Calculations of the ground and excited states of F-type centers in corundum crystals

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The semiempirical intermediate neglect of differential overlap method was used for calculating optical properties of F^+ and F centers (oxygen vacancy trapped one and two electrons, respectively) embedded into large quantum clusters, $Al_{26}O_{39}$. The geometry was optimized for both the ground and excited states of defects. Calculated absorption and luminescence energies obtained for F^+ and F centers are in good agreement with experimental data. Their energy levels lie in the gap between the upper valence band and conduction band, like for similar centers in MgO and alkali halides. It is shown that the oxygen vacancy in corundum crystals is able also to trap a third electron; experimental evidence for this is discussed.

Corundum (α-Al$_2$O$_3$, called also sapphire) crystals have a wide variety of technological applications as a structural, electronic, and optical material. Because of its characteristics such as transparency in middle IR and ultraviolet regions, maintenance of transparency under great doses of γ radiation and high-energy electron beams, corundum is used as a material for fusion applications and optical purposes. Cr-doped and Ti-doped α-Al$_2$O$_3$ is used as a laser material. Undoped α-Al$_2$O$_3$ has applications as an optical window material and as a substrate for epitaxial growth of Si on sapphire for electronic device fabrication. This crystal continues to attract a good deal of attention due to its use in highly sensitive thermostimulated luminescence γ-radiation detectors and in infrared fibers. Therefore, a complete understanding of the electronic structure and the degree of perfection of the crystal lattice of the crystal can help guide developments in many highly technological areas. Technological importance of corundum has stimulated numerous studies of its optical properties performed in the last years.[1−4] However, only few *theoretical* attempts have been made to understand the geometry and electronic structure of electron[5−7] and hole [8−11] centers created in corundum under irradiation. This is caused primarily by the complicated structure of corundum, its large unit cell (ten atoms) and mixed semi-ionic character of chemical bonding.

In this paper, the electronic structure of the two basic electron centers in corundum is studied which are called F^+ and F centers (one and two electrons trapped by an oxygen vacancy). We (i) calculate in a self-consistent way the atomic relaxation around these defects in the ground and excited electronic states, (ii) incorporate covalency effects in the chemical bonding, (iii) discuss the position of energy levels of F^+ and F centers with respect to the bands of the perfect crystals (there are contradictory opinions on this point[6]), and, last, check if the oxygen vacancy in corundum could trap a *third* electron, forming a negatively charged F^- center, similar to the F' center in alkali halides (two electrons trapped by a single-charged halogen vacancy v_a^+). Some experimental evidence for these F^- centers was given in Ref. 12.

The modified semiempirical method of intermediate neglect of differential overlap (INDO) has been used in this study[13] being combined with as large as 65-atom quantum clusters embedded into the electrostatic field of nonpoint charges of the rest of the corundum crystal. This technique based on molecular orbital (MO) approximation theory,[14] and using a new parametrization scheme[15] for calculating the electronic structure of perfect and imperfect crystals, allows us to obtain both optimized geometry and self-consistent electronic structure of point defects in insulating solids, as has been demonstrated recently for F-type centers in alkali halides,[16] Li$_2$O (Ref. 17), and hole centers in corundum.[9−11] Parameters for the pure corundum crystal were fitted[9] to reproduce basic properties of a number of Al- and O-containing molecules as well as the band structure of corundum and lattice parameters using the periodical, so-called *large-unit-cell* (LUC) model. Then a large stoichiometric cluster Al$_{26}$O$_{39}$ (i.e., 13 basic elements, Al$_2$O$_3$, of the corundum structure) was used for defect studies; the O atom in its center was removed and one or two electrons added to the cluster, assuming no *a priori* pattern of the electronic density distribution in the vicinity of the defect under study and about ionic relaxation in the surrounding lattice. Thus we overcame the shortcomings of macroscopic methods. The ions surrounding the O vacancy were allowed to relax in order to achieve a minimum of the total energy. The relevant computer code SYM-SYM, used for these studied, is based on a complete treatment of the system's point symmetry as described in Ref. 18.

