

Theoretical simulations of the radiation-induced defect processes in insulating materials

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The results of two basic kinds of computer simulations of radiation-induced processes in insulating materials, one based on quantum-mechanical and pair-potential (atomistic) approaches, and the other a phenomenological theory of diffusion-controlled reactions, are presented. It is shown that, by combining different techniques (atom–atom potentials and semi-empirical quantum chemical methods) the optimized geometry and the electronic structure of a family of hole centres in crystalline corundum ($\alpha\text{-Al}_2\text{O}_3$) could be found. Their energetics are analyzed; V^{2-} , $V^-V_{\text{Mg}}^-$ hole centres all have a common basic element, namely the diatomic molecule O_2^{3-} , which is responsible for their similar absorption energies. Our calculations provide evidence for the existence of a small-radius two-centre polaron (self-trapped hole, or STH) with an optical absorption energy of around 2.9 eV. The strong covalent bonding of the two O atoms sharing a hole makes this centre analogous to the V_{K} centre in alkali halides. The calculated activation energy for the STH hops (≈ 0.9 eV) between different O triangles is close to the experimental.

1. Introduction

The mechanism and kinetics of radiation damage in insulating materials remains an important topical problem, especially for oxides [1–3]. The atomic structure of the relevant electronic excitations is one of the key points here, including the problem of hole self-trapping, since often self-trapped holes (STHs) serve as cores for self-trapped excitons. Despite the fact that these STHs have been well studied in alkali halides and other ionic materials [4], their possible existence in oxide crystals, and, in particular, corundum ($\alpha\text{-Al}_2\text{O}_3$) is a matter of a long-standing debate [1,5]. These crystals continue to attract a good deal of attention because of their use in highly sensitive TSL α -radiation detectors [6], in infrared fibres [7], and as a laser material [8]. On the other hand, corundum is a useful model material for a wide class of oxides and ceramics, on which different theoretical techniques could be tested and improved. Its semi-ionic covalent bonding and rather complicated structure with ten atoms per unit cell (Fig. 1a) make theoretical studies of defects in corundum not an easy task.

In this paper we will summarize the progress made in the last several years on theoretical studies of STHs and other hole centres in corundum, focusing on the

combined use of atomic simulations and the phenomenological theory of thermostimulated luminescence which arises from the recombination of STHs and electron-excess centres [9,10].

2. Methods used for atomistic simulations

In recent years, two principal approaches to defect modelling in ionic solids have been used, based respectively on pairwise atom potentials [11,12] and on quantum-chemical methods in either semi-empirical or non-empirical versions [14]. The advantage of the former approach is its ability to treat explicitly the relaxation of several tens of ions in the defective region, whereas the latter allows us to study effects when charge re-distribution plays an important role.

In the present study, we used the method of atom–atom potentials as implemented in the CASCADE computer code [15] for non-cubic lattices with potentials from ref. [16]. Note that the latter paper, together with the studies by Mackrodt [17] and Dienes et al. [18] are the only three existing theoretical investigations of the defect properties of corundum. The defective region I in our work contained 300 atomic cores and shells, which is larger than that used in previous studies.

The quantum-chemical semi-empirical method of intermediate neglect of differential overlap (INDO)

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has been used successfully in recent years for defect calculations in oxide crystals, including MgO, SiO₂, Li₂O and α -Al₂O₃ [19,20]. Its parametrization for corundum calculations has been given by Jacobs et al. in ref. [19]. Here we note only that the lattice constant was reproduced with an accuracy of 5% and the bulk modulus to 15%. Several stoichiometric clusters, namely [Al₄O₆], [Al₈O₁₂], [Al₁₄O₂₁] and [Al₂₆O₃₉] embedded into the electrostatic crystal field of a rigid non-point ionic lattice were used for defect calculations. Surface ions were allowed to relax to the equilibrium geometry in order to reduce the effects of the cluster boundary. In the perfect corundum calculation we found the effective atomic charges to be: +2.4e for Al and –1.6e for O. The Mulliken population analysis shows that O–O bonds are not populated at all but that two kinds of Al–O bonds (1.84 Å and 1.98 Å) reveal rather high populations of 0.258e and 0.17e respectively (Table 1). These Al–O bonds are directly responsible for the partly covalent nature of the chemical bonding in corundum.

After calculating perfect corundum, a hole was inserted into the cluster, making no a priori assumptions about the form of its localization, and different modes of ionic relaxation were simulated in order to find the energetically most favourable equilibrium geometry and to calculate the activation energy for its thermally stimulated hopping for a variety of possible migration mechanisms.

