

Theoretical simulations of hole centres in corundum crystals

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Abstract. Atomistic simulations of different hole centres (such as the self-trapped hole, V^{2-} , V^- and V_{Mg} centres) have been performed in order to study theoretically their equilibrium geometry, charge distribution and optical absorption in corundum crystals (α - Al_2O_3). Both the semi-empirical quantum-chemical intermediate neglect of differential overlap method and the atomistic simulation technique based on atom–atom pair potentials (as implemented in the CASCADE code) have been used, and the principal results from these two approaches turn out to be in good agreement with one another. It is shown that the most favourable defect configuration energetically is a hole shared equally between two neighbouring O atoms, and that this is the main factor responsible for the very similar absorption energies of these hole centres.

1. Introduction

α - Al_2O_3 is an important ceramic material (Kingery 1983, French 1990), which is also used as a substrate for thin-film growth and as an optical material. Of possible important applications, its use in single-crystal IR fibres (Merzberg and Harrington 1991) is perhaps the principal one. The theoretical study of pure corundum (sapphire) crystals started only quite recently (Batra 1982, Ciraci and Batra 1983, Nagel 1985, Evarestov *et al* 1980, Causà *et al* 1987, Dovesi *et al* 1989, Salasco *et al* 1991, Xu and Ching 1991) with emphasis mainly on surface properties, interfaces and adsorption (Pisani *et al* 1987, Causà *et al* 1989, Kohyama *et al* 1992). These studies were carried out using a number of quantum-mechanical techniques, both semi-empirical (extended Hückel, CNDO, tight binding) and *ab initio* (Hartree–Fock, OCLAO + LDA), using both cluster and periodical models. The calculations are greatly complicated by the non-cubic structure of the corundum crystal (space group D_{3h}^6 with 10 atoms per unit cell) and its partly covalent chemical bonding (Lewis *et al* 1982). Along with quantum-mechanical studies, the *atom–atom potential* approach, as implemented in the Harwell HADES II (Catlow *et al* 1982) and MIDAS codes, has been successfully applied to pure corundum crystals, their surfaces and impurities (Catlow and Mackrodt 1982, Tasker 1983).

As present, electronic defect properties of corundum have not been studied satisfactorily, especially theoretically (Crawford 1983, Valbis and Itoh 1991). Along with its importance as a potential scintillator material, such a study is of considerable fundamental importance. In particular, the question of whether free holes can be self-trapped in a regular oxide lattice, as they are in alkali halide crystals, has been debated for a long time (Valbis and Itoh 1991, Tale *et al* 1991, Jacobs *et al* 1992).

The purpose of this paper is to simulate by means of the semi-empirical intermediate neglect of differential overlap (INDO) method and atom–atom potentials the spatial and

electronic structure of hypothetical self-trapped holes (STHs) in corundum crystals as well as the V^{2-} centre (a hole trapped by an O atom near an Al vacancy), the V^- centre (two holes trapped by an atom near an Al vacancy) and the V_{Mg} centre (a hole trapped near a Mg atom substituting for an Al atom). These three kinds of hole centre reveal surprisingly close absorption bands centred at 400 nm and their spatial structure has not yet been established. As in recent studies by Grimes *et al* (1989) and Gavartin *et al* (1991), we expect the combination of the two quite different approaches mentioned above to be very useful: the quantum-chemical method gives the charge distribution around a new defect under study and a good idea of its geometry, whereas techniques based on atom-atom potentials allows us to find the displacements of several tens of atoms in the defective region and to calculate the polarization energy due to defect creation.

2. Theoretical methods

The quantum-chemical semi-empirical INDO method has been used successfully to study oxide crystals and defects therein, including MgO (Shluger *et al* 1991a, b), Li_2O (Shluger *et al* 1991c), SiO_2 (Shluger and Stefanovich 1990), and $\alpha-Al_2O_3$ (Jacobs *et al* 1992). This method, modified for defect studies in ionic and semi-ionic solids, is described in detail by Stefanovich *et al* (1990) and Shluger and Stefanovich (1990). For calculations on a pure crystal the periodical large unit cell (LUC) model was used (Evarestov and Lovchikov 1977, 1979, Evarestov and Smirnov 1987), whereas a cluster model (Grimes *et al* 1992) was used for defect calculations since the centres under study are charged with respect to the perfect crystalline lattice.