Unlike alkali halides, F-type centers in the corundum structure have low, C_2 symmetry (Fig. 1) which results in the splitting of the excited p-like state into three levels. The oxygen vacancy has two nearest O atoms (the basic element of corundum is an O triangle with O-O bond length of 2.49 Å) and four nearest Al atoms, forming two kinds of Al-O bonds with lengths of 1.86 and 1.97 Å, respectively (experimental values). The performed relaxation of the atoms in a *perfect* crystal in the INDO calculations gave 1.76 and 1.86 Å for the Al-O bonds, respectively. We found that relaxation of these six atoms contributes predominantly to the lowering of the total energy when doing F-type defect calculations. To extend our basis set for F-type calculations, additional $2s$, $2p$ Slater-type atomic orbitals were centered at the O vacancy.[17] The orbital exponents of these functions were fit to the experimentally observed optical absorption energy ($1A \rightarrow 2A$ transition) and the spin density of the unpaired electron of the F^+ center on the nearest Al atoms.[7] The values of the exponents found, $\zeta(2s)=0.9$ (a.u.)$^{-1}$ and $\zeta(2p)=0.59$ (a.u.)$^{-1}$, are of the same order of magnitude as for the F center in alkali halides.[16] The same basis set was used for calculating absorption and luminescence energies for both F^+ and F centers. These energies were obtained as the difference of total energies for the self-consistent ground and excited states (ΔSCF method).

Table I shows the optimized geometry for both F^+ and F centers and their calculated optical properties. The calculated absorption energy of the F center, 5.9 eV, is in good agreement with the experimental value of 6.1 eV; the same is true for the luminescence energies for both F^+ and F centers. The inward relaxations of the two nearest oxygen atoms towards the vacancy are $\sigma=4.6$ and 2.2 % for the F^+ and F ground states, respectively (in units of the O-O distance in the perfect corundum). This occurs under angles $\alpha=5°$ and 25°, respectively (see Fig. 1). The oxygen displacements for the charged F^+ center naturally are larger than for a neutral F center; the same is true for the outward Al displacements ($\delta=5.2$; $\Delta=5.9\%$ for F^+ and 2.8; 1.8% for F, respectively, for two kinds of Al-v_0 pairs). As seen from Table I the absolute displacements of more distant atoms Al_1, Al_2 (0.12 Å) are *larger* than the relaxation of the closest ones (0.09 Å), which probably confirms the idea of a crystalline
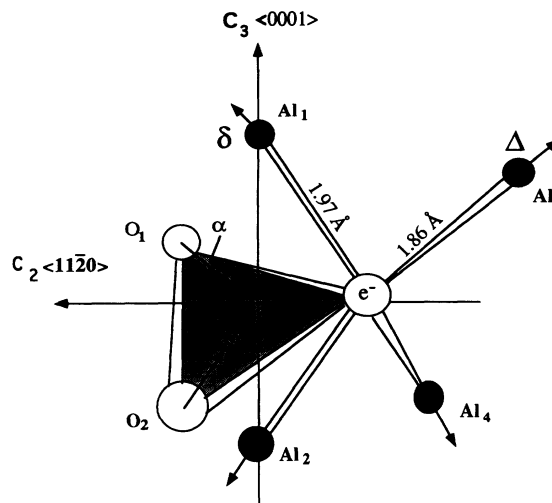

FIG. 1. Relaxation of six nearest atoms surrounding an O vacancy (with trapped electron) involves inward displacements σ of two O atoms from the same basic O triangle (shaded), and outward displacements of two pairs of Al atoms—Al(1), Al(2) (δ) and Al(3), Al(4) (Δ) which form in a regular corundum structure characterized by long (1.97 Å) and short (1.86 Å) Al-O bonds, respectively.

structure as resulting from a set of *structural elements* in the form of molecular units[20] (Al_2O_3, in the case of corundum) with strong atomic interactions inside these elements. This result stresses additionally the role of covalency in corundum chemical bonding which is stronger for short bonds.[11] The wave functions of the ground states are well localized within a vacancy, v_0, but that of the excited state of the F center is delocalized onto the nearest Al atoms. However, the adiabatic potential energy curve of the excited F center has a minimum, corresponding to displacements of surrounding atoms shown in Table I, from which the radiation transition to the ground state occurs (the calculated luminescence energy, 3.0 eV, is close to the experimental, 2.8 eV). The obtained splitting of the $2p$-excited state ($1B$-$1A = 2A$-$2B$) of the F^+ center, 0.3 eV, is twice less than experimental 0.6 eV; it is probably due to the simplified single-exponential wave functions used.

