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Semi-empirical simulations of the electron centers in MgO crystal

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Abstract

Semi-empirical quantum chemical simulations of 125-atom clusters have been undertaken to obtain the self-consistent atomic and electronic structure of the two basic electron defects in MgO crystals – F^+ and F centers (one and two electrons trapped by an O vacancy). The calculated absorption and luminescence energies agree well with the experimental data, the excited states of both defects are found to be essentially delocalized over nearest-neighbour cations. The mechanism of the $F^+ \rightarrow F$ photoconversion is discussed.

1. Introduction

Oxide materials in general, and MgO in particular, are important as catalysts, ceramics and for their relevance to microelectronics and geophysical problems [1–3]. Point defects arise in oxides naturally, under irradiation, and by design, considerably affecting their optical properties. Several kinds of point defect have been identified and studied in the alkali-earth oxide materials like MgO; the two basic electronic defects are called F^+ and F centers [1]. They are respectively one and two electrons trapped by an O vacancy. Especially great theoretical attention has been paid to these centers in recent years, when a number of careful first-principles calculations have been performed [4–10]. However, such calculations are unavoidably restricted to quite small quantum clusters or supercells, so the study of excited states of these centers is not possible. The main unsolved problems of F^+, F centers are [4,11]:

(i) How close are their relaxed excited states to the bottom of the conduction band?
(ii) What is the lowest in energy F-excited state: singlet or triplet, and what are the relevant luminescence energies (only one band has been observed so far experimentally)?
(iii) What is the mechanism of the photostimulated $F^+ \rightarrow F$ conversion?
(iv) Whether an O vacancy could trap the third electron.

If one could answer these questions, the logical continuation of theoretical studies will focus on the H (hydrogen) impurities and related F–H complexes, which seem to play a decisive role in understanding the anomalously delayed luminescence kinetics in MgO [4,11]. Another challenging problem is the optical properties of dimer,

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F_2-type centers in MgO which have been little studied theoretically (see a review article [12]).

All the above demonstrates that there is a great need for a simpler theoretical approach, allowing us to study large quantum clusters (about 100 atoms), complex defects, and it should also be able to optimize the defect geometry (in both the ground and excited states) through a minimization of the total energy, and to calculate reliably the excited states and the relevant absorption and luminescence energies.

Such an approach to defects in ionic solids has been elaborated in recent years in terms of the semi-empirical quantum chemical method of Intermediate Neglect of the Differential Overlap (INDO) [13,14], which has been since then applied very successfully to the defects in many oxide materials, including MgO, SiO_2, Li_2O, ZrO_2, α-Al_2O_3 [15–21]. A similar approach has been used recently for defect studies in semiconductors [22,23].

In this paper, we report INDO calculations of F^+ and F centers in MgO, in order to answer the four questions formulated above.

2. Method

The INDO method is a simplified (semi-empirical) version of the ab initio unrestricted Hartree–Fock formalism based on the linear-combination-of-atomic-orbitals (LCAO) basis set widely used in the quantum chemistry of large molecules and the electronic structure of semiconductors [13]. Its considerable modification for ionic solids is described in detail in Ref. [14]. Briefly speaking, it is a self-consistent field (SCF) theory where the Fock matrix elements read:

$$F_{kk'} = \delta_{kk'} U^{\mathrm{A}}_{kk} + \sum_{ls}^{\mathrm{A}} \left(P_{ls} \langle kk' \,|\, ls \rangle - P^{u}_{ls} \langle kl \,|\, k's \rangle \right) + \delta_{kk'} \sum_{\mathrm{B} \neq \mathrm{A}} \left(\sum_{l}^{\mathrm{B}} \left(P_{ll} \langle kk \,|\, ll \rangle - V^{\mathrm{B}}_{k} \right) \right), \tag{2.1}$$

where k, k' are atomic orbitals (AOs) belonging to the atom A, $\delta_{kk'}$ is the delta symbol. In Eq. (2.1) the symbol u denotes the electron spins (α or β), P^{α}_{kk} and P^{β}_{kk} are the populations on kth AO for electrons with α with β spin, $\langle \cdot\cdot \,|\, \cdot\cdot \rangle$ stands for two-electron integrals [13].

