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Self-trapping at aluminium–alkali centres in α -quartz

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Abstract. We present a calculation of the self-trapping properties in α -quartz of aluminium–sodium centres using a Mott–Littleton calculation. It is found that the hole in $[\text{AlO}_4/\text{M}]^0$ with $\text{M} = \text{Na}$ is most energetically favourable to self-trap at an oxygen atom nearest to the Al ion with a ‘short’ bond. It is also found that the Na ion is in the nearby c -axis channel on the long-bond side of the Al ion. These calculated results agree well with the experimental results. We also found that the hole is also energetically favourable to self-trap at an oxygen ion next nearest to the Al ion. The hole-trapping energies in the two cases are similar and therefore their sites may not be easily distinguished in the experiment.

1. Introduction

Understanding the charge traps in quartz is crucial for reliable fabrication of radiation-tolerant metal–oxide–semiconductor devices. Many studies have been carried out in this field using a variety of experimental [1–8] and theoretical techniques [9–14]. Among the charge traps, the self-trapped hole or self-trapped electron is important in understanding charging and discharging phenomena in insulators [15, 16]. A free charge carrier can lower the ground-state energy of a hole by displacing and polarizing the surrounding lattice. In doing so, the charge carrier is self-trapped and localized. Much work has been done on this interesting topic and a comprehensive review has been given by Schluger and Stoneham [17].

In several polymorphs of silica, there is evidence of self-trapping holes or self-trapping electrons. In quartz, the exciton (a bound electron–hole pair) is self-trapping. This is the basis of the characteristic blue luminescence, with its very large Stokes shift from the ultraviolet band-edge absorption. By using quantum chemistry methods, Fisher *et al* [18] have identified that the hole component of the exciton is located on an oxygen atom and that its two nearest-neighbour silicon atoms are found to relax away from the defect oxygen atom. The electron component of the exciton is localized partly at the defect oxygen atom and partly at a neighbouring silicon atom. The self-trapping exciton also exists in amorphous SiO_2 .

In amorphous SiO_2 , self-trapped holes (STHs) have been identified, and the structural variations will be a contributing factor. Griscom [19] observed two relevant electron spin resonance (ESR) spectra in irradiated silica glasses. This evidence has been supported by semi-empirical and *ab-initio* molecular orbital calculations by Edwards [20]. The underlying problem with most of the quantum chemistry calculations is the small size of the cluster used. In his computational cell, only two silicon and seven oxygen atoms are included in the cluster, although the cluster was embedded either in a fixed cage of $\text{Si}(\text{OH})_3$ units or in an array of point charges. However, hole localization is mainly due to polarization and

distortion energy, both of which are long range in nature. In addition, many defect reactions can only be modelled by including many more atoms explicitly.

Other than a site-to-site variation in the structural properties of glasses, modest amounts of impurity doping, e.g. substitutions of Ge and Al for Si, lead to the trapping of both electrons and holes. Hayes and Jenkin [21] identified an STH in Ge-doped α -quartz but were unable to find analogous STHs in undoped α -quartz. STHs have also been observed experimentally in SiO_2 samples containing defect centres $[\text{AlO}_4/\text{M}]^0$ (where $\text{M} = \text{H}^+$, Li^+ , Na^+ or Ag^+) [22]. After irradiation, each species $[\text{AlO}_4/\text{M}]^0$ formed contains a single unpaired hole occurring mostly in a non-bonding orbital on one of the four adjacent bridging oxygen ions. The centre $[\text{AlO}_4/\text{Na}]^+$ has recently been characterized by ESR [23]. It is formed in α -quartz by x-irradiation at 77 K and contains an Al ion substituted for a Si ion, with an electron hole on a nearest-neighbour oxygen ion, and an interstitial Na ion, which acts as a charge compensator before loss of the electron. Dickson and Weil [23] suggested that the hole is on an oxygen ion linked to the Al ion by a 'short' bond, and that the Na ion is in the nearby *c*-axis channel on the long-bond side of the Al ion. However, the trapping mechanism is complex and is not fully understood.