TABLE I. Optimized displacements of atoms surrounding F-type centers in corundum crystal simulated by a cluster [$Al_{26}O_{38}$] and the relevant optical transitions, in eV. The relevant displacements are shown in Fig. 1. The O atoms relax towards the vacancy under an angle α (shown in the table) and the Al atoms are displaced outwards along a line connecting them with the vacancy. Optical transitions are calculated as the difference of total self-consistent energies in the ground and excited states (ΔSCF method). Due to low symmetry the threefold degenerate $2p$ excited state of the F^+ center is split by the crystalline field into three states: $1B(p_z)$, $2A(p_y)$, and $2B(p_x)$. The asterisk indicates ground state and the double asterisk indicates excited state.

Defect	Displacements, %				Absorption, eV		Luminescence, eV	
	$O_{1,2}$	$\alpha,°$	$Al_{1,2}$	$Al_{3,4}$	Theory	Expt.[a]	Theory	Expt.[a]
	*4.6	5	5.2	5.9	$5.2(1A \rightarrow 1B)$	4.8		
F^+	**4.6	5	6.2	6.5	$5.5(1A \rightarrow 2A)$	5.4	$4.0\ (1B \rightarrow 1A)$	3.8
					$5.8(1A \rightarrow 2B)$	6.0		
F	*2.2	24	2.8	1.8	$5.9(1A \rightarrow 2A)$	6.1	$2.8\ (2A \rightarrow 1A)$	3.0
	**2.8	25	3.9	2.5				

[a]Reference 19.

The insignificant charge redistribution caused by the O vacancy is shown in Table II. The effective charges of both kinds of nearest Al atoms are only slightly decreased and those of two nearest O atoms increased (all by ≤ 0.05 e). Note the considerable deviation of the effective charges in the *perfect* corundum (the first column) from purely ionic charges $+3e/-2e$, which demonstrates clearly the covalency effects in its chemical bonding. In the ground state of the F^+ center 90% of the electron density is localized inside the vacancy, which is typical for F centers in alkali halides. However, in the F center about 0.4 e is spread over atoms nearest to vacancy.

Another test of our theory is the calculation of the activation energy E_a for luminescence quenching. As shown in Fig. 2, this is the distance between the minimum of the excited state and the crossing point of the ground state and excited potential energy curves. Our calculations estimate its value to be ≈ 0.6 eV, which is in good agreement with the experimental finding, 0.4 eV,[19] keeping in mind the many-coordinate character of the potential surfaces whose crossing we are searching for. Figures 2(b) and 2(c) demonstrate how the potential energy surface for the F^+ center depends on the three kinds of basic atomic displacements σ, δ, and Δ, shown in Fig. 1.

Figure 3 shows the position of energy levels of F^+ and F centers with respect to the bands of the perfect corundum crystal; the relevant procedure for placing defect levels is described in detail in Ref. 21. The ground state of the F center lies above that for the F^+ center by ≈ 2.2 eV, which implies that the F excited state falls into the conduction band (both have close absorption energy of ≈ 6 eV). This is in agreement with the experimental observation of photoconductivity observed after F excitation even at 10 K (Ref. 1). Since the relevant wave function of the excited F center is considerably delocalized, the crystalline field does not split this state, unlike the F^+ center. To demonstrate this, Fig. 3(b) shows the *expected* splitting of the F^+ excited state as a function of its Slater-type atomic orbital's exponent $\zeta(2p)$; splitting is rapidly reduced when the wave function is delocalized (the orbital exponent decreases), like it occurs in the F center.

It is important to stress here that our pattern of F-type center levels falling into a gap between the upper valence band and the conduction band is in line with that for F centers in alkali halides[16] and cubic oxides[22] but contradicts the model[6] arguing for an F^+ center ground state

TABLE II. Effective charges on ions surrounding the O vacancy (in units of e).