The first term in Eq. (2.1) describes the interaction of an electron occupying the kth valence AO on atom A with its own core:

$$U^{\mathrm{A}}_{kk} = -E^{\mathrm{A}}_{\mathrm{neg}}(k) - \sum_{m} \left(P^{(0)\mathrm{A}}_{mm} \gamma_{km} - 0.5 P^{(0)\mathrm{A}}_{mm} K_{km} \right), \tag{2.2}$$

where $P^{(0)\mathrm{A}}_{mm}$ are the diagonal elements (initial guess) of the density matrix (= mth AO population), γ_{km} and K_{km} are one-centre Coulomb and exchange integrals, respectively, which are calculated exactly. Finally, $E^{\mathrm{A}}_{\mathrm{neg}}(k)$ is the initial guess of the kth AO energy (the ion's calculated electronegativity). Thus, the effective potential U^{A}_{kk} depends on the three atomic parameters: E_{neg}, the orbital exponent ξ and P^0. An interaction of an electron on the kth AO belonging to the atom A with the core of another atom B entering Eq. (2.1) reads:

$$V^{\mathrm{B}}_{k} = Z_{\mathrm{B}} \{ 1/R_{\mathrm{AB}} + [\langle kk \,|\, mm \rangle - 1/R_{\mathrm{AB}}] \times \exp(-\alpha_{\mathrm{AB}} R_{\mathrm{AB}}) \}, \tag{2.3}$$

where R_{AB} is the distance between atoms A and B, Z_{B} is the core charge of atom B, and the parameter α_{AB} describes the non-point character of this interaction.

Lastly, the so-called resonance-integral parameter β_{kl} enters the off-diagonal Fock matrix elements:

$$F^{u}_{kl} = \beta_{kl} S_{kl} - P^{u}_{kl} \langle kk \,|\, ll \rangle, \tag{2.4}$$

where k belongs to atom A and l to atom B, S_{kl} is the overlap integral between electrons on kth and lth AOs.

Our scheme of parametrization contains the following set of parameters per atom: orbital exponent ξ (O 2s, 2p and Mg 3s in our case) defining the radial part of Slater-type AOs, electronegativities, E_{neg}(s), E_{neg}(p), 'initial electron populations', P^0(s), P^0(p), bonding parameter β and the parameter α. The parameters for Mg and O atoms were fitted earlier [14] to the basic experimentally-observed properties of pure MgO crystal (the lattice spacing, the widths of the O upper s,p valence bands, the forbidden gap, the

Table 1
Optimized INDO parameters for the additional AO of the F center in MgO; the matrix of bonding-parameters β corresponds to the s and p AOs respectively; $\alpha_{FA} = 0$

AO	ξ(at. units)	E_{neg}(eV)	$P^0(e)$	β matrix
				F–Mg
1s	0.55	−2.1	0	−0.60E+00 −0.05E+00
				−0.05E+00 −0.05E+00
2p	0.49	−2.6	0	F–O
				−0.20E+01 −0.20E+01
				−0.20E+01 −0.20E+01
				F–F
				−0.30E+00 −0.30E+00
				−0.30E+00 −0.30E+00

midpoint of the upper valence band, the effective charges on atoms) and of a series of O- and Mg-containing diatomic molecules (mainly, equilibrium distances and the potential energy curves in their vicinity were reproduced for 15 molecules). The large quantum cluster is embedded into the electrostatic field of the non-point infinite rigid lattice, whose effective charges are taken from the INDO supercell calculations [15,16]. In our cluster calculations before the defect is introduced, the equilibrium positions of all cluster ions are obtained by minimizing the total energy of the 'perfect' cluster interacting with the rest of the infinite crystal. We found displacements of ions to be less than 0.5% of the lattice constant, thus confirming that the use of the boundary conditions in the form of the electrostatic field of the ions surrounding quantum cluster is quite an adequate procedure in such ionic solids 125-atom clusters of a cubic shape having high (O_h) point symmetry and modelling 9 spheres of atoms around the coordinate origin, were used in defect calculations. In the F-type center simulations, the O atom in its center has been removed, and one or two electrons added to the cluster, making no a priori assumptions about their localization and the electron density distribution. Then the ions surrounding the O vacancy were allowed to relax in order to get a minimum of the total energy, as well as the self-consistent electronic and atomic structures of the defect. As we found in previous calculations [17], use of the 3s Me AOs in the basis set for the calculation of the F-type centers gives only qualitative agreement with the experimental data since an additional electron is not sufficiently strongly localized by the anion vacancy. We suggest to extend the basis set in such calculations by adding the additional 1s,2p AOs centered at the vacancy [17,18].