3. Results of simulations

3.1. A model for the static self-trapped hole

The INDO calculations show that, when a hole is inserted into a cluster, it occupies the twofold degenerate molecular orbital e'' comprising atomic orbitals of three O atoms in the basic structural triangles of corundum (Fig. 1a). However, the Jahn–Teller effect will reduce the total energy by atomic relaxations,

Table 1

Populations of bonds between atoms in perfect and defective corundum crystals. Atom numbering is shown in Fig. 1. Figures in brackets are the results of ab initio HF calculations [40]. 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	1–4	0.258	0.229	0.267	0.270	0.228
	3–4	0.258 (0.214)	0.210	0.359	0.317	0.282
O–O	1–2	0.002	0.267	0.352	0.363	0.300
	1–3	0.002 (–0.020)	0.001	0.001	0.001	0.001

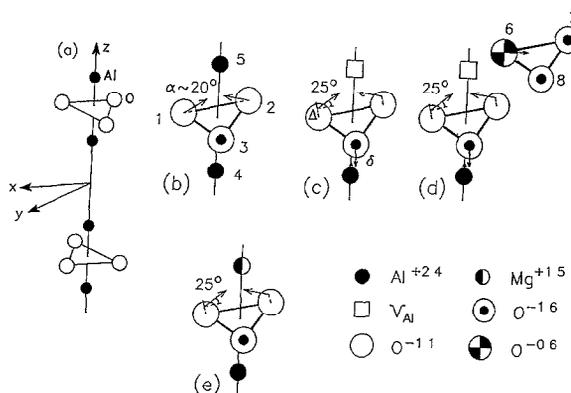


Fig. 1. (a) Contents of the unit cell of corundum showing the location of the Al atoms above and below the plane containing three O atoms which form an equilateral triangle (the so-called “small triangle”); (b) The self-trapped hole; arrows show the relaxation of the two O atoms which share the hole; (c) V²⁻ centre (STH adjacent to a cation vacancy); (d) V⁻ centre (two STHs adjacent to a cation vacancy. The second hole is localized on O atom 6, which relaxes in the direction indicated); (e) V_{Mg} centre (STH adjacent to a substitutional Mg impurity).

which lower the D_{3h} symmetry of the perfect equilateral O triangle. In the Jahn–Teller theory [21] this is the so-called $e \otimes E$ problem and the ionic relaxations promoting the energy reduction will be one of the six normal vibrations of the triatomic molecule with D_{3h} symmetry, or their combination [22].

Since calculations reveal that the hole e'' orbital is antibonding with respect to O atoms and slightly bonding for the two Al atoms on each side of the O triangle along the z axis, we expect an inward O relaxation accompanied by outward Al displacements to give the equilibrium STH geometry. Using a 35-atom cluster, in the INDO calculations we found that a nearly 40% displacement of two O atoms (O₁ and O₂ in Fig. 1b) at an angle of $\alpha = 20^\circ$ (with respect to the straight line connecting O sites), accompanied by a 20% outward relaxation of the two nearest Al atoms, Al₄ and Al₅, is energetically the most favourable configuration and characterized by the large energy gain of about 5.5 eV. 80% of the hole density is localized on these two displaced O atoms. For 65-atom clusters these figures do not change considerably (35% and 12% for the relaxations and a 5.3 eV gain in energy). This shows that a quantum cluster containing 35 atoms (or 7 structural units of Al₂O₃, Fig. 1a) is sufficiently large to achieve realistic results. The populations of the bonds between atoms sharing and surrounding the STH are shown in Table 1. These reveal a high degree of covalent bonding between the two O atoms sharing the hole (Fig. 1b) which is comparable to that between Al and O atoms in pure corundum.