The use of INDO allowed us to perform self-consistent calculations of the electronic structure for quantum clusters as big as $[Al_{14}O_{21}]$. This is a stoichiometric cluster containing seven basic elements of the corundum structural triangle of O atoms with two atoms of Al above and below it. This cluster is embedded into the electrostatic field of non-point ions. The populations of the atomic orbitals (AOs) of these ions outside the cluster are frozen as in the LUC calculation of the perfect crystal. The valence basis set included 3s and 3p AOs on Al and 2s and 2p orbitals on O atoms, and their parametrization is described in detail by Jacobs *et al* (1992). Use of the LUC $[Al_{32}O_{48}]$ (which is the primitive cell extended by a factor of two along all three translation vectors) gives the total E_t a minimum at a lattice constant which is less by $\leq 8\%$ than the experimental value. The calculated bulk modulus $B = \Omega_0 2E_t / \partial \Omega^2 = 352$ GPa (Ω_0 is the volume of the unit cell) is also quite close to the experimental value of $B = 310$ GPa.

In cluster calculations, the peripheral boundary atoms were allowed to relax to the equilibrium geometry (minimum E_t) in order to take into account the effect of their broken bonds with 'atoms' outside the cluster. This point is discussed in more detail in a previous paper (Jacobs *et al* 1992) but the boundary relaxations were typically several per cent of the corresponding perfect crystallographic distance. Then a hole was inserted into a cluster (perfect, or containing an Al vacancy or an Mg substitutional) and different ionic relaxations were imposed in order to find the minimum in E_t without making any *a priori* assumptions about the electron (hole) density distribution, which indeed is a result of our calculations. Typically one calculation with fixed geometry needs 3–4 min CPU time on the CDC-2000 computer at UWO.

We also used the method of atom-atom potentials as implemented in the CASCADE code developed for non-cubic lattices (Leslie 1983, 1985), with Buckingham potentials and shell-model parameters from Catlow *et al* (1982). The defective region I contained 300 atomic cores and shells.

A crucial point in these calculations is the choice of potentials describing interaction among the atoms *inside* the defect (i.e. the O₂ diatomic molecules described below) and between defective atoms and their surroundings. We have fitted these parameters to the INDO potential curve assuming that the charges on two defective O atoms are the same as in the INDO calculations. Note that a quite similar procedure was used before by Monnier *et al* (1977) in their HADES calculations of the STH in alkali halides.

Interactions between the two O atoms, each of which is associated with half a hole, and other Al³⁺ and O²⁻ lattice ions is assumed to be the same as those between Al³⁺ and O²⁻ ions of the perfect structure. In other words, it is assumed that the additional half-hole on each atom of the defect pair does not much perturb the charge distribution of the valence electrons in O²⁻ since it is the overlap of these charge densities on different atoms that give rise to the overlap repulsion. In fact, this cannot be exactly true, but nevertheless seems to be a satisfactory approximation. Recall that HF calculations on O⁻-O⁻ (in a tetrahedral field) may be used quite satisfactorily to generate an O²⁻-O²⁻ potential (Catlow *et al* 1976). For the remaining interactions between Al³⁺ and O²⁻ and between O²⁻ and O²⁻, we used the potentials developed by Catlow *et al* (1982), slightly modified by refitting crystal properties after allowing the perfect structure to relax and release the basis strains that are present if every atom is placed on its crystallographic site (Jacobs and Kotomin 1993). The most important properties to re-fit are the static permittivities and this may be done by changing the core-shell force constant for Al³⁺. Details of potentials and their fit to the properties of corundum may be found in the paper by Jacobs and Kotomin (1993).

