

## Modeling of Point Defects in Corundum Crystals

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Several different approaches including Hartree-Fock *ab initio* cluster calculations, semiempirical INDO calculations, and atom-atom potentials were used for modeling of the spatial and electronic structure as well as migration mechanisms of both intrinsic defects (self-trapped and defect-trapped holes, O and Al vacancies) and impurities (transition-metal ions like Co, Fe, Mg, Mn, Ti). The atomic structure of all hole centers is found to be similar to  $V_K$  centers in alkali halides (two-site model); their formation is energetically favorable. The energy required for  $60^\circ$  hole reorientations inside the basic oxygen triangles is found to be similar to both the energy for hops between such triangles and the experimental activation energy for self-trapped hole migration (0.7 eV). A novel mechanism of hole polaron motion in ionic solids is presented on the basis of quantum-chemical cluster calculations. The role of clustering in the solution of impurities is shown to be crucial. Lastly, five kinds of O vacancy hops are simulated. In several cases the activation energy is lowered considerably when the hopping ion is allowed to deviate from a straight path. Theory predicts the lowest activation energy to be 1.85 eV, in excellent agreement with the value observed experimentally below  $1550^\circ\text{C}$ . Theoretical predictions of the Arrhenius energy for diffusion at high temperatures are also in excellent agreement with Oishi and Ando's experimental values above  $1590^\circ\text{C}$ .

## I. Introduction

DESPITE the technological, mineralogical, ceramic, and catalytic importance of corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) crystals,<sup>1</sup> their fusion and IR fiber applications,<sup>2</sup> and prospects as a laser and dosimeter material,<sup>3,4</sup> point (including electronic) defects in this material have not been well studied so far, especially theoretically (see reviews<sup>5,6</sup> for more details). The main reasons for this are the following: the complicated atomic structure of corundum (10 atoms per unit cell) and the semicovalent chemical bonding observed in X-ray scattering.<sup>7</sup> The first *ab initio* band structure calculations on corundum<sup>8-10</sup> have confirmed the mixed character of the chemical bonding.

The main aim of this paper is to describe calculations of the atomic and electronic structure of several different defects in corundum crystals, including electronic (hole) centers and atomic intrinsic defects (oxygen vacancies) and impurity transition-metal atoms substituting for host cations (Fig. 1). Special attention is paid to the study of defect migration, which is of great importance for the interpretation of the relevant experimental data.<sup>11,12</sup> In our calculations, we combine three different

techniques: *ab initio* Hartree-Fock calculations, semiempirical cluster calculations, and atom-atom pair-potentials. The former two methods allow us to perform self-consistent calculations of the electronic structure of clusters (typically, of 5 and 35 atoms, respectively) embedded into the electrostatic field of the rest of a crystal, and thus to get charge density distributions, and a first guess about the principal atomic displacements around defects. The latter method (being based on the effective defect charge obtained quantum-chemically) permits the explicit automatic relaxation of several scores of the surrounding atoms (150 in our case) and the calculation of relevant polarization energies.

## II. Theoretical Methods

The structure of corundum could be viewed as hexagonal close packing of oxygen atoms (O) with aluminum (Al) atoms occupying two-thirds of the octahedral interstices. The unit cell contains two molecular units, i.e. 10 atoms; the basic structural element is a triangle of O atoms with two Al atoms lying symmetrically above and below it along the Z axis (Fig. 1(a)). These O triangles form O planes<sup>6</sup> separated by a distance of 2.17 Å.

In *ab initio* Hartree-Fock LCAO pseudopotential calculations a small  $[\text{Al}_2\text{O}_3]$  cluster (the molecular unit) was embedded in a point-ion-crystalline field; a 2-1G Gaussian basis set (2s, 2p, O AOs and 3s, 3p, Al AOs) was used. The computer code used, called DICAP, was developed by Dr. V. Puchin at the University of Latvia in Riga.

In semiempirical calculations the modified intermediate neglect of differential overlap (INDO) as implemented in the computer code CLUSTER, developed at the same University, was used; it is described in detail in Refs. 13 and 14. Several stoichiometric clusters were tried in these calculations. We found that 35-atom clusters were sufficiently large for our purposes. For the *perfect* corundum calculations a periodic supercell model was employed. In the pair-potential calculations, the Mott-Littleton two-region strategy, as implemented in the CASCADE computer code<sup>15</sup> for noncubic lattices, was used. Buckingham potentials were employed. Despite reasonably good descriptions<sup>16</sup> of elastic and dielectric properties and low bulk lattice strains, we found the experimental lattice structure to be unstable with respect to ionic relaxations. These relaxations are small but the associated energy makes a significant (and inevitable) contribution to the calculated defect energy which must be allowed for and when this is done defect energies are sensibly independent of the size of the inner region I that contains the defect and near-neighbor ions.<sup>17</sup> Consequently, most of the defect calculations were performed with a fixed region I size of  $\sim 150$  ions (the precise number varying slightly with the defect symmetry). The pair-potentials used for intrinsic defects and for the impurities (Mg, Mn, Fe, Co, Ni, Ti) are described fully in Ref. 17.