As earlier, the relevant parameters were fitted to the experimentally observed optical absorption energy of the F^+ center (5 eV) and the spin density of its unpaired electron on the nearest Mg ions. The optimized parameters are given in Table 1. Note that we use the *same* parametrs for both F^+ and F centers except for E_{neg}; since the F^+ center is charged with respect to the perfect MgO crystal and polarizes the surrounding ions, its E_{neg} parameter has been reduced (compared

Table 2
Optimized displacements of atoms of the three spheres surrounding empty O vacancy (F^{2+}), F^+ and F centers

Atom/Center	F^{2+}	F^+	F
Mg (1, 0, 0)	(1.065, 0.000, 0.000)	(1.047, 0.000, 0.000)	(1.019, 0.000, 0.000)
O (1, 1, 0)	(0.977, 0.977, 0.000)	(0.983, 0.983, 0.000)	(0.999, 0.999, 0.000)
Mg (1, 1, 1)	(1.005, 1.005, 1.005)	(1.003, 1.003, 1.003)	(1.000, 1.000, 1.000)

Coordinates are presented in units of the Mg–O distance of 2.02 Å obtained in the $Mg_{108}O_{108}$ supercell calculations. Clusters used model 9 spheres of atoms around a defect.

Table 3
Effective charges (in units of e) on atoms surrounding the F^{2+}, F^+ and F centers in both their ground state (A) and excited state (B)

Atom/Center	F^{2+}	F^+	F	F^-	Perfect crystal
(A) Ground state					
Mg (1, 0, 0)	1.808	1.823	1.838	1.721	1.831
O (1, 1, 0)	−1.835	−1.826	−1.819	−1.802	−1.829
Mg (1, 1, 1)	1.823	1.828	1.832	1.834	1.831
Vacancy	−0.002	−1.002	−2.002	−2.003	—

Atom/Center	F^+ center	F center	
		singlet	triplet
(B) Excited state			
Mg (1, 0, 0)	1.715	1.701	1.674
O (1, 1, 0)	−1.824	−1.817	−1.816
Mg (1, 1, 1)	1.828	1.832	1.831
Vacancy	−0.476	−1.268	−1.127

with that for the F center) by the value of the electronic polarization potential induced at the O vacancy by the surrounding ions (1.8 eV, e.g. $E_{neg}(1s) = -3.9$ eV for F^+ center). Use of such a polarization correction is necessary since in the INDO approximation displacements of the electronic shells of ions induced by a charge defect (like an F^+ center) are known to be almost negligibly small [13]. The ionic contribution to the polarization energy is taken into account in our calculations via displacements of the ionic cores surrounding the defect. The phenomenological procedure for the electronic polarization calculation and the relevant parameters are described in detail in Ref. [20]. We would like to stress that the defect parametrization plays an important