To check our INDO findings, we used the method of simulating a crystal by using atom–atom potentials, as implemented in the CASCADE code. For the STH calculations O^-O^- short-range potentials were determined from the potential energy curves obtained from INDO calculations, by relaxing two O atoms only and fixing the coordinates of the remaining atoms. This O^-O^- potential curve is given in ref. [22]. Owing to chemical bonding within the STH, the energy minimum is deeper by 3 eV than that for the $O^{2-}O^{2-}$ interaction [16]. In the Buckingham parametrization this deeper minimum is simulated by an increase in the A and C parameters. The optimized geometry obtained with corundum potentials [16] and the INDO O^-O^- potential is qualitatively similar to that from INDO calculations, but now the angle α between the lines joining their lattice sites to the displaced positions of atoms O_1 , O_2 (Fig. 1b), and the straight line connecting their perfect-crystal sites, is only about 6° ; however the third O atom is also displaced in the outward direction by about 11% of the O–O distance. The crystal polarization energy, found using CASCADE, and the INDO equilibrium geometry is 7.2 eV and results from the electronic contribution caused by displacement of the atomic shells of surrounding ions (4.2 eV) and the ionic contribution which is 3 eV. (This latter figure does not include the atomic relaxation within the STH, namely the displacements of the two O atoms O_1 , O_2 and the two nearest Al atoms Al_4 , Al_5 , which are accounted for separately.) Thus, we arrive at a STH model which is very similar to that known as the V_K centre in alkali halides [4,23,24] and also recently discovered in EPR experiments on fused silica [25]; it is a diatomic quasimolecule with a shared hole between the two O atoms. The optical absorption energy, calculated as the difference between the total energy of the STH in its ground and excited state (the so called Δ SCF method) is predicted to be about 2.9 eV.

3.2. Other hole centres

Several hole centres associated with defects have been observed experimentally [26]. These are: the V^{2-} and V^- centres (one and two holes trapped near a cation vacancy) and the V_{Mg} centre (a hole trapped by a Mg impurity substituting for an Al atom). These defects were calculated by us in [27,28] (see Figs. 1c–1e) and the principal results are summarized here briefly.

V^{2-} centre. When an Al vacancy is formed it has an effective negative charge (see the V^{2-} centre shown in Fig. 1c). 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 1 and 2 go up by 0.07 \AA and O atom 3 down by 0.12 \AA . The Al atom 4 on the other side of the O triangle is also shifted up by the same amount, 0.12 \AA . We have simulated new different modes of O atom displacements to check whether and 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 $\alpha = 25^\circ$ (with respect to the straight line connecting the two O atom sites). As one can see in Table 1, the population of this bond (O_1-O_2) is even larger than that in the STH. Partly, this results from the essential charge redistribution caused by the Al vacancy: the effective charges of O atoms 1 and 2 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 3 is displaced down by 0.3 \AA , but Al atom 4 is displaced up by 0.26 \AA .

V^- centre. This centre has two holes trapped by an Al vacancy and thus it was of great interest to find out whether one or both of them will be a di-centre defect. We therefore modelled again the different relaxation modes used earlier for the STH (and also some others) for the O atoms of the basic structural triangle and for O atoms from the nearest triangle lying 2.17 \AA higher along the z axis (in the direction of the vacancy) but displaced in the xy plane (see Fig. 1d). 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 on the atom closer to the second hole being higher by $0.1e$.

V_{Mg} centre. In this centre (Fig. 1e) a hole is trapped by a 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 $2.0e$, in our INDO calculations we obtained $q(Mg) = 1.90e$ whereas for the Al atoms in perfect corundum $q(Al) = 2.34e$; therefore the effective charge is only $-0.44e$. Thus this centre is just a slightly perturbed STH. In particular, the upward shift of O atoms 1 and 2 is negligible, being

0.04 Å only. In CASCADE calculations we found that the Mg atom is also displaced up from the Al site by 0.2 Å and that Al atom 4, which is located along the Z axis on the other side of the O triangle, is also displaced upwards by nearly the same amount.

3.3. Energetics of self-trapping

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 provided atom–atom potentials for defective atoms are fitted in a proper way using 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 same 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 a Mg atom substituting for 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 close absorption energies (2.57 eV; 3.08 eV; 3.08 eV). Our INDO calculations give these energies as about 3.5 eV, but this is only an estimate because we are ignoring any change in the crystal polarization between the ground and excited hole states. Another important problem is whether the formation of these centres is energetically favourable. The key point here is to get a reliable estimate of the so-called hole localization energy, E_{loc} , on a single atom 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 [23–25,29] 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 symmetric and homogeneous upper valence bands constructed entirely from halogen 3p AOs. (If we use this estimate, $E_{loc} \approx 3.8$ –5 eV in corundum crystals.) However, this would not be a correct estimate for partly covalent corundum crystals (as well as for silica) whose valence band has a strong admixture of Al AOs and O atoms form a sharp sub-band near the top of the valence band.

