

## LETTER TO THE EDITOR

# A novel model for $F^+ \rightarrow F$ photoconversion in corundum crystals

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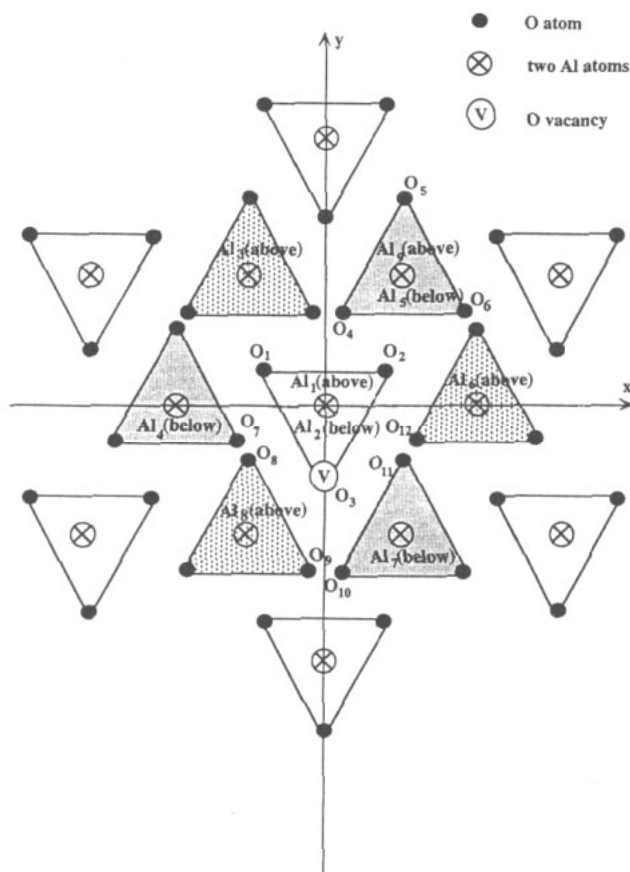
**Abstract.** On the basis of semi-empirical INDO calculations of the atomistic and electronic structure of  $F^+$  and  $F$  centres in corundum crystals, a novel explanation of the old puzzle of  $F^+ \rightarrow F$  photostimulated conversion is suggested. Literature data are presented supporting a quite general character of this phenomenon in ionic solids with defects.

Despite intensive studies of defects in oxide crystals—first of all MgO and corundum ( $\alpha$ - $Al_2O_3$ ) [1–4], which have numerous technological applications—many problems remain unsolved, even as related to the simplest electronic  $F^+$  and  $F$  centres (one and two electrons trapped by the O vacancy, i.e. positively charged and neutral defects with respect to the perfect lattice). In particular, it was observed long ago (see [1], a review article) that excitation of corundum containing  $F^+$  centres (whose excited states lie far from the bottom of the conduction band) by photons with energy close to that of the  $F^+$  absorption bands (4.8, 5.4 and 6.0 eV) results in  $F$ -centre formation. For this process of so-called  $F^+ \rightarrow F$  photoconversion, when a one-electron centre is transformed into a two-electron centre, no clear theoretical explanation has been found, except possibly the *ad hoc* idea [5] that the process could happen if in corundum—unlike MgO and alkali halides—the ground state of the  $F$  centre lies below the upper valence band.

Recently [6], atomistic and electronic structure calculations for the  $F^+$  and  $F$  centres in corundum were performed using the semi-empirical INDO (intermediate neglect of the differential overlap) method and big stoichiometric clusters embedded into the electrostatic field of non-point charges of the rest of a crystal [7, 8]. This technique, based on the molecular orbital (MO) approximation theory, allows us to calculate both the optimized defect geometry (conformation) and the self-consistent electronic structure of point defects in insulating solids. For such partly covalent, low-symmetrical, and complicated structures, like corundum (ten atoms in the unit cell and  $C_2$  symmetry of  $F$ -type centres), it is very important to use as much as possible an automated search of the optimized defect geometry, which is usually—unlike in the case of alkali halides—far from self-evident, as well as to incorporate maximally the point symmetry of the defects, in order to make calculations for as large quantum clusters as possible, thus reducing the boundary effects. Both these conditions are met in a new INDO SYM–SYM computer code [9] used in this letter. This approach gives us a solid basis for the study of optical and dynamical properties of defects in oxides, making no *a priori* assumption about the nature of the chemical bonding and the degree of covalency of the solids under study.

