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Ab initio study of tritium defects in lithium oxide

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Abstract. Lithium oxide has been suggested as a suitable breeder blanket material for fusion reactors. Tritium ions and lithium vacancies are created by neutron irradiation, forming bulk defect complexes whose exact character is experimentally unclear.

We have used *ab initio* total energy pseudopotential methods to study the structure and relative energies of tritium as a substitutional defect, and of the separate tritium interstitial and lithium vacancy. For all stable defect geometries, the formation of an OT^- complex with an O—T bond length of about 1 Å is found to be energetically favoured. In the case of the substitutional defect this bond is found to point towards the vacant Li site, but the direction is fairly free for the interstitial case. The binding energy of tritium to a lithium vacancy is found to be 1.3 eV. Structural relaxation effects are included throughout, and are found to significantly affect the relative energies of different defect geometries. The effects of zero-point fluctuations are estimated and found not to be very significant.

The most probable migration path of interstitial tritium is identified as a jump between nearest-neighbour oxygen ions, with an activation energy of 0.45 eV, in agreement with experimental evidence. The results suggest a picture of thermally assisted diffusion of tritium interstitials and lithium vacancies along the anion and cation sublattices respectively, with the preferential trapping of the two defects into substitutional complexes.

1. Introduction

Lithium oxide, Li_2O, is a leading candidate for use as a blanket material in proposed deuterium–tritium fusion reactors [1]. In addition to its high melting temperature and thermal conductivity, the high density of lithium in this material (twice that of the pure metal) makes it a suitable breeder material to generate tritium. This is because when irradiated with neutrons, lithium vacancies and tritium are formed by the reaction

$$^6\mathrm{Li} + \mathrm{n} \rightarrow {}^3\mathrm{H} + \alpha.$$

The energetic alpha particle flies out of the material, and ^{3}H, i.e. tritium (hereafter designated by T), is left in place of Li in the crystal structure. However, the initial kinetic energy of the tritium is about 2.7 MeV, so it would be expected to recoil and move a substantial distance in the material before thermalization and stabilization as bulk defects in the material. Kudo and Tanaka [2] estimate this distance to be about 30 μm. It is possible that in addition to lithium vacancies and tritium defects, other defects may be created by radiation damage in the material, e.g. F^+ centres [3], but these have not been considered here.

The structure of such tritium defects is not experimentally clear. Although tritium recoils from the lithium vacancy which was produced in association with it, there will be other vacancies in the material due to intrinsic impurities and due to other radiation damage.

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Hence it is even uncertain whether tritium exists as an interstitial or as a substitutional defect. Experimental work by Kudo and Okuno [4, 5, 6] has investigated the charge state (oxidation state) of the defects. This showed that when irradiated samples of Li_2O are dissolved in heavy water (D_2O), most of the tritium is extracted in the form of DTO, and hence can be considered to be in a T^+ state. A review of solubility data by Krikorian [7] clearly shows that the defect species contains only one T atom. Beyond these pieces of work, it has only been possible experimentally to guess more about the form of these defects by drawing inferences from kinetic behaviour, with differing conclusions being drawn by different authors [1, 5].

Theoretical work on this subject has been performed by Schluger *et al* [8] using semi-empirical methods and an embedded-cluster approach. These authors suggest that the substitutional tritium lies between two oxygen ions, off centre from the cation site, and that interstitial T^+ is close to a single oxygen. However, we are not aware of any work which has described the electronic structure of the defects, or their relative stability. In any case it is instructive to re-examine the situation using first-principles methods. Therefore the first aim of this work has been to examine the stable form of the static defects.

The technological importance of tritium defects in Li_2O comes from the possibility of extracting tritium from the material and feeding it into the reactor to help sustain the fusion reaction. It is found experimentally that this release rate is controlled by diffusion of tritium through the bulk material [9]. The activation energy for bulk diffusion is found by various authors [1, 5, 9] to be about 1.0 eV in irradiated samples of Li_2O, and 0.5 eV in samples where tritium has simply been dissolved in the material. However, there appears to be no clear picture of what the diffusion mechanism might be, or to what extent it may be affected by lattice relaxation effects or zero-point quantum effects. These questions have been addressed using first-principles total energy calculations, including *ab initio* determination of the equilibrium ionic geometries. The systematic approximations made in this work (use of pseudopotentials to represent the ionic cores and use of the local density approximation for the electronic exchange and correlation energy) are known from previous work on similar systems [10] to lead to accurate defect energies. Care has been taken to ensure that the calculations were fully converged with respect to the numerical approximations made.