A new refined formalism for calculating E_{loc} in such crystals with mixed valence band has been developed in refs. [30–32]. The method uses the density matrix obtained in self-consistent electronic density calculations and yields for corundum the surprisingly small value of $E_{loc} = 0.5$ –0.75 eV [32]. With this value we can obtain net hole trapping energy, E_{ST} from the relation

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

Here $E_{rel} = -5.5$ eV is the above discussed energy gain due to relaxation of defect atoms caused mainly by their covalent bonding, and $E_{pol} = -7.2$ eV is the

polarization of the crystal due to displacements of both cores ionic contribution ($= -3.0$ eV) and shells (electronic contributions ($= -4.2$ eV) induced by the defect. Finally, one has to subtract from the latter value the electronic polarization caused by a band (free) hole before it is trapped, which is -3.12 eV [32], so that $E_{ST} = -8.8$ to -9.1 eV for the STH. (Note that we estimated E_{rel} from our INDO cluster calculations and all polarization contributions by means of the atom–atom potentials.) The value of E_{ST} turns out to be definitely negative for all hole centres, including the STH, which confirm that hole trapping is energetically favourable and occurs spontaneously. Perhaps the self-trapping energy seems to be rather large, but this is due principally to the large energy change associated with O–O chemical bond formation.

Calculations performed for the one-site hole polaron (in which a hole is trapped by a single O atom which is displaced towards the centre of the basic O triangle) show that it is also an energetically favourable process, but much less so than for the two-site hole localization [22].

3.4. Mechanisms of STH motion

The corundum structure contains equidistant planes of O triangles (with the O–O distance 2.39 Å) organized into stacks along the Z axis in such a way that any O triangle has three nearest-neighbour triangles lying 2.17 Å above it on O planes and arranged symmetrically (Fig. 1). Their end atoms form one of the large triangles ABC with a considerable larger O–O distance, 2.93 Å. STH migration in this structure occurs as a combination of their 60° reorientation inside small triangles (from one pair of O atoms into another pair) and hops either along the Z axis through alternating small and large triangles, or through small triangles only, which lie on different O planes. To simulate these processes we used INDO 35-atom clusters with the STH on the central O triangle [20,22]. Starting from the two-site hole in Fig. 2 path 1, a 60° reorientation is seen to involve a transfer of electronic charge from the third O atom, say c, which is not involved in the original STH, to one of the two O atoms on which the hole resides (say a). Complete transfer of about 0.4e, and simultaneously the return of atom a to its normal lattice site, while b and c undergo the outward relaxation to the STH equilibrium configuration associated with a STH on bc (instead of ab), effects the reorientation. Although the atom movements envisaged may seem elaborate, they are no more than take place in the dynamical change from one Jahn–Teller configuration to an equivalent configuration. The saddle-point configuration is clearly (and confirmed by INDO calculation to be) a state in which the hole is shared by all three O atoms with 50% of the hole

density on the central atom b. Hole charge density and atomic relaxations for the 60° reorientation are shown in Fig. 2, where path 1 indicates the shift in the O–O bond as well as the initial (full lines) and final (broken lines) charge distributions. As in all INDO calculation the final charge distribution in any calculation is obtained automatically for specified atom positions. The 60° reorientation energy was found in this way to be 0.9 eV.

Hole hopping from a small triangle on to a large triangle just above it (see Fig. 2, path 3) requires a very high activation energy of several electronvolts. The reason for this is clear from the electronic density distribution maps in corundum which demonstrated strong bonding inside O octahedra with the Al atoms at their centres, but almost no direct bonding between O atoms. In this respect, large triangles are more a geometrical construction rather than a structural reality since all their O atoms belong to different atomic stacks and the electron (hole) density redistribution which is necessary for a STH hop to a large triangle is hardly possible.

The last possibility for STH hops is that between small O triangles. Qualitatively speaking, it can occur in two ways, as shown in Fig. 3. In the first case (Fig. 3 a), the hop is prepared for by the relaxation of the two O atoms in triangle 2 which is to receive the hole, and only then does the hole hop on to the already relaxed O atoms. In the second case (Fig. 3b), atoms that form

