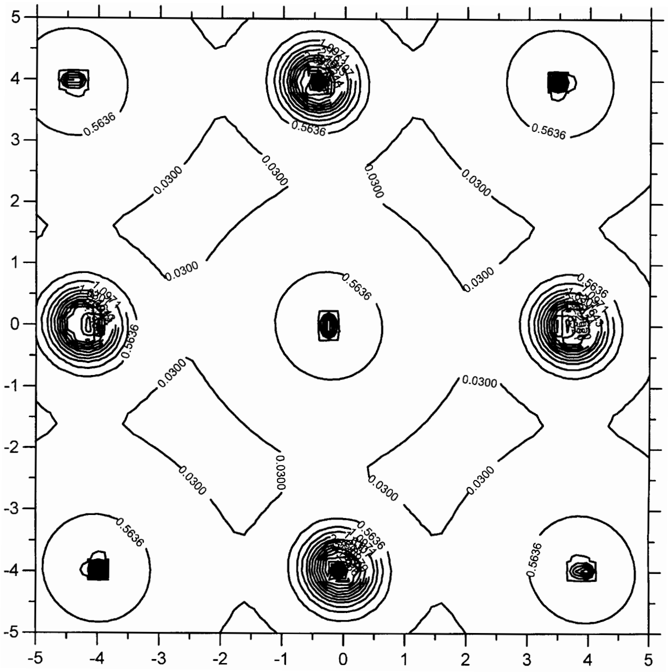

Fig. 3. The contour of charge distribution of MgO ($Z = 0$).

In Figure 3, the plane $Z = 0$ contains five O atoms and four Mg atoms which are seen to be essentially ionic. There is little charge accumulation along the bond lines. This reflects the degree of ionicity, and shows that MgO crystal is an ionic oxide. Also, these results agree reasonably well with the experimental data.

4.2 F^+ center in MgO

On the basis of reasonable calculated results for MgO, we calculate the band energy, bulk total density of states, and energy level of F^+ in MgO. The total density of states and partial density of states of F^+-center in MgO is shown in Figure 4. The main component of valence band and conduction band is still O(2p) and Mg(3s), respectively. It is interesting to examine the forbidden gap, there are two new peaks at VB+ 0.68 eV and CB-3.46 eV which are absent in perfect MgO. Comparing the position and intensity of peaks with the POS of ground-state F^+(1s) and first excited state F^+(2p), the weak peak at VB+ 0.68 eV

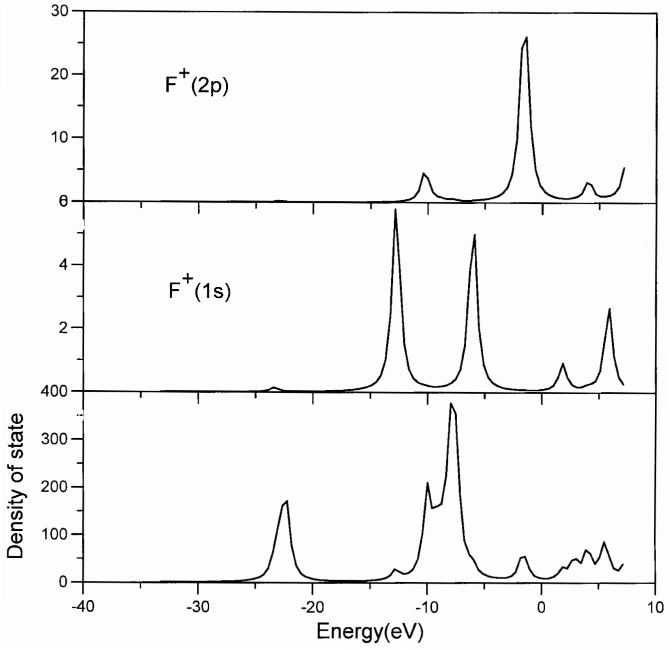

Fig. 4. The total density of states and partial density of states of F$^+$-center in MgO.

