



Radiation-induced point defects in simple oxides

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Abstract

We present a survey of recent theoretical studies of radiation-induced point defects in simple oxides with emphasis on highly ionic MgO, partly-covalent corundum (Al_2O_3) and ferroelectric KNbO_3 . The atomic and electronic structure of the electronic (F^+ and F centers) and hole centers, as well as interstitial atoms therein are discussed in light of the available experimental data. Results for defect diffusion and photo-stimulated $\text{F}^+ \rightarrow \text{F}$ center conversion are also analyzed. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metal oxides have a wide-ranging importance in many areas of physics, geophysics, chemistry and technology. They are important as catalysts, as ceramics, high- T_c superconductors, are potential fusion reactor materials and have relevance to microelectronics. Irradiation of these materials by energetic particles leads to the displacement of an atom into an interstitial position leaving a vacancy behind, and forming what is commonly called a *Frenkel defect* [1–5]. In the oxygen sublattice this could result in the formation of three kinds of Frenkel defect pairs. These comprise a neutral interstitial O_i atom and V_0 vacancy, or a

vacancy with one or two trapped electrons (the so-called F^+ and F centers) and their complementary O_i^- and O_i^{2-} defects. There exist many reports on F-like centers in refractory oxide crystals, including MgO, CaO, BaO [1–7], BeO [8–10], ZnO [11], Al_2O_3 [12–15], Li_2O [16–20], as well as in less-studied ZrO_2 [21], TiO_2 [22], the ternary oxide LiAlO_2 [23], yttria-stabilized zirconia [24], aluminium oxy-nitride $\text{Al}_{23}\text{O}_{27}\text{N}_5$ [25], and other materials.

The characteristic feature of the F-type center is a strong localization of electron(s) inside a vacancy, at least in its ground state. It should be mentioned here that in some oxides (GeO_2 , TiO_2 , BaTiO_3) it is questionable whether the term F center is applicable to the observed defects; because in partly-covalent solids an electron trapped by the V_0 is likely to sit mainly on a ‘broken’ bond (see [26] and references therein, as well as Section 5).

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The simplest F-aggregates are called *dimers*, or F₂-centers. In the cation sublattice one expects formation of pairs comprising interstitial cations and complementary cation vacancies. The latter are known to trap holes created under irradiation and thus readily transform into the so-called V⁻ or V⁰ centers (a cation vacancy with one and two holes, respectively) [2,27].

Formation of Frenkel defects is characterized by their *threshold energies* given in Table 1. (Another analysis for some oxides, SiC and diamond see[12].) Absorption and luminescence energies are collected in Tables 2 and 3. Usually the F⁺ absorption band lies on the long-wavelength side of that for the F center and its energy obeys the simple empirical (Mollwo-like) law [51]:

$$E_{\text{abs}}(\text{eV}) = 44.4a^{-2} - 3.5a^{-1}, \quad (1)$$

where $a = n^{-1/3}$ is a mean distance between two O atoms and n their concentration in the crystal. Of a wide class of binary and ternary oxides we will focus here on three representatives – highly ionic

Table 1
Displacement energy for some oxygen compounds

Material	Displacement energy (eV)		
	Metal	Oxygen	References
Al ₂ O ₃	18	75	[28]
		70	[29]
		90	[30]
	24	79	[31]
		41–53	[32]
MgO	64	53	[33]
		60	[34]
	60	53	[36]
	37	55	[37]
		30	[39]
CaO		58	[38]
		50	[40]
CaO–Mg	65	33	[40]
MgAl ₂ O ₄		59 (77 K)	[41]
		130 (300 K)	[41]
ZnO	57	57	[11]
BSO (Bi ₁₂ SiO ₂₀)		49	[42]
LiNbO ₃		53	[43]
KNbO ₃		64	[44]
BaTiO ₃		60	[45]
BeO		76	[6]
UO ₂	40	20	[7]

MgO, partly covalent corundum (α -Al₂O₃) and the perovskite ferroelectric KNbO₃. The latter has numerous electro-optic and non-linear optic applications [52,53]. As the temperature is lowered, KNbO₃, as most ferroelectrics, undergoes a sequence of phase transitions.

In 1983, Crawford Jr. gave a review talk at one of the first REI conferences [14] summarizing current understanding of defects in oxides (see also his reviews [13]). Crawford has raised a number of questions. In this paper, we discuss progress achieved in recent years due to greatly increased theoretical understanding and computer facilities, and suggest answers to some of these problems.

2. Theoretical methods

Substantial theoretical attention has been paid to the F⁺, F centers in MgO in the last few years, when a number of careful theoretical calculations have been performed, some of them from the *first principles* or ab initio [54]. However, such calculations are unavoidably restricted to quite small *quantum clusters* or periodic systems called *super-cells*, which do not allow the study of excited states. Another technologically important characteristic of electron centers in oxide crystals which cannot be handled by modern ab initio methods is defect *diffusion*. Currently, there is a single theoretical attempt to calculate the activation energy for F⁺ and/or F-center diffusion in MgO crystals.