Our recent Mott-Littleton shell model calculations [24] suggest that it is possible for STHs to be weakly trapped at oxygen ions. Nevertheless, additional stabilization from other causes, such as structural variations in amorphous silica, are important contributing factors. We have also calculated the self-trapping properties of Ge^{4+} in α -quartz using the Mott-Littleton method [25]. Our calculation suggests that it is easier for a hole to be self-trapped at oxygen ions next to a Ge^{3+} ion than at that ion, which is in agreement with the experimental results. The hole self-trapping next to Ge^{3+} is accompanied by a large network distortion. Our results suggest that the distortion in the Si-O-Si bond angle plays a more important role in hole self-trapping than alteration of the Si-O bond length.

Sim and Catlow [26] presented a detailed analysis of the results of Mott-Littleton calculation on defect centres ($[\text{AlO}_4]^-$, $[\text{AlO}_4]^0$, $[\text{AlO}_4]^+$, $[\text{AlO}_4\text{H}]^+$, $[\text{AlO}_4\text{H}_2]^+$ and $[\text{AlO}_4\text{H}]^0$) associated with radiation damage in α -quartz. These results include defect geometry, binding energies and vibrational frequencies calculated for some H^+ -containing centres. A comparison was made with available experimental data for those aluminium centres which are compensated by electron-holes and H^+ . Their results suggested that, in α -quartz, both bound and unbound electron-holes are predominantly localized as polaronic species. Later, Sim *et al* [27] presented an *ab-initio* self-consistent-field (SCF) molecular orbital (MO) calculation on defect centres involved in radiation damage of α -quartz. Various defect centres containing Al^{3+} substitutional ions, and their compensating electron-hole and proton defects were studied. The results obtained for the $[\text{AlO}_4]^0$ centre are in close agreement with ESR data.

In this present work, we aim to study the properties of the STH of the defect centre $[\text{AlO}_4/\text{Na}]^+$ in α -quartz. We performed the Mott-Littleton calculation and discuss the structural change in the STH process.

2. Computational method

We choose to use the Mott-Littleton calculation which can treat the polarization and distortion of a large cluster explicitly. In this calculation, the defective lattice is treated by using a two-region strategy [28]. The crystal is formally divided into an inner region (region I) and an outer region (region II). In the inner region the lattice configuration is evaluated explicitly while the outer region can be viewed from the defect as a continuum. The displacements within the outer region are due solely to the electric field produced by

the total charge of the defect centred at the defect origin. A detailed discussion of this simulation technique can be found in [29].

Our simulation is based on the shell model generalization of the Born model of the solid, with additional three-body angle-dependent terms. The short-range two-body interactions used in this classic simulation are described by the Born-Mayer potential supplemented by an attractive r^{-6} term:

$$V(r) = A \exp(-r/\rho) - Cr^{-6} \quad (1)$$

where A , ρ and C are parameters. The polarizability of individual ions and its dependence on the local atomic environment is treated by the shell model [30], in which the outer valence cloud of the ion is simulated by a massless shell of charge number Y and the nucleus and inner electrons by a core of charge number X . The total charge number of the ion is thus $X + Y$, which indicates the oxidation state of the ion. The interaction between the core and the shell of any ion is deemed to be harmonic, with a spring constant k , and is represented by

$$V(r) = \frac{1}{2}kd^2 \quad (2)$$

where d is the relative displacement of core and shell of ion i . The electronic polarizability of the free ion is thus given by

$$\alpha = Y^2/k. \quad (3)$$

The three-body interactions are expressed as

$$V = \frac{1}{2}k_3(\theta - \theta_0)^2 \quad (4)$$

where k_3 is a three-body interaction constant, θ an angle between the three ions, and θ_0 the equilibrium angle.

In this work, the O ions are treated using the shell model while the Si ions are treated using a rigid model (without shell). We use the potential parameters A , ρ and C and the shell parameters Y and k derived for α -quartz by Sander *et al* [31]. This potential includes a three-body interaction and reproduces the structure of α -quartz in good agreement with the experimental data. It has been successfully applied to the calculation of the energies of point defects in quartz [32]. The Al ions are also treated using a rigid model and Na ions are treated using the shell model. Their potential parameters were taken from [32]. All the potential parameters used in this work are given in table 1. We used a radius for the inner region of 10 Å which includes 570 atoms. The inclusion of a large number of atoms in the inner region is particularly important in the study of the hole-trapping problem. The difference between the defect energies for the inclusion of 100 atoms and of 600 atoms can be as large as about 0.9 eV in α -quartz [24] while the self-trapping energy rarely exceeds several tenths of an electronvolt [17].