We find that for both substitutional and interstitial defects tritium is bound close to a single oxygen ion, with a bonding pattern that suggests the formation of an OT^- species. Relaxation effects of the surrounding lattice are found to be important, but zero-point fluctuations of tritium do not significantly affect the results. The binding energy of tritium to a lithium vacancy is found to be 1.3 eV. We have investigated the diffusion mechanism of the interstitial tritium defects, finding it to involve the hopping of tritium from one oxygen ion to another. The activation energy is found to be 0.45 eV, consistent with experiments on samples in which tritium has been dissolved.

The rest of this paper is arranged as follows. The next section outlines the *ab initio* electronic structure methods used, and some of the issues involved in ensuring accurate results are discussed. We then present our results for static defects and discuss their relative stability. Following this, an estimation is made of how quantum effects might affect the results obtained. Finally the interstitial diffusion mechanism is presented, and the paper ends with a brief conclusion.

2. Methods used

We have used *ab initio* total energy calculations to determine the electronic structure, ionic geometries and energies of various defect configurations. These calculations are carried

out in the framework of density functional theory using the local density approximation. The nuclei and core electrons of lithium and oxygen are represented using non-local norm-conserving pseudopotentials, generated by an *ab initio* method. The strongly localized p orbitals of oxygen can cause convergence problems with plane-wave basis sets, and hence we have used the improved optimized pseudopotentials developed by Lin *et al* [11] and by Lee *et al* [12]. For lithium, a standard Troullier–Martins [13] pseudopotential was used.

Periodic boundary conditions were used to represent the material, with a body-centred cubic supercell corresponding to 48 atoms of the perfect bulk being used for most calculations. Some supporting work was done using a 12-atom simple cubic supercell. The valence electron pseudowavefunctions were expanded in terms of plane waves up to a cut-off of 500 eV. The suitability of this cut-off was checked by monitoring the convergence of the lattice parameter and bulk modulus of the perfect crystal with respect to the number of plane waves. It was found that this cut-off was also sufficient to converge energy differences when tritium, represented by a bare Coulomb potential, was introduced into the system. Brillouin zone sampling was carried out using the Monkhorst–Pack scheme [14], which was found to be converged for $q = 2$ (a single point, corresponding to 32 sampling points in the Brillouin zone associated with the primitive Li_2O cell). We estimate the total error in energy differences due to plane-wave cut-off and sampling to be less than 0.01 eV.

The Kohn–Sham energy functional was minimized by a band-by-band conjugate gradients scheme [15], and the calculations were carried on a parallel computer, using the CETEP code [16]. We have estimated the error due to our use of the LDA by using the charge densities obtained to recalculate the exchange-correlation energies with a gradient corrected functional. We find this changes the energy differences calculated by less than 0.05 eV. The use of a plane-wave formalism allows straightforward, accurate determination of the forces, which can be used for *ab initio* relaxation of ionic positions to the lowest energy configuration. This was carried out at constant volume by a simple steepest descent algorithm, iterated until the residual forces on each atom were less than 0.1 eV $Å^{-1}$.

In some of the defect configurations we have studied the supercell would have contained a net charge. When using periodic boundary conditions the total electrostatic energy diverges for such a case, and so a uniform neutralizing background charge was introduced to preserve overall charge neutrality. Such an arrangement gives rise to fictitious interactions between periodic images, due to the long-ranged electrostatic forces. It can be shown [17] that to leading order this interaction can be calculated as that of a regular array of point charges in a neutralizing dielectric medium. This energy can be analytically evaluated as:

$$\Delta E = -\frac{\alpha q^2}{2\epsilon_r L} \qquad (1)$$

where α is the appropriate Madelung constant for the cell geometry, q the net defect charge, ϵ_r the dielectric constant, and L the cell side length. This expression can then in principle be used to correct the total energy values obtained, improving the convergence with respect to cell size to $O(L^{-3})$. In practice this formula is not completely satisfactory as there is some ambiguity about the correct value to use for the dielectric constant. Strictly speaking one should use a dielectric constant calculated within the LDA and with the same pseudopotentials. Also, for the comparatively small supercell sizes which can be realistically studied with the available computing resources, the assumption of a uniform dielectric medium between the defect images may not be very accurate. However, the errors can be checked by using the above formula with the experimental value for ϵ_r and monitoring the convergence of defect energies with respect to cell size. From the results found, the residual combined error due to the form used for the $O(L^{-1})$ term, and the omission of