This demonstrates that a relatively simple theoretical approach is greatly needed, allowing us to study large quantum clusters (about 100–200 atoms) and complex defects (like dimers). On the other hand, the method should be able to optimize the defect geometry (in both the ground and excited states) through a minimization of the total energy, and to reliably calculate excited states so as to obtain absorption and luminescence energies. Such an approach to large-scale simulations of static and dynamic properties of defects in ionic solids has been elaborated in recent years at the University of Latvia in Riga. This is based on the semi-empirical quantum chemical method of Intermediate Neglect of the Differential Overlap (INDO) [55,56], and it has been applied very successfully to the

Table 2

Experimental measurements of optical properties for single-vacancy centers in oxides, energies are in eV

Material	F center		F ⁺ center	
	Absorption	Luminescence	Absorption	Luminescence
MgO	5.0 [13]	2.3 [13]	4.9 [13]	3.1 [13]
CaO	3.1 [13]	2.1 [13]	3.7 [13]	3.3 [13]
SrO	2.49 [3]		3.0 [3]	2.42 [3]
BaO	2.3 [3]		2.0 [3]	
BeO	6.6 [9]	5.0,3.4 [9,10]	5.4 [9]	3.9 [9]
Al ₂ O ₃	6.0 [14]	3.0 [14]	6.3, 5.4, 4.8 [14]	3.8 [14]
Li ₂ O		3.65 [19]	4.00 [17]	3.26 [19]
LiAlO ₂		4.43 [46]	5.25 [20]	3.26 [46]
MgAl ₂ O ₄	5.3 [14]		4.8 [14]	
Al ₂₃ O ₂₇ N ₅	5.46 [25]		5.00 [25]	
Y ₃ Al ₅ O ₁₂			6.2, 5.28, 3.35 [47]	

Table 3

Experimental measurements of optical properties for dimer centers in oxides, energies are in eV

Material	F ₂		F ₂ ⁺		F ₂ ²⁺	
	Absorption	Lumin	Absorption	Lumin	Absorption	Lumin
MgO	3.63 [48]	3.31 [48]		2.61 [49]	3.82 [49]	2.81 [49]
Al ₂ O ₃	4.1 [50]	2.4 [50]	3.5 [50]	3.26 [50]	2.7 [50]	2.22 [50]
MgAl ₂ O ₄	3.45 [13]	3.3 [13]				
Al ₂₃ O ₂₇ N ₅	4.1 [25]		3.68 [25]	3.13 [25]		
Li ₂ O	3.31 [18]		2.16 [16]			

study of defects in many oxide materials, including MgO, SiO₂, Li₂O, ZrO₂, TiO₂, α -Al₂O₃ etc. The INDO method is based on a Hartree–Fock-type formalism and allows self-consistent calculations of the atomic and electronic structure of point defects and the position of defect levels with respect to the perfect crystal energy bands, as well as the electronic density/spin distribution. This method permits easy calculations of both clusters (CLUSTERD code [57,58]) and periodic defects using the so-called large unit cell (LUC) model (SYMSYM code [59]). The absorption and luminescence energies are calculated as the difference of total energies for the relaxed atomic ground and excited states, respectively (Δ SCF method).

Another very useful method is based on a *shell model* [60] and on pair-potentials (PP). It uses the Mott–Littleton strategy as implemented in the computer code Cascade [61]. Details of this approach are given in [62]. PP calculations allow a

careful account of the ionic relaxation in a very large region around the defect and give accurate estimates for the electronic and ionic polarization of the crystal by a defect. On the other hand, it needs a parametrization for defect atom potentials which could be done with INDO calculations. The latter also control the applicability of the PP approach (which assumes that the charges of ions under consideration are the same as those used in parameterization).

3. Defects in MgO

3.1. Optical properties of F⁺ and F centers

In recent INDO calculations [63,64] of the optical properties of F⁺ and F-centers in MgO 125-atom clusters of a cubic shape with a high (O_h) point symmetry and including nine spheres of atoms

around the defect at the coordinate origin were used. These clusters were embedded into the electrostatic field of a non-point infinite crystalline lattice. In the F-type center simulations, the central O-atom 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. The ions surrounding the O-vacancy were allowed to relax in order to obtain a minimum of the total energy, as well as the self-consistent electronic and atomic structure of the defect. The INDO computer code SYM–SYM is perfectly suited for such computer simulations, as it is based on a complete treatment of the point symmetry and automated defect geometry optimization [65]. The optimized geometry of a bare O-vacancy, and that which trapped one and two electrons, shows that mainly the six nearest-neighbor (NN) cations are displaced in a direction outwards from the vacancy. Naturally, for a double-charged V_0 defect, the surrounding atomic relaxation is the largest, 6.5% of the Mg–O spacing for the nearest Mg ions, but it is reduced to less than 2% for the neutral F center. Atoms of three spheres surrounding O-vacancy are found to be noticeably relaxed, even in the ground state of these F-type centers.

The relevant charge distribution analysis (Table 4) demonstrates clearly the ionic nature of the MgO crystal and that one (two) electrons are well-localized by O-vacancy in the ground state of the F^+ (F) center with a very moderate change in the effective charges on atoms surrounding the vacancy. This is no longer true, however, for their *excited* states: about $0.5e$ is delocalized from the V_0 over the cations surrounding F^+ center, which

results in the reduction of their effective charges (by $0.1e$ on each atom). In the singlet excited state of the F center $0.7e$ is delocalized. An analysis of the spin density distribution for the ground state of F^+ center shows that 90% of the unpaired electron lies inside the O-vacancy but only 44% in its excited state. The INDO calculations place the ground state levels of both the F^+ and F-centers at 3 eV above the top of the valence band. Similar results were recently obtained using the much more refined super-cell multiple-scattering theory. The potential energy curves as a function of the full-symmetry A_{1g} -relaxation for the F^+ and F-centers are discussed in [63,64]. They confirm that the excited states lie very close to the conduction band, in agreement with the experimental data [66–70], placing the F excited state only 0.06 eV below the bottom of the conduction band. This explains why these excited states are delocalized.