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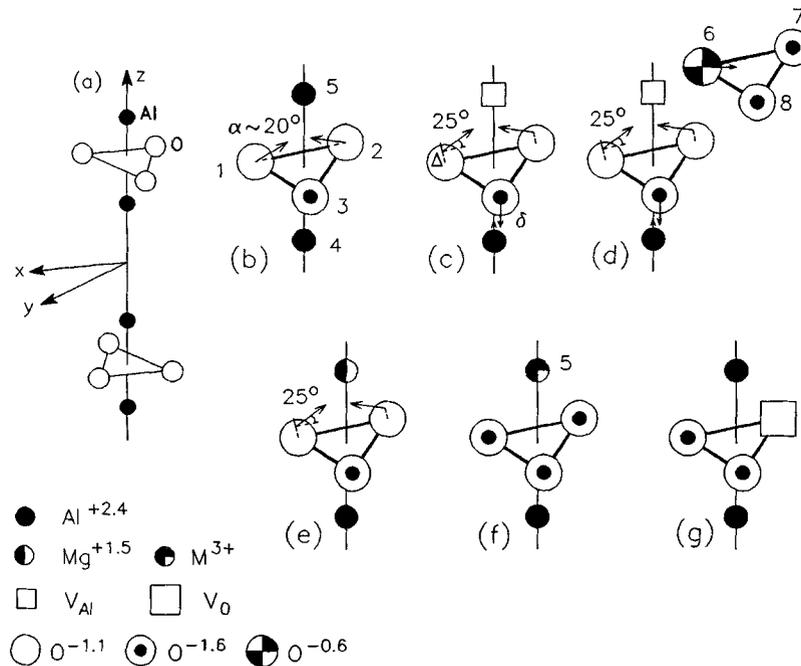


Fig. 1. (a) Contents of unit cell; (b) STH; (c)  $V^{2-}$  center; (d)  $V^-$  center; (e)  $V_{Mg}$  center; (f)  $M^{2+}$  impurity; (g) O vacancy.

### III. Results

#### (1) Hole Centers

We calculated the properties of the basic defects, both electronic and atomic, shown in Fig. 1; most of these have been a matter of long-time debate among experimentalists. First of all is the question of the stability and the structure of the *self-trapped hole* (STH). Despite the fact that STHs in alkali halides have been known since 1955,<sup>18</sup> their analogues in pure oxide crystals have not been identified unequivocally until now.<sup>6</sup> In recent diffusion-controlled luminescence studies<sup>11</sup> on corundum, mobile defects with an activation energy of 0.7 eV were associated with STHs.

In our calculations we found that the formation of a small-radius hole polaron is indeed energetically favorable; the optimized defect geometry (Fig. 1(b)) consists of 40% relaxation of two O atoms in the basic structural O triangle toward each other.<sup>19</sup> Because of the Jahn–Teller effect, the O atoms involved in this bond relax in directions that make an angle of 20° with the line forming two O lattice sites. In the perfect crystal there is no electron density localized between O atoms but for the STHs we found the bond between the two O atoms sharing a hole to be populated by  $0.35e$ , a value which is very close to the population of Al–O bonds in a perfect crystal and which is responsible for the partially covalent nature of the chemical bonding of this material. The change in the effective charges of the two displaced O atoms shows that 80% of hole density is localized on them.

The inward relaxation of two O atoms is accompanied by a 20% outward relaxation of the two Al atoms along the Z axis above and below the O plane. That is, we arrive at a STH model quite similar to that known in alkali halides: a diatomic quasi-molecule  $X_2^-$  with a strong chemical bonding, called also the  $V_K$  center. In the CASCADE calculations potentials for Al–O, O–O interactions were taken from Ref. 16, whereas those for the interaction of two O atoms sharing a hole were fitted to the relevant potential energy curves obtained in INDO calculations. The resulting defect geometry is very close to that obtained quantum-chemically. The STH polarization energies are  $-3.0$  eV (ionic) and  $-5.0$  eV (electronic), so that the total polarization energy gain is 8.0 eV. It is more than enough to compensate for the energy loss ( $\sim 3.8$  eV) required for localization of a

mobile hole on a single O atom before it becomes self-trapped. Lastly, there is another energy gain from the lattice relaxation energy; this consists of  $-3.5$  eV due to the inward relaxation of two O atoms,  $-0.5$  eV from bond bending, and  $-1.5$  eV due to the outward displacement of two Al atoms, giving a total of  $-5.5$  eV and a net trapping energy of about  $-6$  eV.