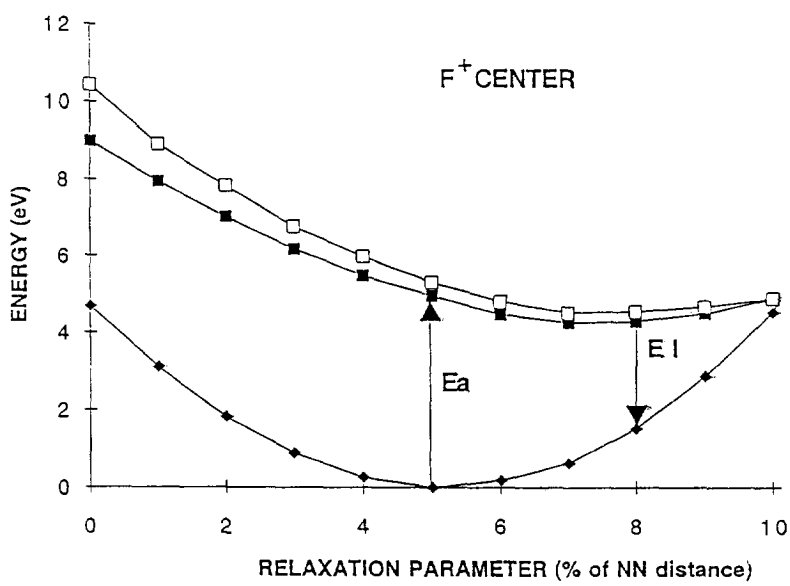

Fig. 1. A_{1g} configuration coordinate curves for F^+ center in MgO (only the effect of the symmetric relaxation of NN atoms is shown): ♦ the ground state; ■ the excited state; □ bottom of the conduction band. E_a, E_l are the absorption and luminescence energies, respectively.

role in such semi-empirical calculations as the present study. In the light of this fact, we varied F-type center parameters over a wide range of magnitudes and found the only combinations describing well the mentioned-above experimental properties. A good test of the quality of these parametrs is a study of dimer (F_2-type) centers which is now in progress. The recently developed INDO computer code SYM–SYM [24] is perfectly suited for our computer simulations, being based on a complete treatment of the point symmetry and the automated defect geometry optimization.

Since in the F^+ and F center calculations we use quantum clusters of different net charges (-2 e for the perfect cluster and that containing the F center, and -1 e for the F^+ center), the relevant patterns for one-electron energy spectra are also shifted in energy – an effect well known for the cluster model [9,10,25]. It is clear, however, that in the case of an isolated defect inserted into a crystal the deep valence band of the latter (O 2s in MgO) must remain unperturbed. This is why for the placing of defect levels with respect to the perfect crystal bands we used the procedure suggested in Refs. [25,26]; it is based on the preliminary matching of the midpoints of the deep O 2s bands in the perfect cluster and that with a defect.

The absorption and luminescence energies were calculated as the difference of total energies for the ground and excited states, respectively (ΔSCF method – see Section 3.1). For this purpose the relevant potential energy curves were calculated, then according to the Frank–Condon principle the absorption energy was calculated as that for a vertical transition from the minimum of the relaxed ground state to the SCF excited state (with fixed atomic coordinates). The luminescence energy was found in a similar way.

3. Results and discussion

3.1. F^+ and F centers

The optimized geometry of a bare O vacancy (F^{2+} center), and of those with one and two trapped electrons (F^+ and F centers respectively) is presented in Table 2, whereas the relevant charges on atoms are shown in Table 3. Naturally, for the doubly-charged F^{2+} defect the surrounding atom relaxation is the largest – up to 6.5% outwards for the nearest Mg ions – but it is

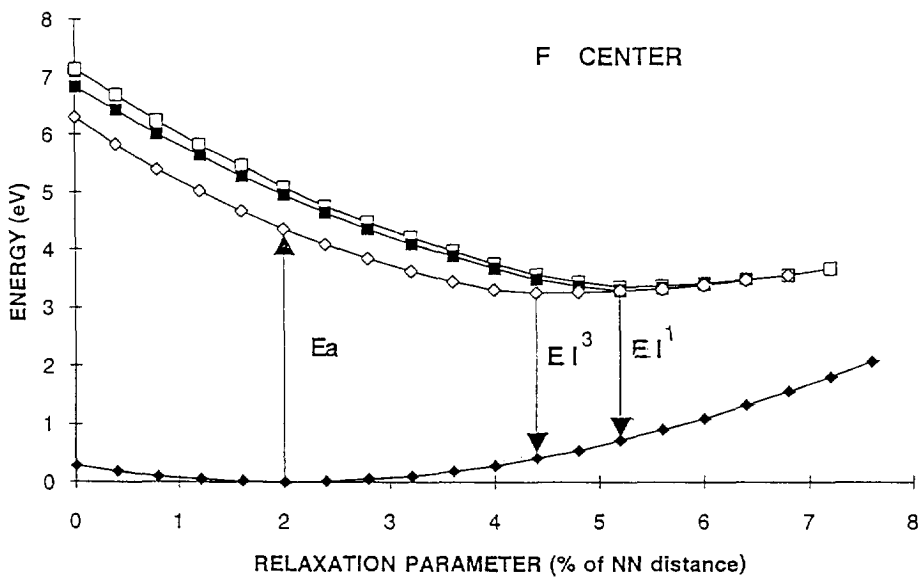

Fig. 2. Same as Fig. 1 for the F center; E_l^1 and E_l^3 denote the luminescence singlet and triplet transitions.

less than 2% for the neutral F center. Atoms of three spheres surrounding an O vacancy are noticeably relaxed even in the ground state of these F-type centers.