In a previous INDO study [6] the calculated energies of the optical absorption and luminescence of  $F^+$  and  $F$  centres turned out to be in good agreement with experimental

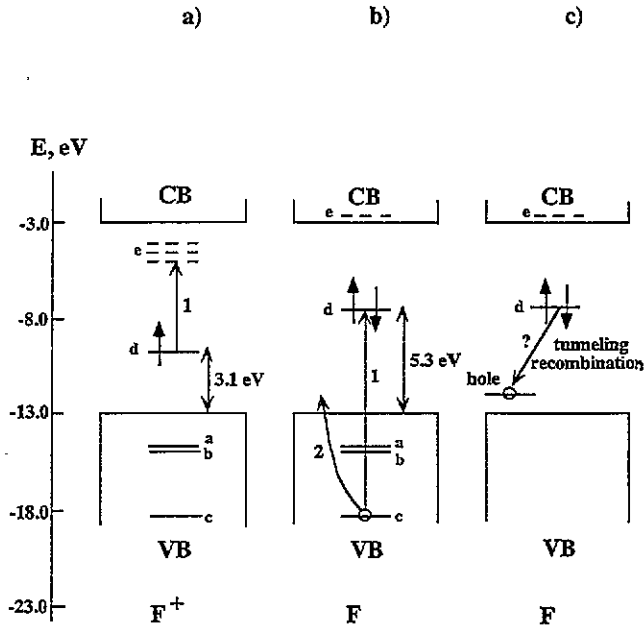
data. An analysis of the positions obtained for the local levels of these centres has shown clearly that the ground states of both  $F^+$  and  $F$  centres lie 3.1 eV and 5.3 eV *above* the top of the upper valence band, respectively—unlike in the hypothesis [5]. Therefore, the explanation of the  $F^+ \rightarrow F$  transformation suggested in the latter paper does not work.



**Figure 1.** A top view of the 65-atom stoichiometric quantum cluster used in the calculations. It contains 13 structure elements (each has two Al atoms and three O atoms). In  $F^+$  ( $F$ ) calculations the  $O_3$  ion is replaced by a vacancy ( $V$ ), and one (two) electrons are added into the cluster. Dotted and shaded O triangles lie 2.17 Å above (below) the  $xy$  plane of white O triangles.

Figure 1 shows the 65-atom quantum cluster used in the present calculations. In this letter we analyse the effects of the positively charged  $F^+$ -centre perturbation of surrounding atoms. Our calculations reveal clearly the existence of several *quasi-local states* located in the upper part of the mixed valence band. These states consist mainly of the atomic orbitals (AOs) of O ions surrounding the  $F^+$  centre (one-electron levels a, b, c in figure 2 and table 1). The predominant contribution to all three states come from the p AOs of the two nearest atoms  $O_1$  and  $O_2$  belonging to the same basic oxygen triangle as a vacancy. Our novel model suggests that the optical transitions 1 of electrons from these levels to the *ground state* of the  $F^+$  centres (d in figure 2(b)) convert them into *two-electron F centres*. The quasi-local nature of a, b, c states makes the transition probability comparable with that

for intrinsic absorption. Simultaneously, a hole is produced on one of the quasi-local levels a, b, c. At the next stage this hole escapes to the valence band to which it is energetically degenerate. To calculate the probability of this process and the relevant energy barrier (if any), one needs to obtain the two potential energy curves of the whole system with a localized and a delocalized (band) hole respectively. This could be done using the technique described in [15] which requires a careful analysis of the contributions of electronic and ionic polarizations of corundum crystal in these two states, which is now in progress.