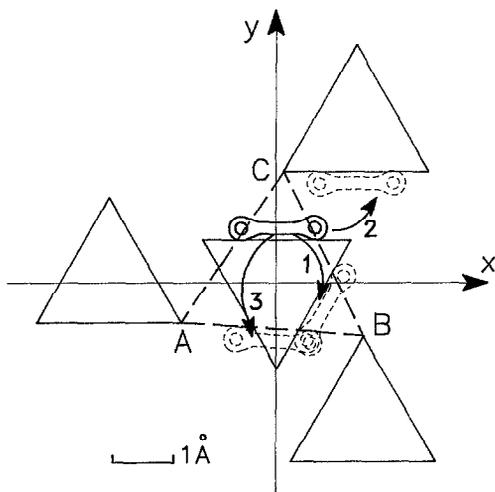


Fig. 2. View down the Z axis of the corundum structure. The central small triangle has three nearest-neighbours (nn) on the next oxygen plane above it, which belong to different z-axis stacks. These three nn form the so-called "large triangle ABC". Potential STH hops include: (1) a 60° reorientation inside small triangles; (2) hopping to a nn small triangle on the plane above the STH; and (3) hopping from a small triangle to a large triangle.

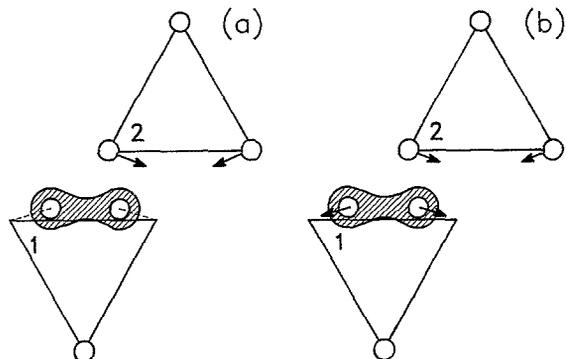


Fig. 3. Two possible mechanisms for STH hopping between small triangles. (a) Two nn atoms in triangle 2 relax to their positions in the STH configuration and the hole then hops to the O atoms in their already prepared positions. (b) The two O atoms in triangle 1 relax half-way to their original lattice sites, while the O atoms in triangle 2 relax half-way to their positions in the STH configuration so that both pairs of O atoms are equally displaced from their regular lattice sites.

the initial and final polaron sites relax in opposite directions and the hole moves at the instant that these two configurations become equivalent, with both being relaxed to 50% of the equilibrium STH configuration. The second model is generally accepted [33] since energetically it seems to be more favourable; the minimum energy required to create the configuration b appears to be $\frac{1}{2}E_p$, whereas that to create the configuration a is E_p (the polaron energy). However, this is only true provided that the constant A defining the lattice deformation energy Aq^2 is the same for both wells, with and without a hole. But as we found in our INDO calculations, this is not the case. Calculations show that the force constants for the O–O interaction are not the same for the perfect crystal and for a STH; this is because of the chemical bonding between the two O atoms on which the STH resides. Both deformations are highly anharmonic but it is clear [22] that the energy gain on relaxing two oxide ions inward in the perfect crystal is much less than the energy required to stretch the bond. The net result is a total activation energy that is as large as about 2.2 eV, which is much higher than that for the first mechanism (Fig. 3b), $E_a = 0.9$ eV. Analysis of charge-density distributions demonstrates that for both mechanisms the hole is delocalized over four O atoms in the saddle point. Another interesting feature of our computer simulations is that bond bending of the two O atoms sharing a hole is an essential feature which lowers the hopping activation energy; if it were absent, the barrier height would be about 2 eV. On the other hand, the bond bending of the two O atoms that receive the hole is less important and lowers the activation energy by 0.1 eV only.

In conclusion of section 3 we should mention that the same simulation techniques were applied also to calculations of the different migration paths of anion and cation vacancies [34] and to transition metal impurities [35].

4. The kinetics of STH recombination

In undoped high-purity crystals with a low concentration of anion defects and related F^+ and F centres (one and two electrons respectively) trapped at V_o , a defect-free hole centre was observed at liquid-nitrogen temperature (LNT) either after X-irradiation or because of photostimulation in the absorption bands of the above-discussed hole centres in samples that had undergone preliminary X-irradiation at 300 K. These new hole centres anneal in the region of 210–230 K, giving rise to the main thermostimulated luminescence (TSL) peak at 220 K. Unfortunately, in the same temperature interval, holes trapped at impurity cations of a lower valence than Al^{3+} (Mg^{2+} , Li^+ and Na^+) are also annealed out but, unlike a Mg-containing specimen, pure undoped corundum crystals show a spectral composition of TSL which coincides with the spectrum of the tunnelling luminescence ($h\nu_{max} = 4.3$ eV) observed at LNT when defects are immobile [5]. A stepwise small (3–5 K) increase or decrease in temperature within the TSL peak results in a change in the recombination luminescence intensity which displays considerable inertia (about 100 s) [36]. By analogy with similar processes in KCl and KBr crystals with STH (V_K centres) this “delayed luminescence” was interpreted and quantitatively analysed in terms of the slow diffusion-controlled motion of small-radius polarons (STH) and their subsequent tunnelling recombination with electron (F) centres [9]. The relevant activation energy for hole hopping was found to be 0.7 eV. It was

assumed that STHs are also responsible for the so-called E luminescence band at 3.8 eV which was considered to result from $(STH + e^-)$ annihilation.