The charge distribution analysis demonstrates clearly that one (two) electrons are well-localized by an O vacancy in the ground state of F^+ (F) center with a very moderate change of the effective charges on the atoms surrounding the O vacancy.

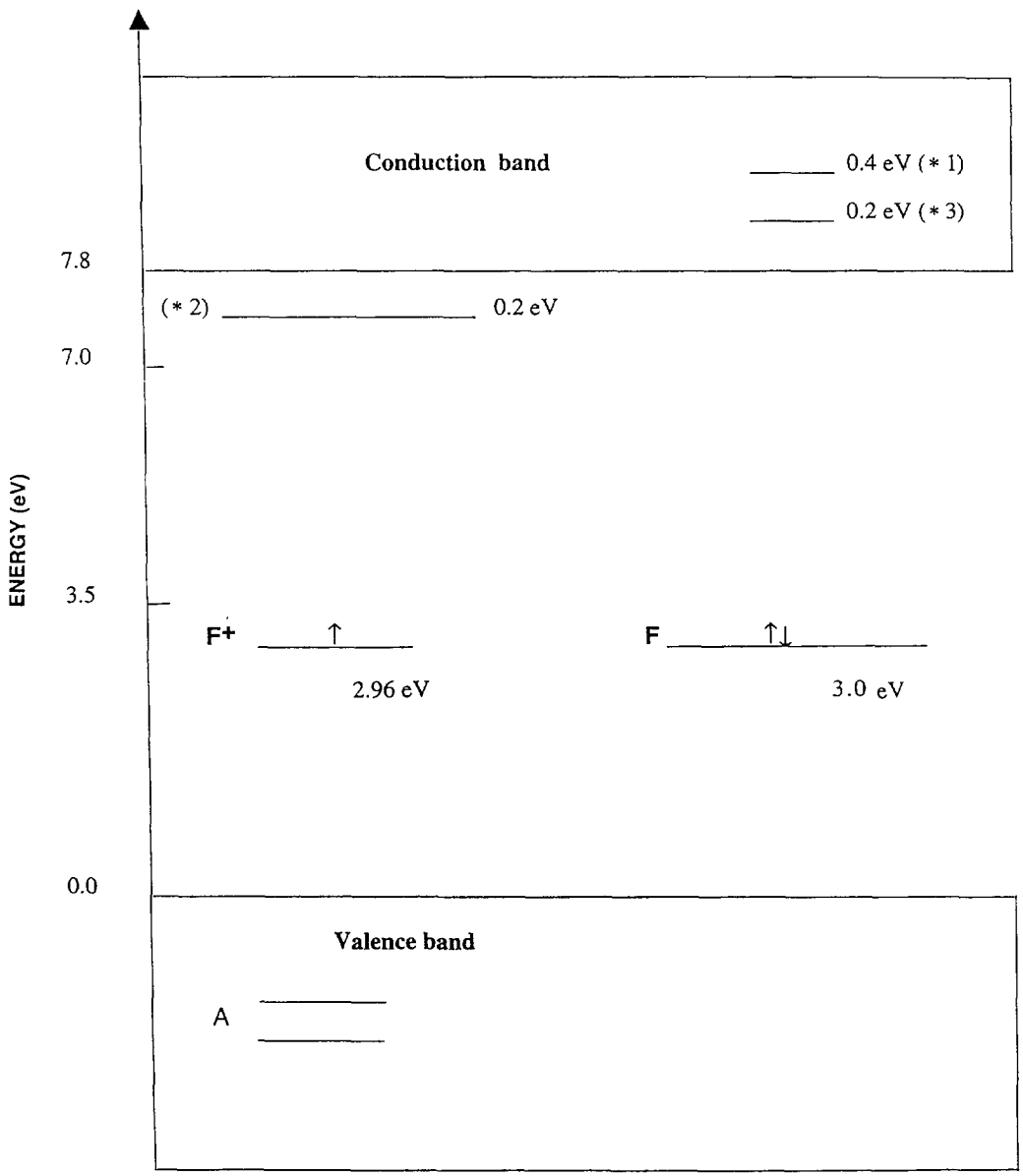

Fig. 3. Position of the one-electron defect levels with respect to the perfect MgO bands; *1, *2, *3 levels denote the singlet, doublet and triplet excited states, respectively. A are two quasi-local state induced by F^+ on two spheres of nearest O ions.

Table 4
Calculated absorption and luminescence energies (in eV); the symbols S and T denote theory for the singlet and triplet bands of the F center

Defect		F^+	F
Absorption:	theory	4.97	4.98 [a]
	expt [4,11]	4.95	5.02
Luminescence:	theory	3.6	2.61 (S); 2.76 (T)
	expt [4,11]	3.2	2.3

[a] Fitted to the experimental value.

This is no longer true, however, for their excited states: 0.5 *e* is delocalized from the O vacancy over the cations surrounding the F^+ center, which results in a reduction of their effective charges (by ≈ 0.1 *e* on each atom). For the singlet state of the F center 0.7 *e* is delocalized. An analysis of the spin density distribution for the ground state of the F^+ center shows that $\geqslant 90\%$ of the unpaired electron lies inside the O vacancy but only 44% in its excited state.

The potential energy curves as a function of the full-symmetry, A_{1g} relaxation of atoms nearest to the F^+ and F centers are shown in Figs. 1 and 2. They confirm that the excited states lie very close to the conduction band, in agreement with experimental data [27] placing the F excited state only 0.06 eV below the bottom of the conduction band. The calculated absorption energies of F^+ and F given in Table 4 practically coincide, again in agreement with the experimental data; the luminescence energy for F^+ exceeds by 0.4 eV the experimental one (3.2 eV).