higher-order $O(L^{-3})$ terms was estimated to be less than 0.1 eV for the defect formation energies. Furthermore it was found that the local electronic structure of the defects were well converged with respect to supercell size, and that in the 48-atom supercell relaxation effects towards the edge of the cell were negligible, suggesting that the finite cell-size effects on the atomic relaxation are negligible at this point. Hence it is likely that in comparing different configurations of a given defect the accuracy is substantially better than 0.1 eV.

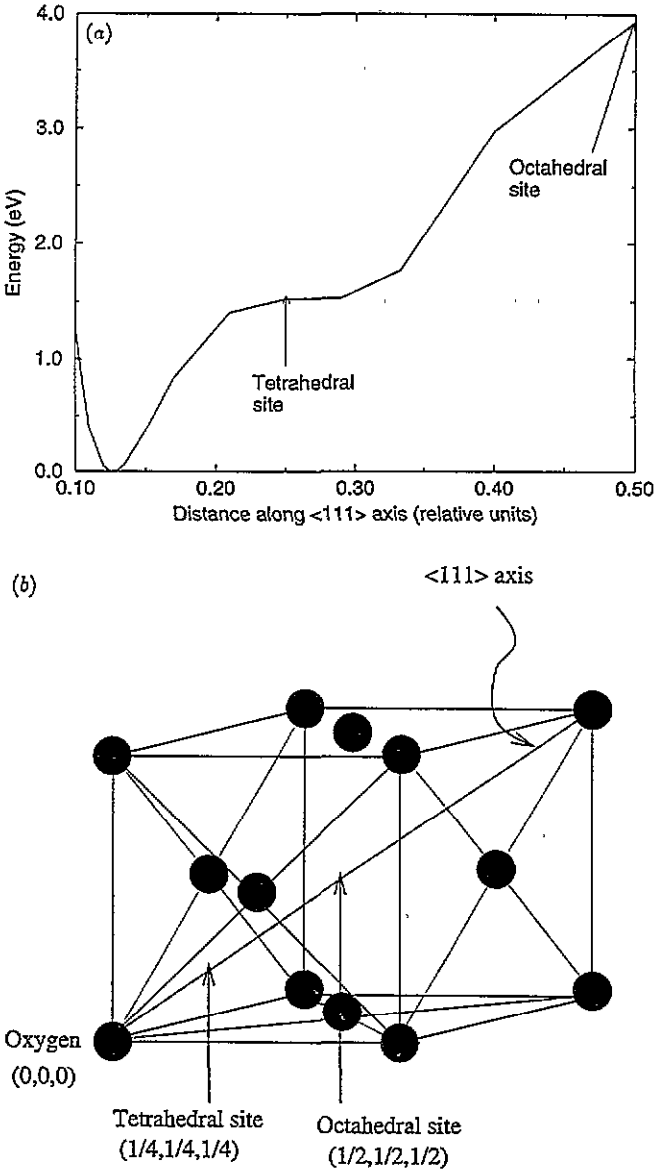

Figure 1. (a) Energy of different sites for substitutional defect along the path shown in (b), starting from an oxygen site as the origin. The lithium ion has been removed from the tetrahedral site shown. The zero of energy is taken as the most stable site.