The STH absorption energy, calculated as the difference in total energies for the STH in the ground state and excited state (the so-called  $\Delta(\text{SCF})$  method), is 2.9 eV. Similar calculations for other hole centers associated with the substitutional Mg atom,  $V_{Mg}$ , or an Al vacancy ( $V^{2-}$  and  $V^-$  centers, or two holes trapped near a vacancy)<sup>20</sup> have demonstrated that in these centers a hole has practically the same structure as in the STH but the two O atoms sharing a hole are displaced along the Z axis because of the Coulomb field of the defect, while the bond bending has an angle of 25° (Figs. 1(c–e)). Because of this, it is no longer surprising that the absorption energies for all three defects are very close (compare the calculated 3.0 eV with the experimental value of 3.5 eV).

Another argument for the existence of STHs comes from our simulation of its motion.<sup>21</sup> INDO simulations have shown that STH hops inside basic O triangles with (60° bond orientation) as well as hops to such triangles lying 2.17 Å above or below (which gives rise to 3D hole motion) require very similar activation energies of ca. 0.9 eV. This value agrees quite satisfactorily with the experimentally observed energy of 0.7 eV.<sup>11</sup> In the second paper<sup>11</sup> the phenomenological theory of the diffusion-controlled recombination between STHs and electron ( $F^+$ ) centers is developed.

#### (2) Oxygen Vacancy Migration

Five mechanisms for the migration of anion vacancies were investigated by methods based on pair-potentials (CASCADE program); three of these were also investigated in the INDO approximation. It is implicit in pair potential calculations that no charge redistribution takes place during the hopping motion of an oxygen atom from a normal lattice site into a vacancy. However, this has seldom (if ever?) been verified. Our INDO calculations show that the effective charge of an O atom in the saddle point ( $-1.63e$ ) does not differ much from that of an O atom on a normal lattice site ( $-1.53e$ ). This justifies the use of the same pair-potentials for ions in saddle points as for ions on normal lattice sites. The five kinds of vacancy hops investigated

are shown in Fig. 2. The first two mechanisms (a1, a2) involve vacancy jumps in directions perpendicular to the  $c$  axis within small and large triangles, respectively. Because of the lack of cylindrical symmetry about these migration paths, one anticipates that the linear path between two lattice sites may not correspond to the lowest activation energy and this indeed proved to be so. For both a1 and a2 jumps the potential energy surface minimum is located at a point displaced by  $\Delta = 0.3$ – $0.4$  Å in a direction normal to the linear path. For these two jumps the agreement between INDO and CASCADE calculations was very satisfactory (Table I).

Mechanisms a3 and a4 consist of jumps approximately parallel to the  $c$ -axis along the shared edge between two occupied octahedra in adjacent vertical stacks (a3) or along a shared edge between filled and empty octahedra (a4). The symmetrical nature of the a3 migration favors a linear path, but the a4 saddle point is not constrained by symmetry to a linear path so that it is again curved, in response to Coulomb interactions. The displacement  $\Delta$  of 0.34 Å is very similar to that for a1 and a2. We also attempted to simulate the a3 path in the INDO program but in this case we failed to relax the near-neighbor ions correctly (this must be done "by hand") so that too high a  $\Delta E$  resulted.

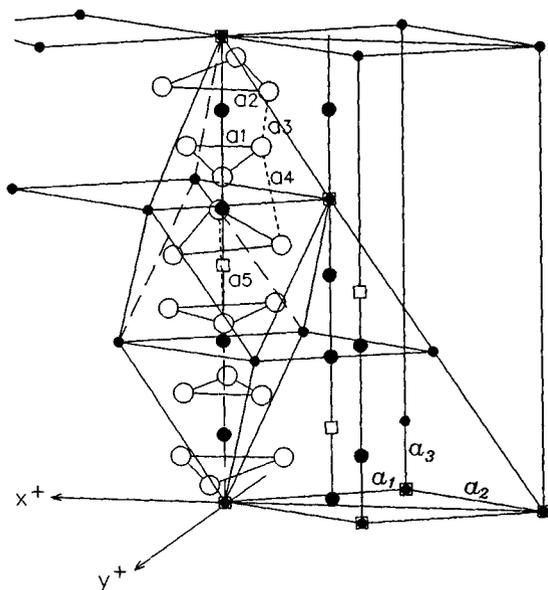


Fig. 2. Relation of rhombohedral unit cell of corundum to hexagonal net.