Calculations of the excited F center predict the singlet luminescence peak at 2.61 eV and the triplet one, at 2.76 eV. The only band observed experimentally so far is at 2.3 eV; probably the singlet and triplet energies are too close to be resolved (the width of the experimental emission band is about 0.6 eV). The calculated minimum energies for the relaxed singlet and triplet states differ by only 0.04 eV; this probably explains why the optically detected magnetic resonance (ODMR) experiments [28] indicate that the emitting state is not predominantly an orbital triplet.

Finally, Fig. 3 demonstrates the calculated positions of the defect levels with respect to the perfect MgO bands which were found following the procedure described above [25,26]. There is some uncertainty related to the magnitude of the gap. The ΔSCF gap value is 10.2 eV, but it does not incorporate the polarization effects due to the electron at the bottom of the conduction band and a hole in the valence band, which are know to reduce the calculated gap additionally [25]. Use of the restricted configuration interaction (RCI) method gives the gap of 7.6 eV [21]; in Fig. 3 we accepted the experimental gap value of 7.8 eV.

Our calculations put both the ground levels – of F^+ and F centers – at about 3 eV above the top of the valence band – similarly to results recently obtained using much more refined super-cell multiple-scattering theory [5]. The relaxed excited states are almost degenerate in energy to the conduction band; their precise positions cannot be found keeping in mind our uncertainty in the gap value.

3.2. F^- (three-electron) center

We also simulated a hypothetical three-electron F^- center negatively charged with respect to the pure MgO crystal. Similar defects exist in alkali halides (two electrons trapped by an anion vacancy) [29] and were predicted theoretically in α-Al_2O_3 (see Ref. [17] and references therein). We have found that the third electron being added to the F center is not localized by an O vacancy but is shared mainly by the nearest six Mg atoms (having in total an extra charge of 0.7 *e* as follows from Table 3). Its energy level is estimated to be almost degenerate with the (experimental) conduction band. More accurate calculations need a careful treatment of the polarization effects due to its very diffused wave-function, which is now in progress.