3. Results

3.1. Perfect crystals

The unit cell of the corundum structure contains 10 atoms in the form of two Al₂O₃ units rotated with respect to each other by 180°. Each of these units consist of an O triangle with two Al atoms situated symmetrically above and below it (figure 1(a)). Each Al atom in this structure is surrounded by a distorted octahedron of O atoms forming two kinds of Al-O bond: 1.93 Å and 1.89 Å. (Only the former are shown in figure 1(b), whereas the latter involve O atoms from nearest-neighbour (NN) atom stacks.) In turn, each O atom has four Al NN atoms at these two distances. The calculated effective charges on the atoms in the LUC calculation (2.34e on Al and -1.5e on O) are in good agreement with recent *ab initio* calculations by Salasco *et al* (1991) (2.02e and -1.35e respectively) and confirm once more the essential covalent contribution to the chemical bonding in corundum.

Table 1. Populations of bonds between atoms in perfect and defective corundum crystals (in *e*). The atom numbering is shown in figure 1. Figures in brackets are the results of *ab initio* HF calculations by Salasco *et al* (1991). Bond populations are calculated as $q_{ab} = \sum_{i \in a} \sum_{j \in b} S_{ij} P_{ij}$, where P_{ij} are the elements of the density matrix and S_{ij} are overlap integrals for $i, j (= s, p_x, p_y, p_z)$ orbitals on atoms a and b.

Bond	Atoms	Perfect crystal	STH	V ²⁻	V ⁻	V _{Mg}
Al-O	2-3	0.258	0.229	0.267	0.270	0.228
	2-5	0.258 (0.214)	0.210	0.359	0.317	0.282
O-O	3-4	0.002	0.267	0.352	0.363	0.300
	3-5	0.002 (-0.020)	0.001	0.001	0.001	0.001

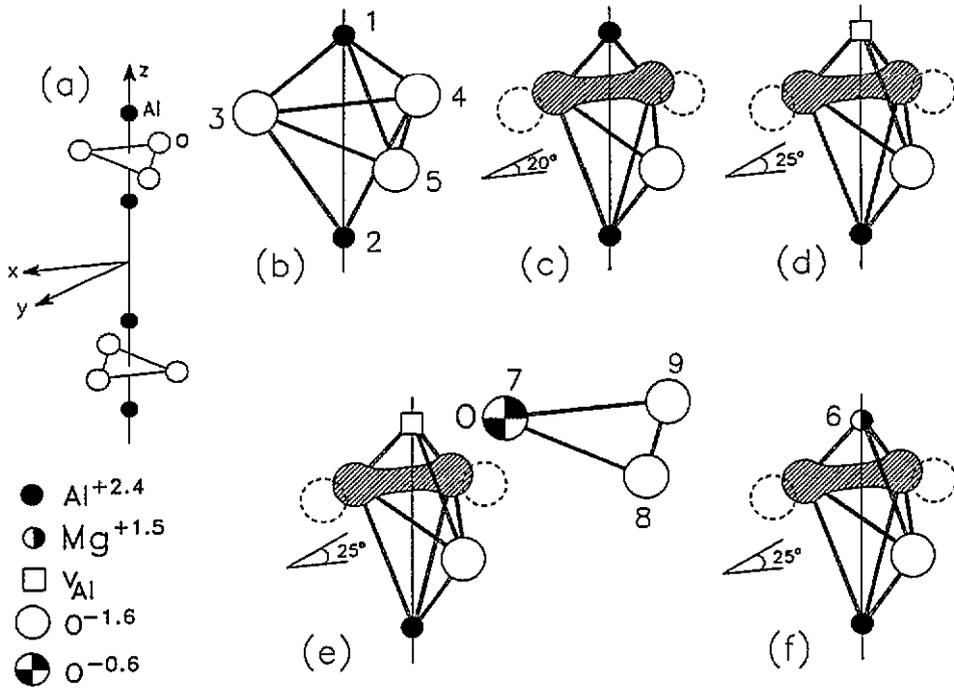


Figure 1. The unit cell of a corundum crystal (a) and the basic atoms defining the spatial and electronic structure of the hole centres (b). The most energetically favourable configuration of the self-trapped hole is shown in (c): it involves a strong inward relaxation of the two O atoms sharing a hole accompanied by an outward z -axis displacements of the two nearest Al atoms. Models of V^{2-} , V^- and V_{Mg} centres are shown schematically in (d)–(f) respectively. A shaded dumbbell denotes hole density equally shared by two O atoms. The bond populations are given in table 1. The circle with alternate quadrants filled denotes the second hole of the V^- centre, which is trapped on one O site in a basic structural triangle (cf (a)) in an adjacent c -axis stack (e).