Table I. Activation Energies ( $\Delta E$ ) and the Displacement of the Saddle Point from a Linear Path ( $\Delta$ ) for O Vacancy Migration in Corundum

Path	CASCADE		INDO	
	$\Delta$ (Å)	$\Delta E$ (eV)	$\Delta$ (Å)	$\Delta E$ (eV)
a1	0.34	0.34	0.42	0.49
a2	0.33	2.50	0.32	2.56
a3		1.85		
a4	0.34	1.37		
a5		5.10		

Anion diffusion perpendicular to the  $c$ -axis requires a succession of a1 and a2 jumps, with a calculated activation energy  $E$  of 2.5 eV, whereas diffusion parallel to  $c$  requires a sequence of a3 and a4 jumps with a calculated  $E$  of 1.85 eV. The a5 jump evidently plays no role in oxygen diffusion (Table I). The lowest activation energy for isotropic diffusion is 1.85 eV for a sequence of a1, a3 jumps. This value is in remarkable agreement with that derived by Oishi and Ando,<sup>22</sup> who recalculated a value of 1.86 eV from the earlier measurements of Oishi and Kingery.<sup>12</sup>

Oishi and Ando's thorough reassessment of oxygen diffusion in corundum<sup>22</sup> also yields results for the activation energy for intrinsic diffusion. Their re-analysis of data for (a) crushed particles (corrected for surface area),<sup>12</sup> (b) diamond-paste polished single crystals,<sup>23</sup> and (c)  $b$ , followed by chemical polishing, with or without Ar in surface bombardment<sup>24</sup> results in values of 6.73, 6.89, and 6.59 eV, respectively, with a mean value of 6.74 eV. Our most reliable calculated defect energies should be those from the Catlow *et al.*<sup>16</sup> potential, refitted after the relaxation of basis strains.<sup>17</sup> This crystal potential resulted in formation energies (per defect) of 4.91 eV for Schottky defects and 5.13 for anion Frenkel defects. A proper analysis of transport data should therefore take both mechanisms into account. This has not yet been attempted for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, but since the formation energies are so close, this hardly matters at this stage. From the Schottky value of 4.91 eV and our calculated oxygen migration energy of 1.85 eV, we arrive at an Arrhenius energy for intrinsic oxygen diffusion of 6.76 eV, again in excellent agreement with the analysis of Oishi and Ando.<sup>22</sup>

### (3) Transition-Metal Impurities

We have also calculated the energy changes on incorporating the transition metals Mn, Fe, Co, Ni (as M<sup>2+</sup>), and also Mg<sup>2+</sup> and Ti<sup>4+</sup> in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> either substituting for Al<sup>3+</sup> ions or in one of the two vacant octahedral sites per unit cell. These sites are generally called "interstitial sites" and are shown as squares in Fig. 2. The effects of cluster formation with O vacancies, M<sub>i</sub> interstitials and Al<sup>3+</sup> interstitials were also investigated. Further details have been published elsewhere,<sup>17</sup> so here we summarize just the main conclusions. Solution of impurities is facilitated by clustering with the interstitial cluster, that is, two substitutional M ions on cation sites separated by an interstitial M<sub>i</sub> at a (normally vacant) octahedral interstice being generally favored. For Mg, a cluster of two M ions with an O vacancy is slightly preferred. The calculated energies of solution shown in Table II indicate that Fe, Co, Ni should dissolve as the M<sub>i</sub> interstitial cluster; Mn and Mg require a favorable entropy of solution but this is apparently the case since Mg is known to dissolve in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

## IV. Conclusion

Results of the combined studies of actual defects in corundum crystals using methods based on quantum chemistry and atom-atom potentials agree well with each other and allow one to obtain more detailed and reliable information.

It follows from our calculations that hole self-trapping in corundum crystals is energetically favorable. Its atomic structure is close to that observed earlier for similar defects in alkali halide crystals ( $V_K$  centers). The experimental activation energy of 0.7 eV<sup>11</sup> is interpreted here as hops between small O triangles and 60° reorientations inside these triangles. The absorption energy is predicted to be at 2.9 eV. It is shown that the similar absorption energies observed for several related hole centers

Table II. Calculated Energies of Solution of Some Divalent Ions M<sup>2+</sup> in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>

	Energy of solution (eV) for M =				
	Mg	Mn	Fe	Co	Ni
As anion vacancy cluster	0.87	0.88	0.53	-1.25	-2.17
As M <sub>i</sub> cluster	1.40	0.51	0.07	-2.35	-3.56

with Al vacancy or substitutional Mg atoms nearby are due to their having the same basic structural element, the diatomic O<sub>2</sub> quasi-molecule.

For the mechanism of oxygen vacancy migration (a matter discussed for many years<sup>1</sup>) we show that the preferred mechanism involves hops within small triangles and hops roughly parallel to *c* along paths that link distorted octahedra in adjacent stacks. An important conclusion drawn from our calculations is that in these hops atoms deviate from the linear path between lattice sites if not constrained by symmetry.

Lastly, we have found that solution of impurity transition-metal ions is accompanied by defect clustering.

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