The luminescence energy for F^+ exceeds the experimental value (3.2 eV) by 0.4 eV (Table 5). Calculations of the excited F-center predict the singlet luminescence peak at 2.61 eV and the triplet one at 2.73 eV. The only observed experimental emission band is at 2.3 eV; very probably singlet and triplet bands are too close to be resolved (the width of the experimental emission band is about 0.6 eV). The calculated energies at the minimum of the relaxed singlet and triplet states differ by only 0.04 eV; this probably explains why the optically-detected magnetic resonance (ODMR) experiments indicate that ‘the emitting state is not predominantly a triplet’ [71]. INDO calculations for electron centers in Li_2O are discussed in [18]. F-type centers in complex oxides (La_2O_3 and ZrO_2) have also been calculated [72,73].

Table 4

Effective charges (in units of e) on atoms surrounding the V_0 , F^+ and F centers in MgO in the ground and excited states. (The basis set for F^+ and F centers included 1s and 2p atomic orbitals centered on the O-vacancy [63,64])

Atom/center	Perfect MgO	Ground state			Excited State		
		V_0	F^+	F	F^+	F (singlet)	F (triplet)
Mg (1,0,0)	1.831	1.808	1.823	1.838	1.715	1.701	1.674
O (1,1,0)	–1.829	–1.835	–1.826	–1.819	–1.824	–1.817	–1.816
Mg (1,1,1)	1.831	1.823	1.828	1.832	1.828	1.832	1.831
Vacancy	–	–0.002	–1.002	–2.002	–0.476	–1.268	–1.127

Table 5

Calculated absorption and luminescence energies in MgO and Al₂O₃ (in eV) [64,65]

	MgO		Al ₂ O ₃	
	F ⁺	F	F ⁺	F
Absorption	4.97	4.98	5.2,5.5,5.8	5.9
Luminescence	3.60	2.61 (singlet) 2.72 (triplet)	4.0	2.8

3.2. F-type center diffusion

In the INDO simulation of defect diffusion, large 224-atom clusters of C_{2v} symmetry were employed [74,75]. They include several spheres of atoms around *both* a vacancy and its NN O-atom with which it exchanges positions. The effective charge of an O-atom in the saddle point (half the distance between two regular O sites along the (1 1 0) axis) which is the top of the energy barrier is found to remain practically the same as at the lattice site. The activation energies for defect diffusion, E_a , are shown in Table 6. The V_0 -energy is very close to the experimental value of 2.4 eV. The other two energies (F⁺ and F) are not well established experimentally. However, it has been observed that in additively colored MgO crystals, the complex (F⁺ + F) absorption band begins to decay only at 900°C [76]. Using the standard expression for the hopping frequency, $\nu = \nu_0 \exp(-E_a/kT)$ with the pre-factor of the order of LO phonons ($\nu_0 \cong 10^{13} \text{ s}^{-1}$) one can estimate that $E_a \cong 3 \text{ eV}$. This is again in qualitative agreement with the calculated values.

Table 6

Calculated activation energies for defect diffusion hops (in eV) in MgO ^a,

Defect	Theory	Experiment
Cation vacancy	2.43	2.1–2.3
Anion vacancy	2.50	2.4–2.6
F ⁺ center	2.72	ca. 3.0
F center	3.13	ca. 3.0
Interstitial cation	0.43 (<i>i</i>), 0.75 (<i>d</i>)	
Interstitial anion	0.54 (<i>i</i>), 1.17 (<i>d</i>)	

^a *d*=direct hops, *i*=interstitialcy mechanism [74,91] (see text for explanations)

3.3. Interstitial oxygen diffusion

Interstitial anions have been reliably identified in alkali halides and alkaline-earth halides (neutral atoms, called the H centers, and ions, called I centers). In oxides, there exist indirect data indicating the radiation-induced production of interstitials as follows. (1) Okada et al. [77] have studied neutron-irradiated MgO : Mn²⁺ and observed that the absorption bands largely differ from those in unirradiated crystals due to the transitions of 3d electrons in Mn²⁺ impurity at the octahedral sites. Supposing that irradiated MgO contains a number of Frenkel defects, it was deduced that interstitial oxygen neighboring the Mn²⁺ ion perturb significantly the d-transitions in Mn²⁺ ions. Besides, a study of the effect of neutron irradiation on d-transitions in MgO : Cr³⁺ suggests also the presence of two types of defects attributable to an *interstitial-Cr³⁺-F center* complex [78]. (2) Halliburton and Kappers [79] demonstrated the presence of interstitial oxygens in neutron-irradiated MgO, which grew slightly in the temperature region from RT to 470 K, and then disappeared in the temperature range 470–640 K, accompanied by the decrease of the F-type centers. (3) Lastly, Evans and Stapelbroek speculated on rather indirect evidence that the absorption band at 4.1 eV in neutron-irradiated corundum is possibly associated with a complex involving an Al interstitial [80].