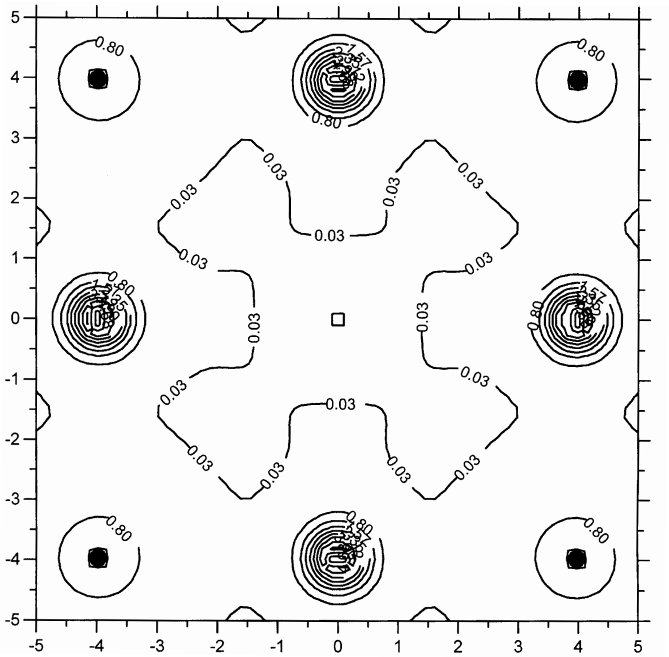

Fig. 5. The contour of charge distribution of F$^+$-center in MgO ($Z = 0$).

is evidently composed of F$^+$(1s), and the stronger peak at CB-3.46 eV is mainly composed of F$^+$(2p). Namely, the F$^+$ center leads into new energy peaks in the forbidden gap. As seen from POS, except for the added peaks in the forbidden gap, F$^+$(1s) state also has some peaks in the range of VB, and F$^+$(2p) state has some weak peaks in CB. The VB has evidently variation as the valence-width broadens to 5.8 eV. We interpret these results as the appearance of F$^+$-center induced band tails, these tail states contain F$^+$(1s) component of the F$^+$ center.

Some calculated energy levels are listed in Table 2. Between VB and CB, there are three energy levels of F$^+$ center. The two excited energy levels at CB-3.46 eV and at CB-3.26 eV are the structure of a defect excited-state energy band. Both of them are shallow acceptor energy levels. F$^+$-center energy levels are consistent with the conclusion of the density of states.

Optical spectroscopy has been one of the primary experimental tools to investigate the properties of defect in ionic material. In MgO the experimentally observed 5 eV optical-absorption band is attributed to F$^+$ and F-center [7]. But, there have been considerable differences in the defect energy level structure. Some papers [4,7,20] consider that this absorption band is a threshold absorption in which electrons are promoted from the defect level to the first excited state which is close in energy to the CB and the defect level is near to the VB. In the calculation of Klein *et al.* [20], the first excited state of F$^+$-center is close to or degenerate with the conduction-band edge.

Our calculated energy levels can explain the optic absorption. Analysing from our calculated results, an optical transition from ground-state of F$^+$-center to excite-state of F$^+$-center needs 4.7 eV energy. This transition energy is in accord with the experimentally observed F$^+$-center absorption energy of 4.9–5.0 eV. Photoionization behavior also depends on the defect energy levels. In our results, photoionization from the first excited-state of F$^+$-center to the bottom of CB needs energy 3.2 eV. In a recent paper, Gribson [8] has found that photoionization needs 4 eV photoelectron yielding energy in defective samples of MgO. So big photoelectron yielding energy can not be explained by the energy level model of Klein.

The map of the distribution of electronic density of the F$^+$-center is directly plotted in Figure 5. There is not a high accumulated center of electronic population in the color center lattice. The moving radius of F$^+$-center electron is 1.89 Å. Also we calculate the H-doped MgO, the electron radius of doped H atom is 0.78 Å. Because the electron of F$^+$-center has no attraction from the nucleus of F$^+$-center, so the radius of F$^+$-center is larger than in doped H atom. Meanwhile, the map reflects that the electronic movement of F$^+$-center is complex.