More detailed analysis of this effect comes from the populations of bonds between different atoms shown in figure 1(b) and given in table 1. This demonstrates clearly that there is no bonding between nearest O ions but that the corundum structure results from strong Al–O bonds.

3.2. Self-trapped holes

When a hole arises in a perfect cluster, it occupies the twofold degenerate molecular orbital built up from AOs of the three O atoms of the basic triangle. Due to the Jahn–Teller effect (Bersuker and Polinger 1983) some asymmetric distortion of this triangle must lower the total energy and give the optimal defect geometry. Some of these distortions are shown in figure 2; they involve displacements of one, two or all three O atoms. Because the hole orbital is antibonding with respect to O atoms and bonding for the two Al atoms on each side of the O triangle, one can expect an *inward* relaxation of O atoms and an *outward* displacement of the two Al atoms along the z axis.

The INDO calculations for 35-atom clusters $[Al_{14}O_{21}]^+$ led finally to the optimized defect geometry and minimum energy in the form of 40% inward displacement of two O atoms

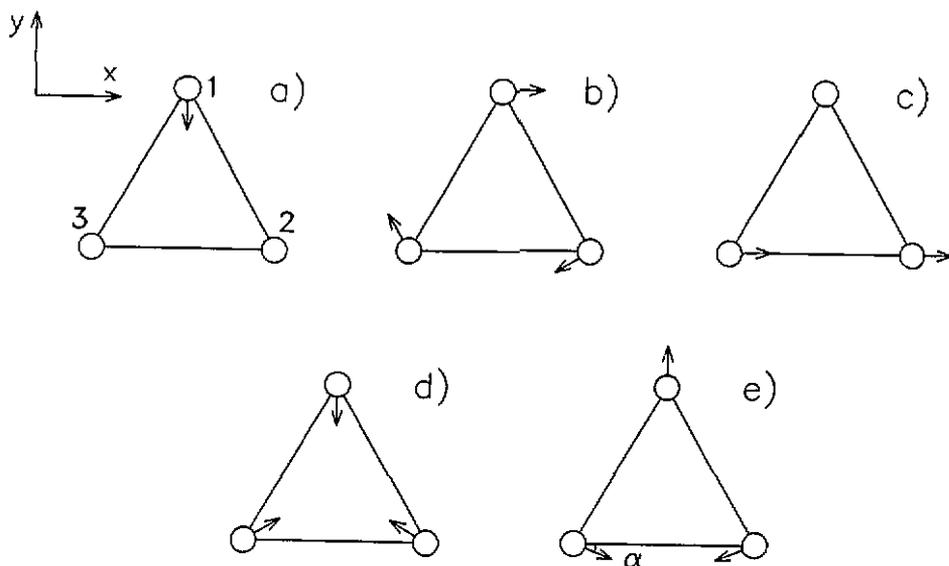


Figure 2. Some possible atomic relaxations inside a basic O triangle which are potentially able to lower the total energy and thus give an optimized geometry for the STH and V^- centres. That of (e) is predicted by the general Jahn–Teller theory for the $e \otimes E$ problem which we have for the STH in corundum.

accompanied by an outward 20% displacement of the two nearest Al atoms on each side of the O triangle (figure 1(c)). The displacement vectors of these two O atoms lie at an angle of $\approx 20^\circ$ with respect to the straight line connecting their perfect-lattice positions: this is also the configuration predicted by the general Jahn–Teller theory (figure 2(e)).

The total energy gain due to hole self-trapping is 5.5 eV; its main contribution comes from linear relaxation of two O atoms (3.5 eV). These O atoms share 80% of the hole density. A closer analysis of the origin of this very strong effect shows that it arises from the *powerful chemical bonding* between the two O atoms sharing the hole: the population of this bond is close to that for the Al–O bond in a perfect crystal (table 1). Calculation of the energy of a hypothetical STH formed by two O atoms belonging to *different* O planes (whose separation is 2.17 Å along the c axis) shows that it is energetically much less favourable than the STH lying within O planes perpendicular to the c axis.