The radiation Frenkel defects complementary to F-type are oxygen interstitials. In his talk Crawford stressed that much more effort is needed to shed light on the identification, formation and aggregation of interstitials in oxides. There is practically no direct experimental information about these defects; also is not clear in what charge state interstitial oxygens leave the vacancy (i.e., O²⁻,

O^- , or neutral atom, O^0). To understand better the situation, several computer simulations were undertaken. The two different techniques were used: for a double-charged oxygen interstitial, O^{2-} , PP method was employed, whereas for a neutral atom which is chemically active and can form a chemical bond with a host O atom, ab initio methods were used.

3.3.1. Charged ion

PP calculations for charged oxygen interstitial [81–84] have shown that Frenkel pairs which are closer than 4th NN are unstable with respect to a recombination which restores the perfect lattice. This could be one of the reasons for the high radiation stability of MgO. Calculations of the interstitial ion diffusion have demonstrated that direct ion jumps along the (0 0 1) axis with a face center as the saddle point (Fig. 1(a)) are not energetically favorable (Table 6). An activation energy lower by a factor of 2 corresponds to the so-called *collinear interstitialcy mechanism* (Fig. 1(b)) when an interstitial moves from a cube center along the (1 1 1) body diagonal and in its saddle point forms a dumbbell with a host ion. Such a low activation energy indicates that such interstitials are highly mobile even at liquid nitrogen temperature. The activation energy for Mg_i^{2+} is close in magnitude to that for oxygen. Lastly, calculations on the vacancy and interstitial dimers and quartets reveal

considerable binding energies thus indicating that radiation-induced bubbles and dislocation loops can form quite efficiently in oxides.

3.3.2. Neutral atom

Calculations for neutral oxygen interstitials were done using the two first-principles methods and (mainly) 16-atom supercells: the Hartree–Fock method [85] and a full-potential linear-muffin-tin-orbital (FP LMTO) method [86] based on a local density approximation for treatment of exchange and correlation. Both methods were earlier successfully used in MgO studies. From calculations for three possible equilibrium configurations of the interstitial oxygen atom—cube center (cc), face center, and a dumbbell on a lattice site – it was found that the dumbbell, O^-O^- , configuration is the energetically most favorable. This dumbbell is a result of chemical bonding between atoms and is remarkably similar to interstitial halide atoms (H centers) in alkali halides [5]. The fact that the dumbbell is accommodated readily in the MgO lattice seems to be the reason why no appreciable volume change occurs in irradiated MgO [87].

Both methods agree in this conclusion and even in the equilibrium distance between the two O atoms (Table 7). In a model of a 16-atom supercell a dumbbell is oriented along the (1 1 1) axis (this is why it is called also a volume dumbbell, vd).

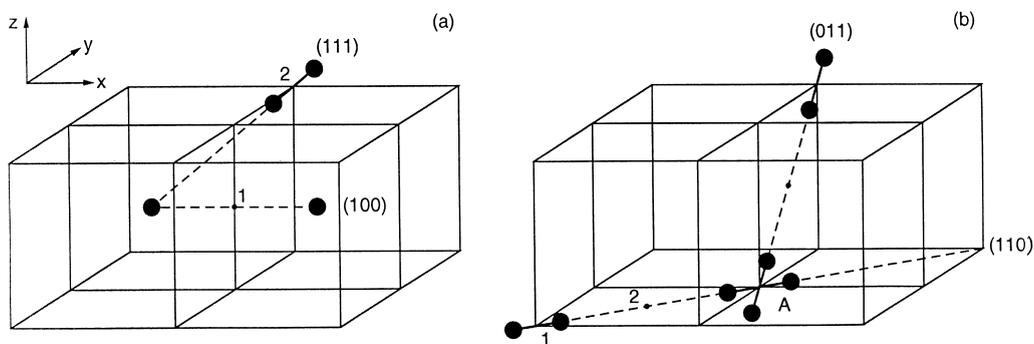


Fig. 1. A schematic of possible configurations of interstitial oxygen atoms in MgO. (a) Diffusion hops of charged interstitial ions along the (1 0 0) axis by a direct diffusion mechanism, with 1 as the saddle point. The alternative collinear interstitialcy mechanism with hops along the (1 1 1) axis, 2 is the relevant saddle point. (b) Proposed diffusion mechanism for a neutral interstitial atom forming a dumbbell configuration. 3D diffusion is a combination of dumbbell rotation in a lattice site A and hops along the (1 1 0) axis with the saddle point 2.

Table 7
Energetics and geometry for the interstitial oxygen atom in MgO, in various configurations

Defect configuration	E (eV)		d (Å)	
	HF	LMTO	HF	LMTO
f	2.30	1.45	–	–
fd	0.09	0.15	1.38	1.37
vd	0	0	1.39	1.36

^a d is the distance between two atoms in a dumbbell. Defect energies are given with respect to the ground state [88]. Notations: v = volume-centered, f = face centered, d = dumbbell

LMTO [89,90] gives the (1 1 0) oriented dumbbell (face dumbbell, fd) to be by 0.15 eV higher whereas HF [83,91] estimates the difference as 0.09 eV only. (It should be stressed that the energy balance between the two dumbbell orientations is a very delicate problem which depends in particular on the size of the supercell and the number of surrounding atoms allowed to relax: Very time-consuming HF calculations for 32 atom supercells reveal that the (1 1 0) configuration becomes lower in energy, with the hop energy of 2 eV [83,91].) The 3D diffusion of dumbbells (Fig. 1(b)) happens by the sequence $vd \rightarrow fd \rightarrow f \rightarrow fd \rightarrow vd$ (where f is the interstitial atom in the face center position) with occasional rotation of the dumbbell on a site. The $fd \rightarrow f$ hop is the limiting factor; its activation energy lies between 1.45 eV (LMTO) and 2.3 eV (HF), which is much larger than that for a charged interstitial. It is interesting to note that the calculated diffusion energy of 1.45 eV is close to the activation energy of 1.6 eV observed in [87] and ascribed to the diffusion-controlled recombination of O-related defects. In all three configurations (fd, vd and cc) oxygen atom attracts electron density from neighboring atoms and transforms into something like O^- ion, an effect which cannot be found in PP calculations.