By comparing carefully Figures 5 and 3, we find there are some distortion in shape of electron population of Mg^{2+} ion and O^{2-} ion. In the lattice site, the electron population of Mg^{2+} changes from rhombus in Figure 3 to hexagon in Figure 5. This phenomenon shows that F$^+$-center electron disturbs the electric field distribution and there is strong interaction between F$^+$-center and lattice ions. Also, we know that the energy level is decided by the distribution of electronic field, so the distortion of the distribution qualitatively explains the movement of energy level and broadness of band gap. This is consistent with our above conclusion.

Table 2. Partial calculated energy levels of F^+, F center in MgO.

	F^+ center					F center			
			Energy level	charge				Energy level	charge
	5	A2 .1	−7.5559	2.00000		5	A2 .1	−6.4664	2.00000
	10	B2 .1	−7.5506	2.00000		10	B2 .1	−6.4572	2.00000
	11	B1 .1	−7.4559	2.00000		11	B1 .1	−6.3642	2.00000
	23	E .1	−7.0428	2.00000		23	E .1	−6.2483	2.00000
	23	E .2	−7.0428	2.00000		23	E .2	−6.2483	2.00000
O(2p)	6	A2 .1	−6.7468	2.00000	O(2p)	6	A2 .1	−5.71616	2.00000
F^+(1s)	18	A1 .1	−6.0600	1.00000	F(1s)	18	A1 .1	−4.8245	2.00000
	24	E .1	−1.6129	0.00000		24	E .1	−0.3734	0.00000
F^+(2p↑)	24	E .2	−1.6129	0.00000	F(2p↑)	24	E .2	−0.3734	0.00000
F^+(2p↓)	19	A1 .1	−1.4232	0.00000	F(2p↓)	19	A1 .1	−0.0767	0.00000
Mg(3s)	20	A1 .1	1.8557	0.00000	Mg(3s)	20	A1 .1	2.6603	0.00000
	12	B1 .1	2.8980	0.00000		12	B1 .1	3.3736	0.00000

4.3 F center in MgO

Meanwhile, we calculate the bulk total density of states, energy level of F center in MgO. The total density of states and partial density of states are shown in Figure 6. The main component of valence band and conduction band are still O(2p) and Mg(3s), respectively. But, there are two new peaks in the forbidden gap which are absent in perfect MgO. The weak peak is at VB+0.91 eV and the stronger peak is at CB- 3.03 eV. According to the energy level analysis, F-center leads into three new energy levels in the forbidden gap, one F(1s) occupational energy level is at VB+0.91 eV, one F(2p) excited-state energy level is at CB-3.03 eV and one F(2p) doubly degenerate energy level is at CB-2.73 eV.

According to calculated results of the energy level, see Table 2, we assign the optic transition model of F center. An optical transition from ground-state F(1s) to first energy level of F(2p) needs transition energy 4.8 eV. This energy value is in good agreement with optical absorption spectroscopy values of 4.8 eV–5.0 eV [6,7]. And the calculated photoelectron yielding energy is 3.03 eV (from first excited energy level of F(2p) to bottom of CB). This conclusion is similar to the F^+-center.

In Figure 7, it is evident that there is not an accumulated center of electron in the F-center site, the moving radius of F-center electron is 2.5 Å around a quadrilateral constructed by nearest-neighbor Mg^{2+} ion. The radius of F-center is bigger than F^+-center. This result agrees with the conception that the F-center consists of one oxygen vacancy containing two electrons. By carefully analyzing Figure 7, we find there are some distortion in shape of electron population of Mg^{2+} ion and O^{2-} ion. In the lattice site, the electron population of Mg^{2+} turns to hexagon. This phenomenon shows F-center disturbs the electric field distribution, and reflects that there is strong interaction between F-center and near ions. This conclusion is consistent with our above conclusion for F^+-center.