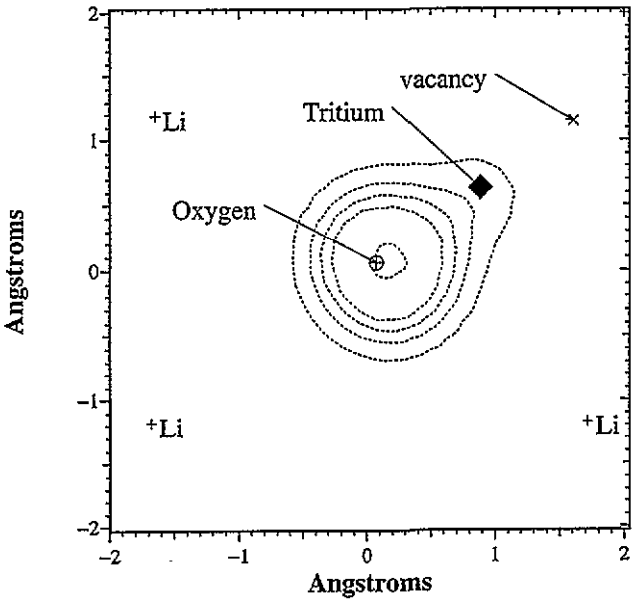

Figure 2. Valence charge density of the stable substitutional defect, in a ⟨110⟩ plane containing the O—T bond and vacant Li site. Contours at densities of 0.1, 0.2, 0.3, 0.4 and 0.5 e Å^{-3}.

3. Structure of defects

Tritium is produced in association with a lithium vacancy, from which it recoils. We have studied both the combined substitutional defect, and the separate interstitial and vacancy pair.

3.1. Substitutional defect, T_{Li}

Lithium oxide is an ionic material, with the anti-fluorite structure. It can be thought of as a face-centred cubic lattice of O^{2-} ions, with tetrahedral sites that contain Li^+ ions, and vacant octahedral sites. However, we find that when one of the lithium ions is substituted by a tritium ion, it is unstable at the tetrahedral site. Figure 1 shows the energy of the T_{Li} defect at different sites if the rest of the lattice is kept rigid. The lowest energy is obtained when T is at a distance of about 1 Å from an oxygen ion. Different orientations of the O—T bond were investigated, and it was found that there is a strong preference for it to point in the direction of the vacant Li site, with an energy penalty of several eV for other orientations. This can be explained by strong repulsion of tritium by other Li^+ ions in the lattice.

When the whole structure is allowed to relax, the tritium ion remains close to the oxygen ion. However there are some small relaxations of the neighbouring ions, which reduce the energy of the defect by about 0.6 eV. The oxygen ion nearest to the tritium is displaced towards it by 0.08 Å, and the O—T equilibrium bond length is 0.99 Å. The three Li^+ ions neighbouring the vacant Li site and furthest from the tritium ion are each displaced by 0.15 Å towards the vacant site.

Figure 2 shows the valence charge density of the substitutional tritium defect in the ⟨110⟩ plane. Note that on such a plot the lithium ions are not visible—this is because the

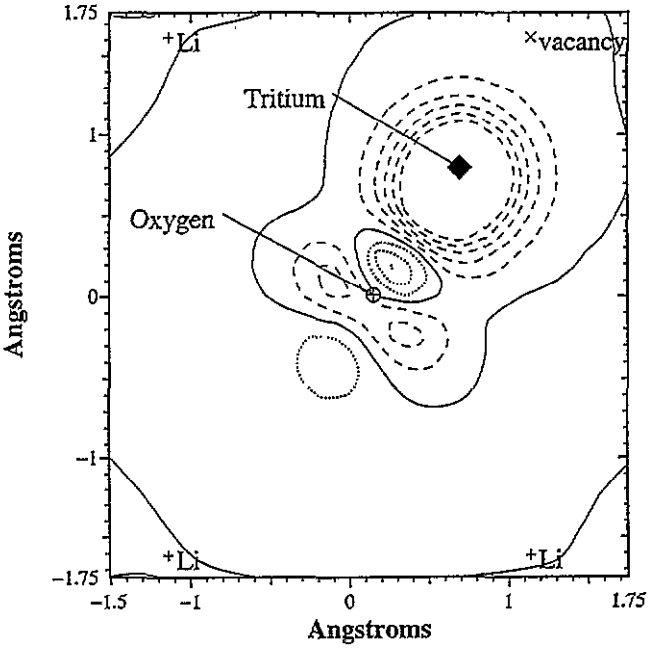

Figure 3. Valence charge density difference between the stable substitutional defect and perfect bulk, in a ⟨110⟩ plane containing the O—T bond and vacant Li site. This is calculated for the unrelaxed ionic configuration in order to show only changes due to differences in electronic configuration. Contours at intervals of 0.1 e Å^{-3}, dotted lines show negative change, solid line zero change and dashed line positive change.

material is almost completely ionic, and hence the valence charge density is almost entirely concentrated on the oxygen cores. From this picture it can be clearly seen that tritium lies in the charge cloud of an oxygen ion, suggesting that it exists in the form of a tritiated hydroxide ion, OT^-. The O—T bond stretching frequency was calculated using the frozen phonon technique, and found to be 2030 cm^{-1}. This can be compared to typical O—T bond lengths of 0.97 Å and bond stretching frequencies of 2000–2200 cm^{-1} found in hydroxides, supporting the conclusion of formation of OT^-. Figure 3 shows the difference in charge density between the perfect bulk and the substitutional defect. The chemical bond between O^{2-} and T^+ is seen to be formed by distortion of the oxygen 2p orbital pointing along to the bond, with charge transfer from it to the 1s orbital of the tritium.