3.4. Bound hole polarons

The basic defect in the cation sublattice of MgO is a vacancy which has trapped one or two holes (V^- and V^0 centers, respectively and called also a bound *small-radius hole polaron* and *bi-polaron* [5]). Interest in polarons and bi-polarons in oxides

has greatly increased in recent years due to their possible relevance to high- T_c superconductivity. The atomic structure and optical properties of V^- and V^0 centers were calculated by the INDO method [92] using large 104-atom stoichiometric clusters. It is found that an O^- ion on which a hole has been trapped in V^- center is closer by 3% of the Mg–O distance in the perfect crystal to the cation vacancy than the other five O^{2-} ions surrounding the vacancy. In the bipolaron, V^0 center, in its singlet state (lowest in energy) the two O^- ions on which two holes are sitting are located on the opposite sides of the cation vacancy. They are shifted towards the vacancy by 2% of the Mg–O distance. The calculated absorption energies are in excellent agreement with the relevant experimental data for V^- and V^0 : $E_{\text{abs}} = 2.3$ and 2.18 eV, to be compared with the experimental values of 2.3 and 2.3 eV, respectively. The same is true for the thermal ionization energies: 1.6 and 0.8 eV (cf. with experimental 1.4 and 0.95 eV, for V^- and V^0 , respectively) [93].

4. Defects in corundum

In corundum each O atom is surrounded by four Al atoms forming two kinds of Al–O bonds of length 1.86 and 1.97 Å. This is why in corundum – unlike alkali halides – F-type centers have low C_2 symmetry. Besides, an O vacancy has two nearest neighbor O atoms, forming the basic O triangle with O–O band length of 2.49 Å in a perfect corundum. Thus, the F-type centers are surrounded by *six* nearest atoms which determine mainly their optical properties.

4.1. F^+ and F centers

Calculations of atomic and the electronic structure of F-type centers were performed by means of INDO method using 65 atom clusters [94]. Table 4 shows the calculated absorption and luminescence energies for F^+ and F centers. Due to the low local symmetry, the $1s \rightarrow 2p$ absorption band of the F^+ defect is split into three sub-bands (Fig. 2) whose energies are reasonably well reproduced in our INDO calculations. Theory reproduces very well the luminescence energies of both F^+ and F cen-

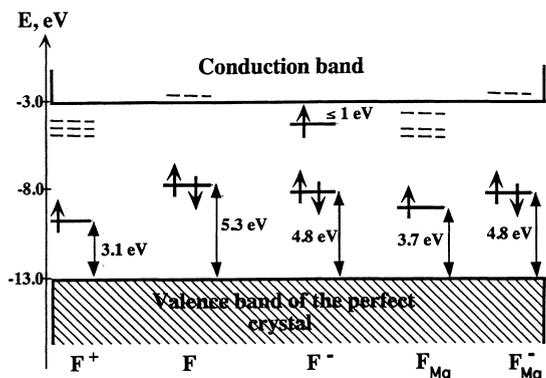


Fig. 2. Calculated positions of F-type center levels with respect to the perfect corundum bands. Dashed lines are excited states.

ters, and the activation energy for the F^+ luminescence quenching, $E_a \cong 0.6$ eV (the experimental value is 0.4 eV) [12–14]. Positions of the local energy levels for F-type centers in corundum are shown in Fig. 2. It shows that the excited states of the F^+ center are well localized within the gap, whereas the excited state of the F center is degenerate with the conduction band. This is in agreement with the photoconductivity observed after F excitation even at 10 K. Since the relevant wavefunction of the excited F center is considerably delocalized, the crystalline field does not practically split its 2p state, resulting in a single absorption band. It is important to stress here that our pattern of F-type center levels falling between the conduction band and valence band is in line with that for F centers in alkali halides and cubic oxides, including MgO but contradicts the model [95] arguing for the F center ground state position below the upper valence band.

We simulated also a hypothetical F^- center (O vacancy with *three* electrons) and found its ground state level to be about 1 eV below the bottom of the conduction band. The existence of this defect was discussed in [2]; in [96], thermostimulated luminescence and electron emission peaks at 255–260 K were ascribed to this center. Analysis of the effective charges of ions shows that in a perfect crystal they are Al 2.35e and O $-1.57e$, i.e., far from expected in the purely ionic model (Al $+3e$ and O $-2e$). Formation of the O vacancy does not affect much this charge distribution since in

the ground state of the F^+ and F centers 90% and 80% of the electron density is localized within vacancy, respectively.