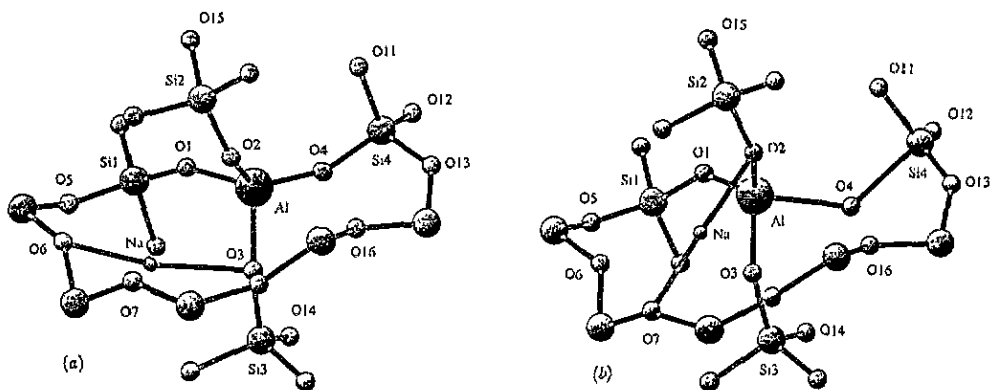
3. Results and discussion

Our model of a system of Al-doped α -quartz is made by substituting Al for one of the 24 basis Si atoms in α -quartz, with charge compensation attained by introducing an Na ion. The system is then run using the computer code CASCADE [33] until the system reaches equilibrium. This equilibrium system is used as the model system of Al-doped α -quartz. The coordinates and structural parameters of the atoms in Al-doped α -quartz at equilibrium (called the natural position) are given in tables 2 and 3, and the structure of this model system is shown in figure 1(a) (in all the figures shown in this paper, the atom pairs with

Table 1. Potential parameters.

Ion	k (eV Å ⁻²)	Y (e)	
Shell-model parameters			
Si		Rigid ion	
Al		Rigid ion	
O	74.92	-2.848	
Na	96.44	2.128	
Interaction	A (eV)	ρ (Å)	C (eV Å)
Two-body potential parameters			
O-O	22 764.0	0.1490	27.88
Si-O	1283.9073	0.3205	10.6616
Al-O	4986.0	0.385 23	0.0
Na-O	1226.80	0.3065	0.0
Interaction	k_3 (eV rad ⁻²)	θ_0 (deg)	
Three-body potential parameters			
O-Si-O	2.097	109.47	
O-Al-O	2.097	109.47	

interatomic distance less than 2.30 Å are connected by 'bonds' for convenience in showing the structural changes). The replacement of Si by Al changes the SiO₄ tetrahedra only slightly, whereas the AlO₄ tetrahedron has three longer bonds (Al-O(1), Al-O(2) and Al-O(3)) with a bond length of 1.70–1.77 Å, and one shorter Al-O(4) bond of 1.60 Å, which is comparable with the Si-O bond in the SiO₄ tetrahedron. It is noted that the Na ion is on the side of the three longer Al-O bonds, which agrees with the experiment [23].

Figure 1. The structure of Al³⁺-doped α -quartz (a) before and (b) after hole trapping at O(4).

The two shortest Na-O distances (Na-O(3) and Na-O(6)) are about 2.2 Å, as expected for the case of a tetrahedron [34]. The Hartree-Fock SCF MO calculation [35] gives an unrealistic Na-O distance of 1.4 Å. The reason may be that the calculation uses only a ten-atom cluster [Al(OH)₄Na]⁺ to model the centre [AlO₄/Na]⁺.