For further CASCADE calculations we have fitted O^-O^- short-range Buckingham parameters to the INDO potential curve for the cluster total energy versus the distance between the two relaxed O atoms. The relevant STH geometry that results from a CASCADE energy minimization was found to be very similar to the above-described INDO result, except that the angle of bond bending α is slightly smaller, and the third O atoms is slightly displaced outwards. This remarkable agreement of two different approaches argues that chemical bonding is the main driving force in hole self-trapping while Coulomb interactions of the defects with the rest of the crystal are less significant.

The STH model obtained in our calculations is very similar to that known for a long time as the V_K centre in alkali halides (Kabler 1972). Similar diatomic centres have also been discovered by Griscom (1989) in EPR experiments on fused SiO_2 glass.

3.3. V^{2-} centres

When an Al vacancy is formed it has an effective negative charge (see the V^{2-} centre shown in figure 1(d)). So, one can easily foresee that the two O atoms sharing a hole will be displaced towards the Al vacancy whereas the third atom of the O triangle will relax in the opposite direction along the z axis. Both INDO and atom-atom calculations confirm this electrostatic effect. In the quantum-chemical calculations of the energetically most favourable configuration, O atoms 3 and 4 go up by 0.07 Å and O atoms 5 down by 0.12 Å. The Al atom 2 on the other side of the O triangle is also shifted up by the same amount, 0.12 Å. We have simulated anew different modes of O atom displacements (figure 2) to check whether an Al vacancy can make the one-site hole localization energetically more favourable. However, our calculations confirmed the two-site model of hole trapping with essentially the same 40% inward relaxation and a slightly increased angle $\alpha \approx 25^\circ$ (with respect to the straight line connecting the two O atom sites). As one can see in table 1, the population of this bond (O3–O4) is even larger than that of the STH. Partly, this results from essential charge redistribution caused by the Al vacancy: the effective charges of O atoms 3 and 4 have increased by $0.3e$ each.

In CASCADE calculations (with potentials optimized by the INDO STH results) we found atomic displacements having the same directions and order of magnitude; e.g. O atom 5 is displaced down by 0.3 Å, but Al atom 2, up by 0.26 Å.

3.4. V^- centres

These centres have *two* holes trapped by an Al vacancy and thus is was of great interest to simulate whether one or both or them will be a di-centre defect. With this objective in mind, we modelled again the different relaxation modes shown in figure 2 (and also some others) for O atoms entering the basic structural triangle and for O atoms from the nearest triangle lying 2.17 Å higher along the z axis (in the direction of the vacancy) but displaced in the xy plane (see figure 1(a)).

The main result was that one hole is shared by two O atoms—exactly as in the STH, whereas 80% of the second hole is trapped by a *single* O atom of the upper triangle nearest to the negatively charged vacancy. This O atom has the effective charge $-0.65e$ —and is displaced by 5% of the O–O distance towards the centre of this triangle. Hole localization on a single O atom has mainly an electrostatic origin since this atom is essentially closer to the negatively charged V_{Al} than the other two O atoms of the O triangle. Hole distribution within the O_2 molecule in the lower triangle turns out now to be slightly asymmetric: the charge of the atom closer to the second hole is higher by $0.1e$.

3.5. V_{Mg} centres

In these centres (figure 1(f)) a hole is trapped by an Mg atom having a smaller charge than an Al atom which it substitutes for, so effectively it is a negative charge with respect to the perfect corundum lattice. In a purely ionic model its charge would be $-1e$, in our INDO calculations we obtained $q(Mg) = 1.90e$ whereas for an Al atom in perfect corundum $q(Al) = 2.34e$; therefore the effective charge is only $0.44e$. Thus this centre is simply a slightly perturbed STH. In particular, the upward shift of O atoms 3 and 4 is negligible, being only 0.04 Å. In CASCADE calculations we found that the Mg atom is also displaced up from the Al site by 0.2 Å and Al atom 2, located along the z axis on the other side of the O triangle, is also displaced upwards by nearly the same amount.

4. Discussion and conclusion

The results of our *parallel* quantum-chemical and atom-atom simulations of hole centres in corundum has demonstrated that their results agree well even for defects with a strong electron density redistribution if atom-atom potentials for defective atoms are fitted in a proper way using the quantum-mechanical results.