4.2. Photo-stimulated electron center conversion

In his talk [14] at the REI meeting in 1983, Crawford Jr. called a *puzzle* the effect that optical excitation of one-electron F^+ centers in corundum and MgO crystals results in the formation of two-electron, F centers. This process of color center photoconversion is accompanied by the formation of *hole* centers [97,98]. The latter excludes the simple explanation that thermal ionization of excited F^{++} centers is followed by a further electron trapping by another F^+ center. In order to shed more light on this phenomenon, we have performed large-scale semi-empirical simulations of oxide crystals with F-type centers [63,64,99]. Based on these calculations, the following model is suggested (Fig. 3). The positively charged F^+ centers perturb surrounding atoms which results in the formation of several quasi-local energy levels in the upper part of the oxygen valence band shown as *a*, *b*, *c* in a panel *a* of the Fig. 3. These states consist mainly of the atomic orbitals of O atoms surrounding the F^+ centers. Optical excitation can result not only in the intrinsic transition **1** to the excited states (panel *a*), but in the electron transition from quasi-local levels *a*, *b*, *c* to the *ground* state level of the F^+ center which transforms it into the F center – see the panel *b*. Simultaneously, a *hole* is produced on one of the quasi-local levels *a*, *b*, *c* (panel *c*). At the next stage the hole escapes to the valence band (to which it is energetically degenerate) and either becomes self-trapped, or trapped by a cation vacancy or an impurity. Tunneling recombination of this hole with an electron of a nearby F center is then very probable [99]. Our model is supported not only by the hole center observation but also by the fact that the energy spectrum of the $F^+ \rightarrow F$ transformation in corundum not only covers the region of the F^+ intrinsic absorption (4.8–6.0 eV) but extends to *both* longer and shorter wavelengths, as follows from our calculations. The application of this model to MgO and corundum is discussed in [63,99].

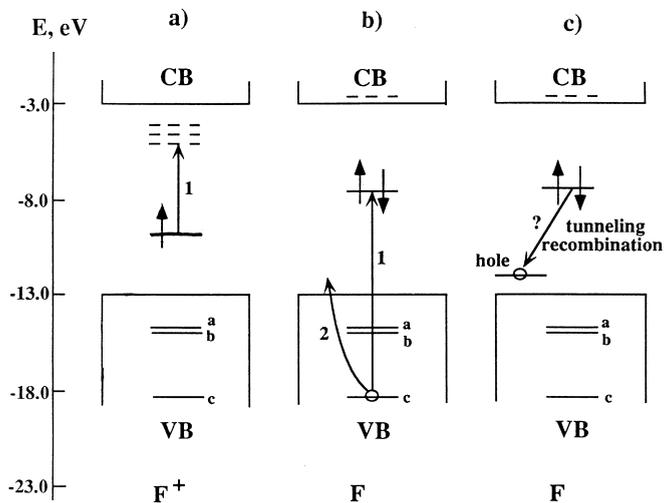


Fig. 3. A proposed mechanism of the $F^+ \rightarrow F$ center conversion under photostimulation in the F^+ absorption band in corundum [99]. Full lines are ground states and broken lines are excited states, a , b , c stand for the quasi-local states in the valence band induced by a charged F^+ center.

4.3. Dimer centers

In the corundum structure two kinds of dimer, F_2 centers could arise – those with oxygen vacancies lying in the same basal plane, and in two adjacent planes along the c -axis. Only the latter dimers, characterized by high optical anisotropy, have been observed experimentally up to now [100,101]. Both kinds of dimers were simulated by means of the INDO using 65 atom clusters [65,102]. Depending on the number of electrons trapped by two vacancies, three different charge states of each dimer were studied: neutral F_2 (four electrons), F_2^+ (three electrons), and F_2^{2+} (two electrons in two vacancies). For both kinds of dimers (vacancies in the same O-plane and adjacent-plane vacancies) we found that absorption and luminescence energies *decrease* considerably with the decrease in the number of trapped electrons. Three absorption bands are predicted to exist for each dimer center with a splitting ≤ 1 eV. Besides, for the F_2^{2+} center we predict an additional band in the IR region, as is characteristic of M centers in alkali halides.

In the series $F_2^{2+} \rightarrow F_2^+ \rightarrow F_2$ the ground state energy levels move monotonically up in the optical gap and their excited states become closer and closer to the conduction band. Charge distribution

analysis shows that in the ground state $0.5e$ of four electrons is delocalized over the atoms surrounding the F_2 center, but $0.3e$ for F_2^+ and $0.1e$ for F_2^{2+} .

4.4. F_{Mg} centers

In Mg-doped corundum F-type centers are observed in which a Mg^{2+} ion substitutes for a regular Al^{3+} nearby the O vacancy [15]. The fundamental problem is, what is the net charge of this defect; i.e., is it Mg^{2+} near an F^+ (a neutral F_{Mg} center) or near an F center (negatively charged F_{Mg}^-)? To answer this question, INDO simulations were undertaken [65,102,103]. The main finding is that the two defects reveal quite different absorption and luminescence bands and only the *neutral* center fits the experimental data. The effect of a Mg^{2+} ion is to lower the absorption and luminescence energies of the F^+ center by ≈ 0.2 eV. Additionally, the third absorption band around 6 eV is predicted for this defect, similar to an isolated F^+ center.