The work of Schluger *et al* [8] suggested that T_{Li} was most stable when tritium was midway between two oxygens. However we have tested this hypothesis and found such a configuration is at least 0.6 eV higher in energy than the singly bonded configuration. We also found in our work that the doubly bonded configuration is actually unstable, representing a transition state between two equivalent singly bonded sites.

3.2. *Interstitial tritium, T_i^+*

It has been found that Li^+ interstitials in Li_2O occupy the vacant octahedral sites in the lattice [18, 19]. However, we have found that interstitial T^+ is unstable at such a site. Instead it is again found to be most stable at a distance of about 0.99 Å from an oxygen ion—the energies for the possible stable sites are shown in table 1. It can be seen from this that, if the lattice is kept rigid, there is a strong preference for the O—T bond to lie along

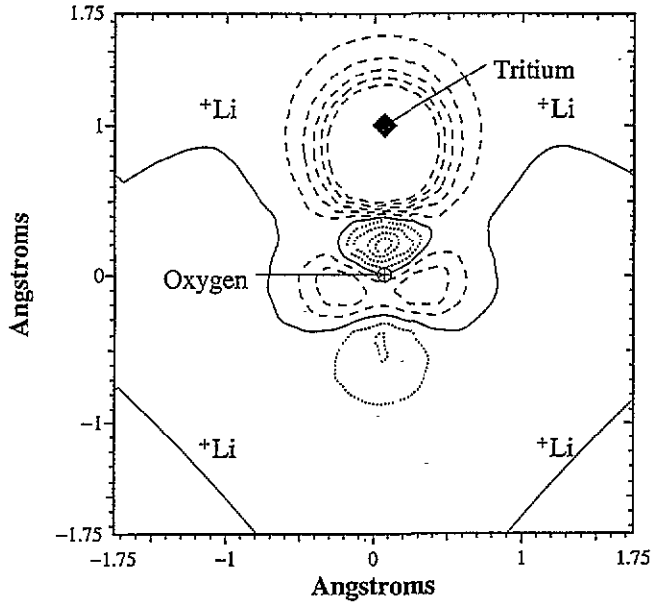

Figure 4. Valence charge difference between most stable interstitial defect and perfect bulk, in a ⟨100⟩ plane containing the O—T bond. Contours as for figure 3.

the ⟨100⟩ axis, i.e. pointing towards the octahedral site. This can be understood in terms of minimizing Coulombic repulsion from surrounding Li^+ ions. However, when the crystal structure is allowed to relax around the defect there is remarkably little energy difference between the different sites. The relaxation energies can be seen to be quite large. The similarity between the energies of the relaxed structures shows that for each orientation of the O—T bond the system can minimize the structural energy of the defect by a suitable pattern of ionic displacements. The Li^+ ions move in such a way as to minimize the repulsion of the tritium ion—for example, for the ⟨111⟩ site, the nearest Li^+ is displaced by 0.7 Å away from the tritium. When tritium is on the ⟨110⟩ axis the two nearest Li^+ are displaced from the tritium by 0.3 Å in the xy plane, and 0.25 Å in the z direction. For the case of tritium on the ⟨100⟩ axis, the four nearest Li^+ are displaced by 0.2 Å from the tritium.