Our calculations support the idea that the basic element of a model of the STH and related hole centres is essentially the diatomic molecule with the hole density shared equally between the two atoms of the O₂ quasi-molecule. This pattern is only slightly modified by the presence of an Mg atom substituting for the nearest Al atom (V_{Mg} centre), or an Al vacancy (V²⁻, V⁻ centres). In the light of these results it is not surprising now that V_{Mg}, V²⁻ and V⁻ centres have very close absorption energies. Our INDO calculations give an estimate of these energies as about 3.5 eV. This is a difference of total energies for the ground and excited defect states and, remembering that we ignore a change in the polarization energy, this result can be considered in good agreement with the experimentally observed value (3.10 eV). For the STH absorption band we predict a slightly lower energy (~3.0 eV). Another important problem is whether the formation of these centres is energetically favourable. The key point here is to obtain a reliable estimate of the so-called hole localization energy E_{loc} , which is an intermediate state between a free valence band hole and the STH. The existing estimates made earlier for the STH in alkali halide crystals (Kabler 1972, Stoneham 1975, Shluger *et al* 1992a, b, c) vary between 0.5 and 0.375 of the width of the upper valence band E_W and are based essentially on a pattern of purely ionic chemical bonding with the upper valence bands constructed entirely from halogen 3p AOs. However, this is not true for partly covalent corundum crystals (as well as for silica), whose valence band has a strong admixture of Al AOs (Salasco *et al* 1991). A first attempt to solve this problem has been undertaken recently by Shluger and Heifets (1992) and Kantorovich *et al* (1993) and we hope to apply their approach in the future to a more accurate analysis of hole defects in corundum. However, if we take, as an *estimate* $0.375E_W$ for the hole's localization energy, we can obtain the net hole trapping energy E_{ST} from

$$E_{ST} = E_{loc} + E_{rel} + E_{pol}$$

where E_{rel} (< 0) is the energy gain due to relaxation of defect atoms caused by their covalent bonding, and E_{pol} (< 0) is the polarization of the crystal due to displacements of both cores (ionic contribution) and shells (electronic contributions) induced by the defect. Finally, one has also to incorporate a correction for the electronic polarization caused by a band (free) hole before it is trapped. If the total energy balance is negative ($E_{ST} < 0$), hole trapping is energetically favourable and can occur spontaneously. We estimated E_{rel} from our INDO cluster calculations and polarization contributions by means of the atom-atom potentials.

The main results are presented in table 2. First, hole trapping in STH, V²⁻ and V_{Mg} hole centres is found to be energetically favourable. Since this is actually observed experimentally for V²⁻, V⁻ and V_{Mg} centres, this lends considerable support to the correctness of our calculations for the STH. Secondly, note that E_{rel} is largest for the STH and smaller for other hole centres; this arises partly from the considerable (~0.75 eV) contribution of the displaced Al atom lying above the oxygen plane. Ionic polarization for the STH is relatively small because the lowering of the total energy due to inward displacement of the two O atoms constituting the STH is also included in their E_{rel} . Thirdly, unfortunately we cannot estimate E_{ST} for the doubly charged V²⁻ centre because E_{loc} and E_{pol} cannot be estimated at present for a centre with two holes. It is certainly not sufficient to assume that these quantities depend linearly on the number of holes.

Table 2. Different contributions (in eV) to the energetics of hole trapping in the STH , V^{2-} and V_{Mg} centres in corundum. Defect charges with respect to the perfect crystalline lattice are shown as superscripts.

Defect	$[\text{STH}]^+$	V^{2-}	$[\text{V}_{\text{Mg}}]^\ominus$
Relaxation energy	-5.5 ^a	- 4.2	-4.0
Ionic polarization	-3.0	- 3.8	-4.4
Electronic polarization	-5.1	- 9.6	-3.3
Localization energy	+ 3.8	+ 3.8	+ 3.8
Loss in polarization due to free hole	+ 3.7	+ 3.7	+ 3.7
Net hole trapping energy	-6.1	-10.1	-4.2

^a Including -1.5 eV due to outward relaxation of two Al atoms and -0.5 caused by O-O bond bending after relaxation.

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