By assuming that the hole is localized on an oxygen atom, as suggested by experimental

Table 2. Equilibrium coordinates for the neutral and positively charged clusters in Al^{3+} -doped α -quartz.

	Positive position (\AA)			Natural position (\AA)			Displacement (\AA)
	X	Y	Z	X	Y	Z	
O(1)	0.0666	-1.3822	2.6806	0.2613	-1.4219	2.4973	0.2704
O(2)	1.7023	0.7104	2.1662	2.0679	0.4559	1.9580	0.4917
O(3)	2.0674	-1.6974	0.8120	1.9552	-1.7667	0.2767	0.5513
O(4)	0.0243	-0.2617	-0.3582	0.0000	0.0001	0.0000	0.4444
O(5)	0.9472	-3.3185	4.2144	0.9192	-3.2259	4.2316	0.0982
O(11)	-0.3731	2.4079	0.4775	-0.3139	2.5075	0.5255	0.1254
O(12)	-2.0300	1.1443	-1.1153	-1.9564	1.1700	-1.0720	0.0892
O(13)	0.6340	1.8602	-1.8678	0.5584	1.8094	-1.8222	0.1019
O(14)	0.6654	-3.1405	-0.9518	0.6834	-3.4871	-1.2205	0.4390
O(15)	0.7214	1.9597	4.2003	0.8053	1.7177	3.9150	0.3834
O(16)	3.0344	0.9920	-0.9175	2.9798	1.0399	-0.9883	0.1015
Si(1)	-0.2334	-2.8341	3.2371	-0.2756	-2.6878	3.2240	0.1528
Si(2)	2.0353	1.7557	3.3352	2.2121	1.4501	3.1559	0.3960
Si(3)	2.1045	-2.8452	-0.2899	2.1128	-3.0284	-0.6290	0.3855
Si(4)	-0.5696	1.6435	-0.9022	-0.4319	1.3526	-0.6165	0.4304
Al	0.9442	-0.6863	1.5889	0.9879	-0.5635	1.1270	0.4799
Na	3.5792	-0.5391	2.3264	2.2707	-2.7119	-2.2132	2.5389

fact, we then calculate the formation of a hole at various oxygen atoms at the vicinity of an Al impurity atom. Two energy terms are involved in the calculation. The first is an elastic energy and the other is an electronic energy. The elastic energy is contributed by lattice distortion as well as by lattice polarization. Again, the polarization energy is composed of displacement and electronic components. We made an estimate of the two components of the polarization energy arising from the localized hole on the oxygen atom, by performing two calculations: firstly a 'thermal' calculation in which a full equilibrium of the lattice surrounding the defect is performed; secondly an 'optical' calculation in which only relaxation of the shells is allowed. The defect energies corresponding to the two calculations in the model system are listed in table 4. The difference between the 'optical' and 'thermal' calculations gives the displacement polarization energy. However, to obtain the electronic polarization energy, a third calculation is performed to give a reference energy by restricting the relaxation of both shell and core. We note that substitution of an O^- for the oxygen ions (O(2), O(3) and O(4)) bonded to the Al ion causes substantial displacement polarization energies of 9.1–9.6 eV, while the substitution of an O^- at O(1) (which also is an oxygen ion bonded to the Al ion) causes a smaller displacement polarization energy of 8.11 eV. All four of these oxygen ions have a large electronic polarization energy of 2.50–2.71 eV. Compared with the case of α -quartz, the substitution of O^- for O ions causes a displacement polarization energy of 8.33 eV and an electronic polarization energy of 2.31 eV [24], which are smaller than the corresponding values in the case of Al-doped α -quartz. The oxygen ions which are not bonded to the Al ion, except O(5) and O(11), all have smaller displacement polarization than O(2), O(3) and O(4); however, these values are almost the same as those in α -quartz. For the case of a hole localized at O(5) and O(11), the displacement polarization energies have relatively large values of 10.0–10.6 eV.

Table 3. Equilibrium geometry for the neutral and positively charged clusters in Al³⁺-doped α -quartz.