4.5. Hole centers

One of the long-debated problems in oxides is whether holes could be self-trapped as in alkali ha-

lides, or not [15]. For this purpose, a series of the INDO and PP studies were done [104,105] (see a review in [106]). Briefly, theory supports self-trapping which is energetically favorable, in the form of a two-site, molecular polaron similar to the V_K center in alkali halides. Formation of small-radius hole polarons in corundum is supported also by thermostimulated experiments [107]. However, direct evidence like Raman experiments is absent at present.

Besides, the atomic structure of holes trapped by Mg impurities has been studied [108–110]. The choice is between a one-site (*atomic*) polaron with a hole localized by a single O^- atom, and a *molecular* polaron where a hole is shared by the two O atoms. To make the calculations more reliable, both 65-atom clusters and 80-atom supercells were used in large-scale simulations. Both models agree that one-site and two-site polarons are energetically favorable and can coexist, but give preference for the molecular polaron as lowest in energy. (Due to the complicated lattice structure we cannot calculate a barrier between two configurations.) The only stable one-site V_{Mg} configuration found is that where a Mg impurity is in the next NN cation position with respect to the O^- ion. As to the molecular form of the V_{Mg} , the supercell model favors the Mg ion in the NN position whereas a cluster model gives a preference to Mg in the next NN position. Interpretation of experimental data [111] for this defect is suggested.

4.6. Defect creation and diffusion

As in the case of irradiated MgO, very little is still known about interstitial aluminum atoms, Al_i , which are complementary defects to cation vacancies (V-centers). One possible reason for the paucity of experimental evidence for the interstitials is that as such they may be unstable already at moderate temperatures (this is the case for anion interstitials, I centers, in alkali halides). In [112], we have performed semi-empirical INDO cluster calculations for the primary Frenkel defects in the cation sublattice of corundum crystals. These V_{Al} and Al_i radiation defects form a sequence of Frenkel pairs ranging from NN to 4NN. The main results obtained for 130-atom sto-

ichiometric clusters are as follows. (1) NN pairs are unstable and immediately recombine. The threshold energy for the formation of 2NN–4NN pairs increases from 15.9 to 26 eV, respectively. This is in a good agreement with experimental estimates ranging between 18 and 24 eV [28,21]. (2) Neglect of the ionic relaxation along the Al_i path increases the threshold energy up to 32 eV. (3) The barrier energy for Al_i back recombination even for 4NN is small and could be estimated as 0.26 eV. In other words, first four kinds of Frenkel defects are unstable at moderate temperatures since Al_i are highly mobile around the liquid nitrogen temperature. (4) In the interstitial position Al_i attracts considerable electron density from nearest O ions. Thus, in the 3NN position its effective charge is just $0.63e$ to be compared with $2.42e$ for a regular Al ion in a corundum lattice site. This demonstrates that the atom–atom potential technique could be hardly used for such simulations and only quantum chemical formalisms are adequate for this problem.

We also performed calculations for O vacancy diffusion [113–115], in order to identify its limiting stage and mechanism. As is well known [113], five types of O vacancy jumps are possible in the corundum structure. 3D migration can occur via a combination of hops inside small basic O triangles in a direction perpendicular to the c -axis, and between small triangles in adjacent O planes, parallel to the c -axis. The INDO calculated energies are 0.49 and 3.50 eV, respectively demonstrating that the inter-plane hops is a limiting factor. The PP calculations gave 0.34 and 1.85 eV, respectively. The large difference in energies between INDO and PP for the second type of hops very likely is due to incomplete INDO lattice relaxation which in this case was done ‘by hand’ whereas it is always automated in the PP simulations.

One of the principal conclusions of these calculations is that in the quite loose corundum structure a hopping O atom deviates from a straight path which can reduce the activation energy by a factor of 2. The experimental value for the O vacancy activation energy of 1.86 eV [116] is in good agreement with PP calculation. INDO calculations show also that the effective charge of the hopping O atom does not change very much compared with

that in a regular lattice site ($-1.63e$ and $-1.53e$, respectively) which justifies the use of PP for the saddle-point configuration.

5. F-type centers in KNbO_3

Recently, electron defects (tentatively, F-type centers) were observed under electron irradiation in several perovskites – LiNbO_3 , [43,117], BaTiO_3 [45] and, lastly, KNbO_3 [44]. Their absorption bands are consistent with threshold energies for O atoms (Table 1). To our knowledge, in perovskite-type crystals until recently there existed only very simplified calculations for the F^+ center absorption energy (in LiNbO_3 and LiTaO_3 [118]). These were based on point-ion or semi-continuum models and neglected lattice relaxation around the defect and a self-consistent treatment of the electronic density distribution. Nevertheless, the qualitative theory for the F centers in perovskite ferroelectrics [119–121] predicts considerable delocalization of the electron density from V_0 towards the two nearest Nb atoms.

To answer these questions, as well as to clarify an assignment of the 2.7 eV absorption band in KNbO_3 [44], we have performed INDO calculations [122] of the atomic and electronic structure for the F^+ and F centres in KNbO_3 crystal. As a starting point we used recent INDO studies of the pure KNbO_3 and KTaO_3 crystals [123,124] where their electronic structure, the equilibrium ground state structure for several ferroelectric phases as well as Γ -phonon frequencies were reproduced in surprisingly good agreement with both ab initio calculations and available experimental data. A considerable covalency of the chemical bonding in pure KNbO_3 was also observed therein which might be expected from intuitive electronegativity considerations and the fact of a strong overlap between O 2p and Nb 4d orbitals and partial densities of states. A 40-atom supercell was used to simulate the F center. In the perovskite structure each O atom is surrounded by two Nb atoms, four K atoms and eight O atoms. In the high temperature cubic phase all O atoms are equivalent and have the local symmetry C_{4v} whereas in the room temperature (RT), ortho-

rhombic phase there are two kinds of non-equivalent O atoms whose symmetry is lower, C_{2v} or C_s .