	Perfect crystal	F^+ center	F center
Al(1),Al(2)	2.35	2.30	2.32
Al(3),Al(4)	2.36	2.29	2.26
O(1),O(2)	-1.57	-1.55	-1.54
Vacancy[a]		-0.90	-1.57

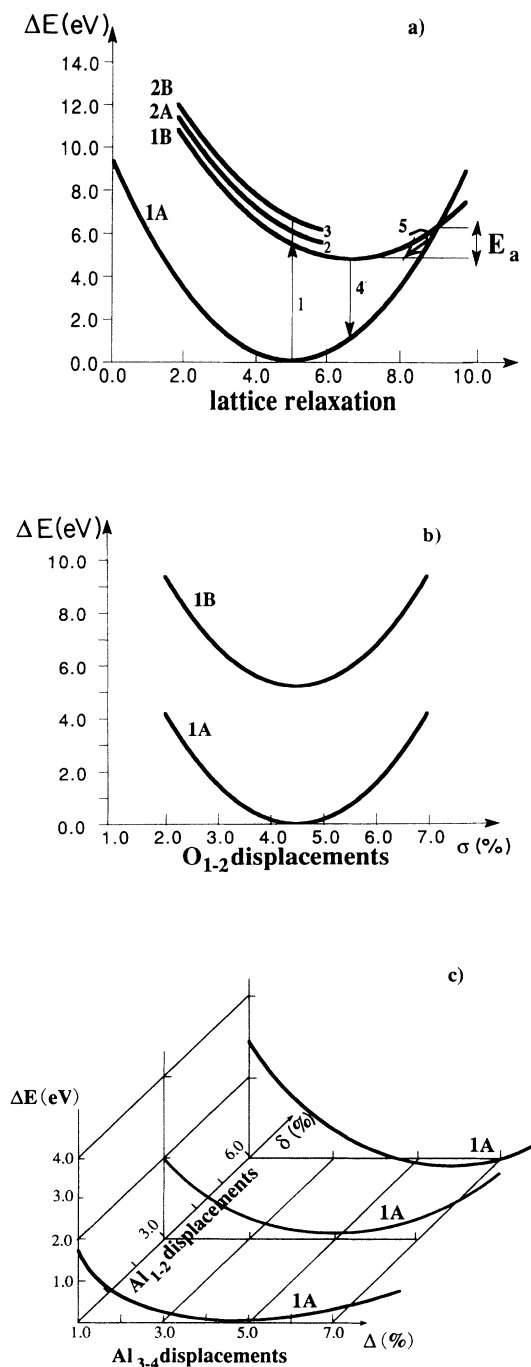[a]A number of electrons localized by a vacancy. Mulliken population analysis is used.

FIG. 2. (a) General sketch of the potential energy curves for an F^+ center showing three absorption bands (1,2,3) corresponding to transitions $1A \rightarrow 1B$, $2A$, $2B$, respectively, as well as the luminescence transition 4 $(1B \rightarrow 1A)$. Thermal quenching of the luminescence is shown by arrow 5; the relevant activation energy E_a is shown. Numerical results are given in Table I. Note that x coordinate denotes a lattice relaxation combining *three* kinds of displacements (σ, δ, Δ) of six nearest atoms. (b) The same as (a) as a function of displacement σ of the two O atoms (in units of the distance between two regular O sites, 2.49 Å). (c) The same as (a) as a function of two kinds of cation displacements: of closer atoms Al_3, Al_4 (δ) and more distant atoms Al_1, Al_2 (Δ), in units of the lengths of regular Al-O bonds.
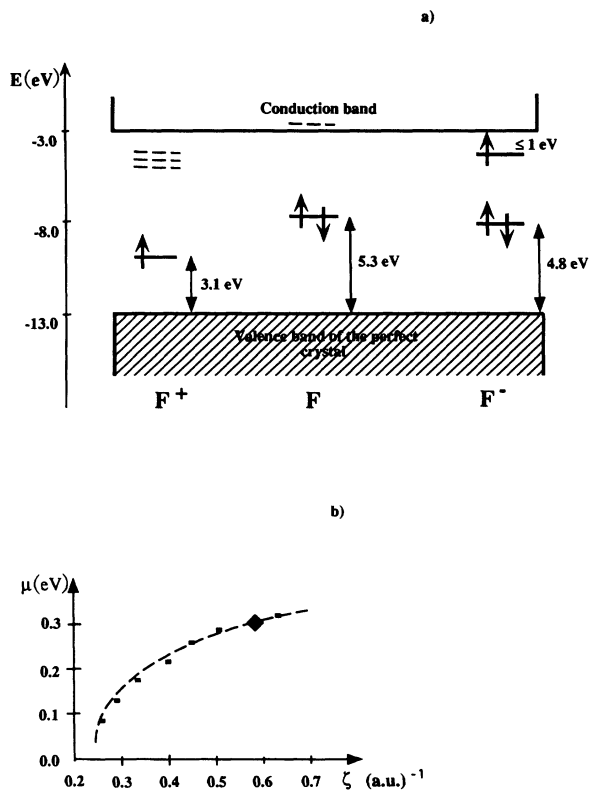
FIG. 3. (a) Position of levels of F-type centers with respect to the perfect corundum bands. Dashed levels are for the unoccupied states. (b) The energy splitting of threefold degenerate F^+ excited state μ $(2A\text{-}1B \cong 2B\text{-}2A)$ as a function of the degree of localization of the excited state, measured by $\zeta(2p)$. ◆: Optimized value.