	Bond length (Å)			Bond angle (deg)	
	Neutral	Positive		Neutral	Positive
Al-O(1)	1.7727	1.5641	O(1)-Al-O(2)	99.94	112.38
Al-O(2)	1.7018	1.6908	O(1)-Al-O(3)	105.51	115.17
Al-O(3)	1.7625	1.6993	O(1)-Al-O(4)	117.49	118.04
Al-O(4)	1.6012	2.1949	O(2)-Al-O(3)	107.27	110.56
			O(2)-Al-O(4)	121.63	109.33
			O(3)-Al-O(4)	103.85	89.23
Si(4)-O(4)	1.5479	2.0684	O(4)-Si(4)-O(11)	108.67	100.32
Si(4)-O(11)	1.6284	1.5895	O(4)-Si(4)-O(12)	106.21	90.57
Si(4)-O(12)	1.6015	1.5580	O(4)-Si(4)-O(13)	111.78	93.98
Si(4)-O(13)	1.6257	1.5582	O(11)-Si(4)-O(12)	110.45	112.87
			O(11)-Si(4)-O(13)	106.06	112.06
			O(12)-Si(4)-O(13)	113.64	133.15
Na-Al	2.7277	2.7403	Al-O(2)-Si(1)	153.74	139.42
Na-O(2)	3.1845	2.2605	Al-O(3)-Si(2)	144.45	151.73
Na-O(3)	2.1779	2.4333	Al-O(1)-Si(3)	152.50	139.56
Na-O(6)	2.2206	2.4981	Al-O(4)-Si(4)	139.47	122.13
Na-O(7)	3.2088	2.2301			

Table 4. The calculated defect energies in Al³⁺-doped α -quartz.

O ⁻ substitution position	Displacement polarization energy	Electronic polarization energy	$E_s = E_d + E_e$ (eV)	Hole- trapping energy (eV)
	E_d (eV)	E_e (eV)		
O(1)	8.11	2.71	10.82	-0.90
O(2)	9.16	2.48	11.64	-1.60
O(3)	9.09	2.62	11.71	-1.49
O(4)	9.63	2.50	12.13	-2.21
O(5)	10.00	2.18	12.18	-1.82
O(11)	10.63	2.41	13.04	-2.24
O(13)	8.54	2.43	10.97	-0.90
O(14)	8.49	2.47	10.96	-0.95
O(15)	8.79	2.22	11.01	-0.84
O(16)	8.84	2.28	11.12	-1.79

Next, we proceed to calculate the total defect energy E_{vk} arising from lattice distortion caused by a hole localized on the oxygen atom. In order to examine the stability of the self-trapped oxygen hole relative to a hole in its lowest-energy state in the valence band of an undistorted crystal, we follow the criteria proposed by Norgett and Stoneham [36] that the hole is self-trapped if the energy

$$E_s = \frac{1}{2}E_v + E_{vk} - E_M \quad (5)$$

is negative. Here E_{vk} is the calculated 'thermal' defect energy of the hole, E_v is the width of the valence band in the undistorted crystal and E_M is the anion Madelung energy. In

our case of O^- substituted for O(4), E_{vk} is 19.27 eV and E_M is 31.48 eV. The value of E_s can thus be estimated from the relation

$$E_s = \frac{1}{2}E_v - 12.21 \text{ eV}. \quad (6)$$

The available experimental value of E_v for α -quartz is about 20 eV [37–40]. If we use this E_v for the calculation in equation (6), we obtain an E_s of -2.21 eV. The negative value of E_s indicates that self-trapping of a hole at O(4) is energetically favourable. Compared with the other three O sites (O(1), O(2) and O(3)), which can also self-trap a hole, the O(4) site is the most energetically favourable for self-trapping to occur. This result is in good agreement with the experimental results that the hole is on an oxygen ion linked to the aluminium ion by a 'short' bond [23]. The hole-trapping energy E_s for the other O sites, which are not bonded to Al, are also calculated. Our results show that self-trapping of a hole on other oxygen ions near the Al ion is also possible. It is found that, among these sites, O(11) is energetically most favoured to trap a hole with an E_s of -2.24 eV. We note that O(11) is a next-nearest oxygen ion to Al. Our results give support to the experimental results of Meyer *et al* [41] that the possible placement of the hole is on a next-nearest oxygen atom for $[AlO_4]^0$ in α -quartz. This agreement between theory and experiment suggests that the possible placement of the hole on a next-nearest oxygen atom for $[AlO_4]$ in α -quartz should be considered when one interprets the ESR spectra.