3.3. $F^+ \rightarrow F$ photoconversion

It has been observed experimentally [11] that the optical excitation (photostimulation) in the region of F^+ (one-electron) center absorption results in their transformation into the F (two-

Table 5
The coefficients of AOs in the molecular orbitals for the two quasi-local states induced by the F^+ center in the valence band (energy levels A in Fig. 3)

Atom	Distance from the top of the upper VB	
	1.17 eV	2.01 eV
O(1, 1, 0)	$P_x = -0.204$	$P_x = -0.041$
	$P_y = 0.204$	$P_y = -0.044$
	$P_z = -0.137$	$P_z = 0.000$
O(2, 0, 0)	$P_x = 0.000$	$P_x = 0.307$
	$P_y = -0.035$	$P_y = 0.000$
	$P_z = 0.000$	$P_z = 0.000$

electron) centers and creation of hole (V) centers. A similar phenomenon is known also in corundum crystals [1]. It is very likely that F centers do not arise owing to the trivial thermal release of the excited electrons to the conduction band with further trapping by other F^+ centers (thus transforming them into F centers) since in this case no hole centers could be expressed to arise.

We propose the following explanation of this phenomenon. As follows from our calculations, a charged F^+ center induces in the upper part of the valence band two quasi-local states. Their nature is shown in Table 5 – they consist mainly of the AOs of O atoms of the two nearest spheres around the F^+ center (Fig. 3, levels A). Therefore, the reasonable idea suggests itself that the optical transitions from these levels A to the ground state of the F^+ center convert it into an F center. Because of the quasi-local nature of the induced states the transition probability is comparable with that for intra-center absorption. Simultaneously, a hole produced on a quasi-local level. It escapes to the valence band and moves until it is trapped by a cation vacancy in a form of a V center (indeed it has been observed experimentally [30]) or by an impurity, e.g. $F^{+*} + Fe^+ \rightarrow F + Fe^{2+}$ [31].

From our calculations the photon energy needed for the transition between quasi-local states and the ground state of F^+ is close to that used in the so-called photostimulated conversion experiments (≈ 5 eV). Recently, we have used the same model successfully for interpreting experimental data for corundum and a number of other ionic solids with charged defects [32].

4. Conclusion

Our calculations have demonstrated that the semi-empirical INDO approach combined with large quantum clusters allows us to treat successfully static and dynamic properties of the basic electron (F^+ and F) centers in MgO. We found that their ground states are well localized but excited states are quite diffuse with the relevant energy levels close to the bottom of the conduction band. This is in agreement with the experimental arguments and earlier ab initio calculations [4,5]. We predict that both singlet and triplet minima of the F excited states have very close energies and result in overlapping luminescence bands around 2.61 and 2.76 eV – hardly resolvable on the background of the 0.6 eV wide experimental emission band. Lastly, we have analyzed the mechanism of $F^+ \rightarrow$ F center photoconversion and suggested a novel model. These findings give us confidence in the reliability and flexibility of the present INDO formalism; the study of other types of defect in MgO crystal (H-related and dimer centers) is now in progress.