Let us discuss results obtained for the two different KNbO_3 phases. The positions of 14 atoms surrounding the F and F^+ center in a cubic phase after lattice relaxation to the minimum of the total energy are given in [122]. The main conclusion is that the largest relaxation occurs for two nearest Nb atoms which are strongly displaced outwards from the O vacancy along the (0 0 1) axis. This is accompanied by a much smaller, outward displacement of K atoms and by an inward displacement of O atoms. The two Nb atoms give the largest (80%) contribution to the lattice relaxation energy of 4.6 eV whereas O atoms give most of the rest of the energy gain (1 eV). In the F^+ center the two nearest Nb atoms are relaxed by 35% less (mainly along the (0 0 1) axis) than in the F center, with the total energy gain less by 0.94 eV.

The analysis of the effective charges of atoms surrounding the F center shows that of the two electrons associated with the removed O atom only $-0.6 |e|$ is localized inside the V_0 . A similar amount of the electron density is localized on the two nearest Nb atoms. For the F^+ center these quantities are $-0.3 |e|$ and $-0.3 |e|$, respectively. Such a small portion of the electron density localized inside the O vacancy explains the large lattice deformation around the (formally neutral) F center; the NN cations repelled from V_0 where charge is $+1.4 |e|$. This is in sharp contrast with F center calculations in MgO (Section 3.1) where both electrons are well localized and the lattice deformation is 2% only. The F center in KNbO_3 produces a local energy level, which lies ca. 0.6 eV above the top of the valence band. Its molecular orbital contains primarily contributions from the atomic orbitals of the same two nearest Nb atoms.

The orthorhombic phase of KNbO_3 is important since it is stable in a broad temperature range around RT and thus has been subject of most studies and practical applications. The displacements of Nb atoms nearest to the V_0 for both kinds of F centers existing in this phase are very similar in magnitude and also close to those found for the cubic phase. The relevant relaxation energies are slightly less than for the F center in the cubic phase. Since the effect of the phase transition

on the local lattice deformation is small, we studied its consequences only for the F center. Because of the C_{4v} local symmetry of the F-type centers in the KNbO_3 cubic phase, its excited 2p-type state splits into *two* levels, one of which remains two-fold degenerate. Around RT, in the orthorhombic phase, there exist two kinds of F-type centers associated with two non-equivalent O atoms of the C_{2v} and C_s symmetry. The corresponding *three* absorption bands for F-centers are also given in Table 8. Their difference is largest for the lowest energy band (0.16 eV) and negligible for the other two bands.

As it was stated in Section 1, Eq. (1) (the Mollwo-type relation) holds for many F^+ centers in ionic oxides. However, its application to KNbO_3 gives an absorption energy greatly exceeding the optical gap (3.8 eV). This demonstrates once more that perovskites are a special case. Indeed, our results for the electronic density distribution are in a sharp contrast with what is known for the F centers in ionic oxides (in particular, in MgO) where the two electrons are well localized by the V_0 in the ground state of the F center. Evidently, this discrepancy arises from a considerable degree of covalency in the chemical bonding in KNbO_3 which is neglected in most models of defects in this material (as well as in similar ABO_3 perovskites, e.g. [125]; the only exception we know is an X_α cluster calculation on the F center in LiNbO_3 [126]. Electron defects similar to what we have observed are also known, in particular, in partly-covalent SiO_2 crystals. For example, in the so-called E'_1 center an electron is also not localized inside V_0 but sits on the sp^3 orbital of a neighboring Si atom [127]. To our knowledge, the only experimental study (accompanied by a semi-quantitative analysis) of the phase transition effect on the opti-

Table 8
Calculated absorption energy (in eV) for the F^+ and F centers in KNbO_3 [122]

Defect	Symmetry	E_{abs}		
F center	C_{4v} , cubic	2.73	2.97	
	C_s , orthorhombic	2.56	3.03	3.10
	C_{2v} , orthorhombic	2.72	3.04	3.11
F^+	C_{4v} , cubic	2.34	2.66	

cal properties of F-type centers was performed for KCN and NaCN [128]. This has demonstrated how a single Gaussian absorption band in the high-temperature, cubic phase splits into three components in the low-temperature, orthorhombic phase.

Summing up, the present INDO calculations demonstrate that the broad 2.7 eV absorption band observed in electron-irradiated KNbO_3 crystals [44] could be due to *both* the F^+ and F centers, and predict existence of two more absorption bands for both centers at RT. A recent ab initio supercell study of the F center in KNbO_3 [129] performed using the local density approximation (LDA) for an FP-LMTO scheme confirms the main INDO findings for defect geometry and the electron density distribution.

6. Conclusion

In conclusion, we believe that quantum chemical methods (in particular, INDO) combined, when necessary, with the pair-potential approach and ab initio formalisms, is a very efficient tool for the study of static and dynamic properties of complex defects in oxide materials. With their help we have been able to suggest the explanation for several puzzles and we have also made several predictions for future experiments.

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