These experimental results strongly motivated us to perform the present atomistic simulations of the mechanism and activation energy of STH motion in corundum. The above-presented agreement of the calculated activation energy for STH hops (0.9 eV) and the experimental value of 0.7 eV argues strongly for the identity of our small-radius polarons and the hole centres observed experimentally. In order to extract more information from the TSL experiments, we developed the theory discussed briefly below.

First of all, the very effect observed of a very slow and inertial increase in recombination intensity after an instantaneous (small) temperature increment, cannot be understood in terms of either an electron delocalization from traps, or the usual diffusion-controlled recombination of mobile defects. The long-time change of intensity indicates clearly that a relatively slow spatial defect redistribution takes place. For instance, in the standard theory of diffusion-controlled reactions, the change of concentrations with time is characterized by the reaction rate $K = 4\pi DR_0$ (D is the diffusion coefficient and R_0 is the recombination radius); a stepwise change of temperature leads here to the synchronous inertialless change of $D = D_0 \exp(-E_a/kT)$ (E_a is the activation energy), whereas the relative spatial distribution (and the joint density) of dissimilar defects, remains unaltered: $Y(r) = 1 - R_0/r$ [38]. This is why such delayed kinetics can arise only if the joint density $Y(r)$ is dependent on defect mobility $D(T)$. This is true for the tunnelling recombination of electron and hole defects [39], observed, in particular, for STHs in corundum, as described above. In terms of this theory, which is described in detail in ref. [9], the observed effect is due to the slow transition between two different joint densities corresponding to the two

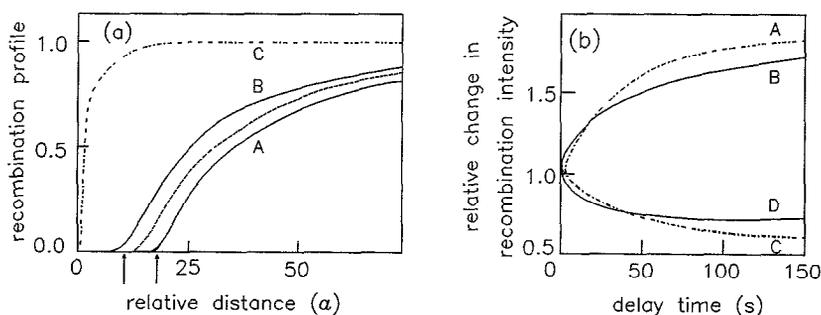


Fig. 4. (a) Schematic recombination profiles for diffusion-controlled tunnelling recombination at two temperatures. The temperature increases from A to B; the dashed line shows the transient profile. C is the profile if no tunnelling recombination occurs. The relative distance is measured in units of the half Bohr radius of the electronic centre involved in of the tunnelling recombination. (b) Relative change in the recombination luminescence intensity, I/I_0 , in corundum crystals after stepwise temperature increase from 198.2 K to 201.5 K (B) and cooling from 204.4 K down 201.5 K (D) [36]. The dotted-dash curves A, C show results of theoretical calculations [9].

respective temperatures before and after the stepwise temperature change (due to either cooling or heating). The recombination profile is defined by a balance between the mutual approach of defects by diffusion and their tunnelling recombination, the probability of which depends exponentially on the relative distance between the combining pair of defects. For instance, if a sample is heated, rapidly moving STHs recombine with electron centres, at shorter distances, and the $Y(T)$ shifts from the profile A, Fig. 4a, to a new equilibrium position B.