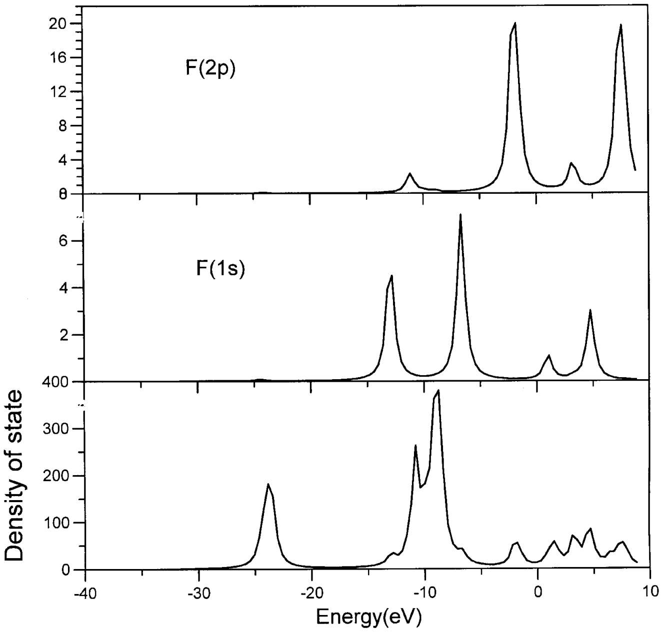

Fig. 6. The total density of states and partial density of states of F-center in MgO.

In general, F and F^+ center in MgO have similar phenomenon in electronic density distribution and the bulk total density of state. Their optic transition model is also alike. These are attributable to the to similar structure of F^+ and F center which both are oxygen vacancies with electrons.

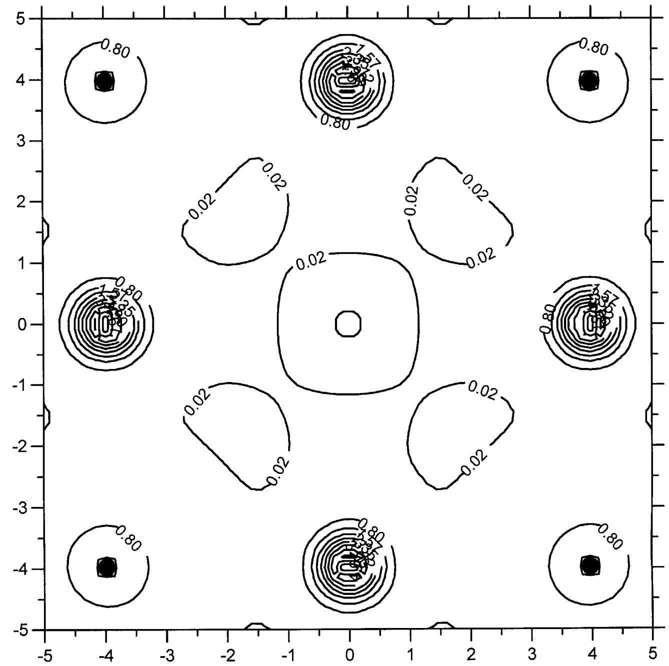

Fig. 7. The contour of charge distribution of F-center in MgO ($Z = 0$).

5 Conclusion

Using the embedded-cluster discrete variational method and H-like wave function of color center, we calculate the electronic structure of perfect MgO crystal, F and F^+-center in MgO. These results include color center energy band and optical transition energy.

In MgO, the forbidden gap is 7.8 eV, the width of VB is 5.8 eV and separation of two peaks in VB is 1.7 eV, which is in good agreement with XPS. We find that there is hybridization between Mg(3s) and O(2p). The map of electron density distribution shows the typical ionicity of MgO crystal.

In our results, F^+ and F-center have three defect energy levels in the fundamental gap. The ground-state energy level of F^+-center is at VB+0.68 eV. The excited-state F^+(2p) energy level is at CB-3.46 eV and CB-3.27 eV. The ground-state energy level of F-center is at VB+0.91 eV, The excited-state F(2p) energy levels are at CB-3.03 eV and CB-2.73 eV. Our results reasonably explain the experimentally observed optic absorption and large photoelectron yielding energy in MgO. The density of electron population has been plotted. The map directly shows the behavior of color center electrons. The agreement between our calculation and the experiment is quite reasonable and we are confident that the embedded cluster model containing the H-like wave function is a good approximation for electronic structure calculations of color centers in crystals.

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