lying *below* the upper valence band (which may result from overestimated Madelung field used in the calculations[6]).

Last, we have simulated a hypothetical F^- center adding one more electron to the F center. We found that the ground state of the F center does not shift considerably,

whereas an additional electron occupies the local state close to but below the bottom of the conduction band. The existence of such a center was discussed in Ref. 23, whereas in Ref. 12 to this center thermostimulated luminescence and electron emission peaks at 255–260 K were ascribed. Absence of the relevant absorption peak is clear from Fig. 3(a)—we expect it to fall into the IR optical region.

In summary, we have demonstrated in this paper that due to the semi-ionic character of the chemical bonding the interaction between atoms within the structural element $(Al_2O_3$ molecular unit) is stronger than between atoms belonging to different structural units. This is seen from the larger displacements of the Al(1) and Al(2) atoms belonging to the basic molecular unit which contains O vacancy as compared to the relaxation of the Al(3) and Al(4) which are closer to the O vacancy. As a whole, the magnitudes of the atomic displacements are similar to those in alkali halides[16]—anions are moving towards vacancy while cations are relaxing away from it by several percent of interatomic distance. The observed splitting of the excited F^+ center state is due to its deep position in the energy gap (≈ 1 eV below the bottom of conduction band). We came to this inference due to simulation of the delocalization of the wave function of the excited F^+ center state as a function of its orbital exponent, ζ. When reducing ζ the distance between the F^+ center excited state level and the conduction band diminishes and the wave function becomes more diffuse and the simultaneous reduction of the splitting of the excited state happens as shown in Fig. 3(b). Obviously, the effect of low local symmetry is thus reduced and leads to only a broadening of the F^+ absorption band. The calculation of the F^- center demonstrates clearly the existence of such a defect which is formed from the F center by trapping the third electron.

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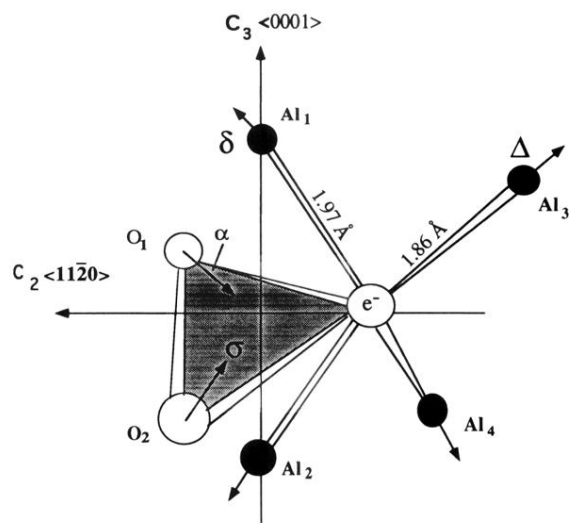
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