The long delay time observed ($\cong 150$ s, Fig. 4b) arises directly from the slow defect diffusion. In pure or slightly doped wide-gap insulators this is a strong indication of the presence of small-radius polarons having high activation energies for thermally-activated hops. This effect was observed earlier in a number of insulators including AlN, $\text{Ba}_3(\text{PO}_4)_2$, the Na-salt of DNA, KCl, KBr [9]. The mathematical formalism is described in detail in ref. [9]; we will stress here only that fitting the theoretical curve to the experimental change in recombination intensity allows us to obtain the parameters a^2/D and E_a which define the diffusion and tunnelling recombination of defects involved in the recombination. The value of E_a , defining the relative increment in the intensity I , as $t \rightarrow \infty$, was found to be close to the value of 0.7 eV obtained from TSL [36]. The second parameter a^2/D , which determines the delay time, was found to be 30 ± 10 s. It could be used to calculate the diffusion-coefficient pre-exponential factor $D_0 = \nu_0 \lambda^2 / 6$ (λ is the hopping length, ν_0 is the hopping frequency factor) but this requires a knowledge of the parameter a which could be found from calculations on the electron F^+ centres in corundum. These calculations are in progress. In this manner we found for the STHs in KCl (V_K centres) a value of ν_0 of $4.1 \times 10^{13} \text{ s}^{-1}$, in very good agreement with that from optical dichroism measurements [4,23] and in satisfactorily close agreement with the LO phonon frequency in this material. If we scale the value of a for KCl by a factor of 2, because of the higher dielectric constant of alumina, and use a value for λ of 3.5 \AA (which is the polaron hopping distance between closest triangles in adjacent stacks) we find $\nu_0 = 7 \times 10^{15} \text{ Hz}$, which is again in satisfactory agreement with the LO phonon frequency in corundum, $2.5 \times 10^{16} \text{ Hz}$ [41], given the $\pm 33\%$ uncertainty in a^2/D . Note in conclusion that a more refined formalism incorporating the discreteness of small-polaron hops in a crystalline lattice has been presented in ref. [10] and applied to V_K centres in KCl crystals.

5. Conclusion

In this paper, we have shown that by combining different computer-simulation techniques, the atomic

and electronic structure of point radiation defects in general, and small-radius polarons in particular, could be found and their optical properties, the migration mechanism, and the relevant activation energy for thermally activated hops, determined. We have concentrated here on hole centres in corundum crystals; recent progress in small-polaron studies on MgO and KCl is reported in refs. [29,37]. Development of new theoretical methods, in particular embedding techniques, will be an important element of further point defect calculations in semi-ionic solids.

The second point we wanted to stress in this paper is that atomistic simulations can be combined with the phenomenological theory of reactions between defects which lead, in particular, to the thermostimulated luminescence observed experimentally. We have demonstrated here the good argument between these quite different approaches, using self-trapped holes in corundum as an example.

In the particular case of oxide crystals (like MgO and $\alpha\text{-Al}_2\text{O}_3$), the next important theoretical steps to be taken are the following: (i) a study of the luminescent centres (likely related to C substitutional atoms) in corundum dosimeters [6]; (ii) calculations of the quanta and mechanism of tunnelling recombination between F^+ centres and self-trapped holes, in order to interpret experimental data [36]; (iii) the investigation of different atomic configurations of self-trapped excitons in corundum crystals [5]; (iv) calculations of the formation energy of short-lived and long-lived primary Frenkel defects and the study of how this is affected by vacancies and other defects in MgO and corundum crystals [1,3].

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References

- [1] J. Valbis and N. Itoh, *Radiat. Eff. Defects in Solids* 116 (1991) 171.
- [2] N. Itoh, *Radiat. Eff. Defects in Solids* 110 (1989) 19.
- [3] E. Aluker, V. Gavrilov, A. Sitdikov, S. Chernov and D. Erts, *Sov. Phys-Solid State* 33 (1991) 209; *Opt. Spectr.* 70 (1991) 75.
- [4] A.L. Shluger and A.M. Stoneham, *J. Phys.; Cond. Matter* 5 (1993) 3049.
- [5] I.A. Tale, P. Kulis, Z. Rachko, M. Springis and J. Jansons, *Radiat. Eff. Defects in Solids* 119–121 (1991) 963.
- [6] M.S. Akselrod, V.A. Kortov, D.J. Kravetsky and V.I. Gotlib, *Radiat. Prot. Dosim.* 32 (1990) 15.