**Figure 2.** Positioning of one-electron levels with respect to the bands of perfect corundum. Full lines are ground states (d) and broken lines excited states (e) of  $F^+$  and F centres. The quasi-local states induced by a charged defect are denoted as a, b, c. The basic idea of our explanation is that the  $F^+ \rightarrow F$  transformation occurs not because of the intrinsic one-electron transition in 1 in a, but because of the transition 1 in b from the valence band.

A hole thus created in the valence band becomes in the next moment either self-trapped (as follows from calculations [4]) or trapped by an impurity/defect not far from the F centre (process 2 in figure 2(b)).

From our calculations, several characteristic features of this model, which could help to check it, arise as follows. (i) The energetic spectrum of the  $F^+ \rightarrow F$  transformation covers the region of the  $F^+$ -centre absorption (4.8–6.0 eV) and extends to *both longer and shorter* wavelengths. This is in agreement with the photostimulated transformation actually observed down to 4.1 eV as well as the photoconductivity structureless tail extended below 4 eV [1]. (ii) Hole centres should be spatially correlated with F centres, which, in particular, could result in their *tunnelling recombination* (probably observed in [10]). The very fact of hole formation has been recently concluded from photo-induced thermostimulated electrical conductivity [11].

In conclusion, we want to stress that the proposed model is quite general for ionic solids where charged point defects strongly disturb surrounding ions. In particular, it holds for

**Table 1.** The coefficients of AOS in MOS for three localized states (a to c in figure 2) induced by the  $F^+$  centre in the valence band. Only atoms different in symmetry terms are presented.

The distance		1.8 eV,	2.1 eV,	5.5 eV,
from the top of		level a	level b	level c
the upper VB				
Vacancy	$p_x$	0.05	-0.03	-0.26
	$p_y$	-0.11	-0.04	-0.14
	$p_z$	0.26	0.29	0.04
O <sub>2</sub>	$p_x$	-0.05	0.03	0.26
	$p_y$	0.11	0.04	0.14
	$p_z$	0.26	0.29	0.04
O <sub>7</sub>	$p_x$	-0.10	0.07	0.01
	$p_y$	0.06	-0.17	-0.01
	$p_z$	0.07	-0.16	0.01
O <sub>8</sub>	$p_x$	0.01	-0.09	0.01
	$p_y$	-0.07	0.04	-0.01
	$p_z$	-0.08	0.02	0.05
O <sub>9</sub>	$p_x$	-0.02	0.13	-0.01
	$p_y$	0.04	-0.03	0.01
	$p_z$	-0.01	—	0.03

$Tl^{2+}$ -centre absorption (and for that of other mercury-like charged activator centres in alkali halides) resulting in  $Tl^+$  and self-trapped hole formation (see experimental results [12, 13] and theory [13–15]). A similar model was considered theoretically for  $LiF:Mg$  [16]. There is also some experimental argument for hole formation under  $F^+$  excitation in  $MgO$  crystals [17, 18].

Finally, we have observed in our F-type calculations that along with the quasi-local states inside the valence band just discussed, these defects also perturb surrounding cations— $Al_1$ ,  $Al_2$ ,  $Al_7$  and  $Al_8$  (figure 1)—which results in the additional splitting of several states by 0.6–2.0 eV below the conduction band. This is in agreement with the experimental observation of  $F^+$ -related absorption bands at around 7–8 eV [19], present along with the three ‘classical’ bands in the region 4.8–6.0 eV. However, these results could be reinterpreted in terms of the so-called  $\alpha$ - and  $\beta$ -bands well known in alkali halides [20] and arising due to the exciton absorption perturbed by the empty anion vacancy and F centres, respectively. In particular, the two bands observed at around 7–8 eV and ascribed to  $F^+$  intrinsic absorption [19] could, in fact, be considered as analogues of  $\beta$ -bands induced by  $F^+$  centres; due to low symmetry the relevant excitonic excitations could differ in their conformation and thus also absorption energies.

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