The core positions of some selected ions around the hole site (O(4)) before and after hole trapping are shown in figures 1(a) and 1(b). Their corresponding coordinates are given in table 2. It is observed that trapping a hole on O(4) gives rise to a large displacement of this ion by 0.44 Å. It also causes the nearest silicon ion Si(4) and the Al ion to have large displacements, 0.43 Å and 0.48 Å, respectively. It is noted that both of these ions shift away from the O^- ion and that the Al ion shifts more than the Si(4) ion. These structural changes are similar to those that occur in α -quartz [24]. We note that the Na ion shows a huge displacement of 2.54 Å in moving closer to the O(2) ion. It is not known to what degree this huge displacement contributes to the large polarization to self-trap a hole on O(4).

We calculate the equilibrium geometry (table 3) for the neutral cluster and for the positively charged cluster, which correspond, respectively, to the structure before and after oxygen O^- is substituted for O(4). We find that both the Si(4)–O(4) and the Al–O(4) bond lengths change significantly, from 1.55 and 1.60 Å, in the neutral configuration to 2.07 and 2.19 Å, respectively, in the positively charged configuration. The bond angle Al–O(4)–Si(4) also undergoes a large change (of about 17°), from 139.47° in the neutral configuration, to 122.13° in the positively charged configuration. We find that, except for the elongation of Al–O(4) and Si(4)–O(4), all other silicon–oxygen bonds in the AlO_4 and $Si(4)O_4$ tetrahedra are shortened. The bond angles in AlO_4 and $Si(4)O_4$ tetrahedra have also been calculated. It is found that the angles O(2)–Al–O(4) and O(3)–Al–O(4) decrease by 12–14° whereas the other three angles in the AlO_4 tetrahedron increase by 1–12°. The bond angles of the $Si(4)O_4$ tetrahedron undergo similar changes as those in the AlO_4 tetrahedron. The bond angles O(4)–Si(4)–O(11), O(4)–Si(4)–O(12) and O(4)–Si(4)–O(13) decrease by 8–18°, whereas the other three angles in the $Si(4)O_4$ tetrahedron increase by 2–20°. We note that the bond angle O(12)–Si(4)–O(13) increases by almost 20° after hole trapping. All the other bond lengths and bond angles in this model system have smaller changes than those mentioned above. The large structural changes in the AlO_4 and $Si(4)O_4$ tetrahedra, and the Na ion are shown in figure 1(a) and 1(b).

4. Conclusion

It can be clearly seen from our calculation that the hole can be trapped on oxygen atoms (O(1), O(2), O(3) and O(4)) which are nearest to the impurity Al^{3+} atom as well as on oxygen atoms (O(5), O(11), O(13), O(14), O(15) and O(16)) which are next nearest to the impurity atom. The most stable STH is located at O(4), among the nearest oxygen atoms, and at O(11), among the next-nearest oxygen atoms. In both cases, the polarization energy created is the largest in their respective groups. When a hole is located at an oxygen atom near the Al^{3+} atom, the contribution from the displacement polarization energy to the hole-trapping energy is large. This is because the polarizabilities of the atoms concerned are in the ratio of $\text{Na} : \text{Al} : \text{Si} = 10 : 3.5 : 1$. However, since the number of Al^{3+} atoms is small, the variation in the electronic polarization energy with hole location at different sites is smaller than 0.5 eV (table 4). We therefore conclude that, to self-trap a hole on an oxygen atom, the Si–O bond of the oxygen atom has to be extended significantly. For example, the length of the Al–O bond is increased from 1.60 to 2.19 Å in the case of a hole located at O(4). (Note that the results shown in table 4 are the results of structural changes caused by hole self-trapping on O(4). When the hole is self-trapped on O(11), we also found a significant extension of the Si(4)–O(11) bond.) The hole-trapping energies in the case of O(4) and O(11) are similar, and therefore their sites may not be easily distinguished in an experiment.

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