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References

[1] H. Crawford, Jr., Structure and Properties of MgO and Al_2O_3 Ceramics; Advances in ceramics 10 (1983) 793; Nucl. Instrum. Methods B1 (1984) 159.
[2] Point Defects and Related Properties of Ceramics; Ceramic Transactions 24 (Westerville, Ohio, 1990).
[3] Metal–Ceramic Interfaces, ed. M. Rühle, A.G. Evans, M.F. Ashby and J.P. Hirsh (Pergamon, Oxford, 1990).
[4] G.P. Summers, T.M. Wilson, B.T. Jeffries, H.T. Tohver, Y. Chen and M. M. Abraham, Phys. Rev. B27 (1983) 1283.
[5] B.M. Klein, W.E. Picket, L.L. Boyer and R. Zeller, Phys. Rev. B35 (1987) 5802.
[6] R. Pandey and J.M. Vail, J. Phys: Condens. Matter. 1 (1989) 2801.
[7] Q.S. Wang and N.A.W. Holzwarth, Phys. Rev. B41 (1990) 3211.
[8] K. Jackson, M.R. Pederson and B.M. Klein, Phys. Rev. B43 (1991) 2364.
[9] A.V. Bezel' and V.A. Lobach, Sov. Phys. – Solid State 33 (1991) 744;
A.B. Sobolev, Sov. Phys. – Solid State 36 (1994) 1557.
[10] V.S. Stepanyuk, B.L. Grigorenko, A.A. Katsnel'son, O.V. Farberovich and V.V. Mikhailin. Sov. Phys. – Solid State 36 (1990) 342.
[11] G.H. Rosenblatt, M.W. Rowe, G.P. Williams Jr. and R.T. Williams, Phys. Rev. B39 (1989) 10309.
[12] B. Henderson, CRC Crit. Revs. in Solid State and Mater. Sci. 9 (1980) 1.
[13] J.A. Pople and D.L. Beveridge, Approximate Molecular Orbital Theory (McGraw-Hill, New York, 1970);
A.H. Harker and F.P. Larkins, J. Phys C 12 (1979) 2487.
[14] E.V. Stefanovich, E.K. Shidlovskaya, A.L. Shluger and M.A. Zakharov, Phys. Stat. Sol. B 160 (1990) 529;
A.L. Shluger, Theor. Chim. Acta 66 (1985) 355;
A.L. Shluger and E.V. Stefanovich, Phys. Rev. B 42 (1990) 9664.
[15] P.W.M. Jacobs, E.A. Kotomin, A. Stashans, E.V. Stefanovich and I. Tale, J. Phys: Condens. Matter 4 (1992) 7531.
[16] P.W.M. Jacobs and E.A. Kotomin, Phys. Rev. Lett. 69 (1992) 1411.
[17] E.A. Kotomin and A.L. Shluger, Phys. Status Sol. B 109, (1982) 75;
A.L. Shluger and N. Itoh, J. Phys: Condens. Matter 2 (1990) 4119.
[18] A. Stashans, E.A. Kotomin and J.-L. Calais, Phys. Rev. B 49 (1994) 14854.
[19] J.L. Gavartin, C.R.A. Catlow, A.L. Shluger, A.N. Varaksin and Yu.N. Kolmogorov, Modeling and Simul. in Mater. Sci. Eng. 1 (1992) 29.
[20] A.L. Shluger, E.A. Kotomin and L.N. Kantorovich, J. Phys. C 19 (1986) 4183.
[21] E.V. Stefanovich, A.L. Shluger and C.R.A. Catlow, Phys. Rev. B 49 (1994) 11560;
A.L. Shluger, R.W. Grimes, C.R.A. Catlow and N. Itoh, J. Phys: Condens. Matter 3 (1991) 8027.
[22] P. Deak, L.C. Shyder and J.W. Corbett, Phys. Rev. B 45 (1992) 11612.
[23] P. Deak, B. Schröder, A. Annen and A. Scholz, Phys. Rev. B 48 (1993) 1924.
[24] L.N. Kantorovich and A.I. Livshicz, Phys. Status Sol. B 174 (1992) 79;
L. Kantorovich, E. Heifets, A. Livshicz, M. Kuklja and P. Zapol, Phys. Rev. B 47 (1993) 14875;
L. Kantorovich, A. Stashans, E. Kotomin and P.W.M. Jacobs, Int. J. Quant. Chem. 52 (1994) 1177.
[25] R.A. Evarestov, E.A. Kotomin and A.N. Ermoshkin, Molecular Models of Point Defects in Wide-gap Solids (Zinatne, Riga, 1983).
[26] A.N. Ermoshkin, E.A. Kotomin and R.A. Evarestov, Phys. Stat. Sol. B 103 (1981) 581.
[27] R.W. Roberts and J.H. Crawford, J. Nonmetals 2 (1974) 133.
[28] P. Edel, B. Henderson and R. Romestain, J. Phys. C 15 (1982) 1569.
[29] E. Sonder and W.A. Sibley, Point Defects in Solids, vol. 1 (Plenum, New York, 1972) p. 208.
[30] Y. Chen and R. Gonzalez, Opt. Lett. 10 (1985) 276.
[31] L.A. Kappers and E.B. Hensley, Phys. Rev. B 6 (1972) 2475.
[32] E.A. Kotomin, A.I. Popov and A. Stashans, J. Phys: Condens. Matter 6 (1994) L569.