- [7] G. Merzberg and J. Harrington, *Infrared Fibre Optics III*, Proc. SPIE, vol. 1591 (SPIE, Bellingham, Washington, SPIE, 1990) p. 13.
- [8] E.R. Martynovich, V.I. Baryshnikov and V.A. Grigorov, *Opt. Commun.* 53 (1985) 257.
- [9] E. Kotomin, I. Tale, V. Tale, P. Butlers and P. Kulis, *J. Phys.; Cond. Matter* 1 (1989) 6777.
- [10] E. Kotomin, I. Tale, V. Tale and L. Kantorovich, *J. Phys.; Cond. Matter* 4 (1992) 7429.
- [11] C.R.A. Catlow, R. James and W.C. Mackrodt (eds.), *Computer Simulations of Solids* (Berlin, Springer, 1982).
- [12] J.H. Harding, *Rep. Progr. Phys.* 53 (1990) 1403.
- [13] R.W. Grimes, C.R.A. Catlow and A.L. Shluger (eds.), *Quantum Mechanical Cluster Calculations in Solid State Studies* (World Scientific, Singapore, 1992).
- [14] J. Vail, *J. Phys. Chem. Sol.* 51 (1990) 589.
- [15] M. Leslie, *Physica B* 131 (1985) 145.
- [16] C.R.A. Catlow, R. James, W.C. Mackrodt and R.F. Stewart, *Phys. Rev. B* 25 (1982) 1006.
- [17] W.C. Mackrodt, *Adv. Ceram.* 10 (1983) 62.
- [18] G.J. Dienes, D.O. Welch, C.R. Fisher, R.D. Hatcher, O. Lazareth and M. Samberg, *Phys. Rev. B* 11 (1975) 3060.
- [19] P.W.M. Jacobs, E.A. Kotomin, A. Stashans, E.V. Stafanovich and I.A. Tale, *J. Phys.; Cond. Matter* 4 (1992) 7531.
- [20] P.W.M. Jacobs and E.A. Kotomin, *Phys. Rev. Lett.* 69 (1992) 7411.
- [21] I.B. Bersuker and V.Z. Polinger, *Vibronic Interactions in Crystals and Molecules* (Nauka, Moscow, 1983).
- [22] P.W.M. Jacobs, E.A. Kotomin, A. Stashans and I.A. Tale, *Philos. Mag. B* 67 (1993) 557.
- [23] A.M. Stoneham, *Theory of Defects in Solids* (Oxford University Press, London, 1975).
- [24] P.E. Cade, A.M. Stoneham and P.W. Tasker, *Phys. Rev. B* 30 (1984) 4621.
- [25] D.L. Griscom, *Phys. Rev. B* 40 (1989) 4224.
- [26] J.-M. Spaeth and F.K. Koschick, *J. Phys. Chem. Sol.* 52 (1991) 1.
- [27] P.W.M. Jacobs, E.A. Kotomin, A. Stashans and I.A. Tale, *Model. Sim. Mater. Sci. Eng.* 2 (1994).
- [28] P.W.M. Jacobs, E.A. Kotomin, A. Stashans, I.A. Tale and E.V. Stafanovich, *Proc. Int. Conf. on Defects in Insul. Materials* (World Scientific, Singapore, 1993).
- [29] A.L. Shluger, E.N. Heifets, J.D. Gale and C.R.A. Catlow, *J. Phys.; Cond. Matter* 4 (1992) 5711.
- [30] E.N. Heifets and A.L. Shluger, *J. Phys.; Cond. Matter* 4 (1992) 8311.
- [31] L. Kantorovich, E. Heifets, A. Livshic, M. Kuklja and P. Zapol, *Phys. Rev. B* 47 (1993) 14875.
- [32] L. Kantorovich, A. Sashans, E. Kotomin and P.W.M. Jacobs, *Int. J. Quantum Chem.*, to be published.
- [33] N.F. Mott and E.A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1979) p. 75.
- [34] P.W.M. Jacobs and E.A. Kotomin, *J. Solid State Chem.* 106 (1993) 27.
- [35] P.W.M. Jacobs and E.A. Kotomin, *Philos. Mag. B* 67 (1993) 557.
- [36] P. Kulis, Ph.D. thesis, Riga (1987).
- [37] A.L. Shluger, L.N. Kantorovich, E.N. Heifets, E.K. Shidlovskaya and R.W. Grimes, *J. Phys.; Cond. Matter* 4 (1992) 7417.
- [38] T.R. Waite, *Phys. Rev.* 107 (1957) 463.
- [39] E.A. Kotomin and A.B. Doktorov, *Phys. State Solids B* 114 (1982) 287.
- [40] L. Salasco, R. Dovesi, R. Orlando, M. Causà and V.R. Saunders, *Molec. Phys.* 72 (1991) 267.
- [41] H. Bialas and H.J. Stolz, *Z. Phys. B* 21 (1975) 319.