Table 1. Total energies in eV of a 48-atom supercell contain T_i^+ defect at different possible stable sites, after applying the correction of equation (1). In all cases except for the octahedral site only the direction of the O—T vector was constrained—the defect was found to be most stable with an O—T distance of 0.99 Å in all three cases; for the octahedral site the T ion was constrained to be at the centre of the site

Interstitial site	Rigid lattice	Relaxed lattice	Relaxation energy
⟨100⟩	−7136.84 eV	−7138.04 eV	1.20 eV
⟨110⟩	−7135.74 eV	−7137.99 eV	2.25 eV
⟨111⟩	−7133.62 eV	−7137.99 eV	4.37 eV
Octahedral	−7135.33 eV	−7135.58 eV	0.25 eV

Calculations were made to examine the energy profile between the different sites given in table 1 for tritium bound close to an oxygen. We constrained only the orientation of

the O—T bond to correspond to a series of points along the trajectory between two sites, otherwise allowing T to be completely free to move. Between any two of the three sites the energy was found to vary smoothly and continuously with no intervening minima or maxima in the energy, both when the rest of the lattice was kept rigid, and when the whole lattice was allowed to relax.

Figure 4 shows the difference in charge density between the most stable interstitial defect configuration and the perfect bulk. This shows a striking similarity to the bonding pattern of the substitutional defect, with tritium in the charge cloud of the nearest O^{2-} ion, again suggesting the formation of OT^-. This similarity is confirmed by a calculation of the O—T bond stretching frequency, which is found to be 2080 cm^{-1}.

Hence we can see that the substitutional defect and interstitial defect are in many ways very similar in their electronic structures, with the tritium at a distance of about 0.99 Å from an oxygen ion, binding to form OT^-. The main difference between the two defects comes from the electrostatic repulsion of tritium by surrounding cations, which affects the direction of the O—T bond. The substitutional defect has a strong preference to point towards the vacant Li^+ site, but for the interstitial there is little difference in the repulsion felt for different orientations when the lattice is allowed to relax fully.

3.3. Lithium vacancy v_{Li}^-

The nuclear reaction which forms tritium creates an equal number of lithium vacancies. Therefore, if there is a T_i^+ defect in the material, there will also be a corresponding negatively charged lithium vacancy elsewhere. This defect has been studied previously [18] but we have repeated it here including *ab initio* relaxation of the ionic positions. The calculated energies are included in table 2.

3.4. Dissociation of substitutional defect

When comparing the relative energy of the substitutional defect to that of the separate interstitial and vacancy, care must be taken to compare the total energy of the same amount of material. We calculate this by taking the energy of one supercell containing T_{Li} plus one supercell of perfect bulk, and subtracting from this the energy of one supercell containing T_i^+ and a supercell containing v_{Li}^-. The appropriate values are tabulated in table 2. From this it can be seen that the binding energy of tritium to a lithium vacancy is 1.3 eV, i.e.

$$T_{Li} \rightarrow T_i^+ + v_{Li}^- \qquad \Delta E = +1.3 \text{ eV}.$$

Hence if the defects are fully thermalized, we would expect all the tritium to be in the form of substitutional defects.

Table 2. Energies, after the correction of Equation (1), of a 48 atom supercell containing different defect configurations, used to calculate the relative stability.

	Rigid lattice	Relaxed lattice
Perfect bulk	−7119.51 eV	
T_{Li}	−7125.48 eV	−7126.17 eV
T_i^+	−7136.84 eV	−7138.04 eV
v_{Li}	−7105.33 eV	−7106.30 eV

One might also consider the possibility of the substitutional dissociating into a pair of neutral defects, i.e. $T_i^0 + v_{Li}^0$. However preliminary calculations on a smaller 12 atom

supercell showed such a pair to be much higher in energy (about 10 eV) than the charged pair, so this possibility was not investigated further.

4. Quantum effects on tritium

The previous calculations have treated the nuclei and core electrons for each atom as a classical point particle. The low atomic mass of tritium suggests that quantum effects may be important for the T^+ ion, and we have attempted to investigate this issue. A full quantum mechanical solution for the tritium nucleus would be computationally very expensive, so we have used an approximate method to investigate these effects. The force constants were obtained for small displacements of tritium from the most stable configuration by the frozen phonon method, in the approximation that the other atoms were held rigid. These force constants were used to model the tritium as a 3D harmonic oscillator, from which the zero-point energy and rms displacements were obtained. The results are shown in table 3.

Table 3. Zero-point energies and rms displacements for tritium, calculated in the harmonic approximation.

	Zero-point energy	rms displacement along O—T bond	rms displacement transverse to O—T bond
T_{Li}	0.17 eV	0.04 Å	0.14 Å
T_i^+	0.18 eV	0.06 Å	0.12 Å

The similarity of the results for the two defects is again indicative of the similarity of the bonding in both. Care should be taken not to take these results too literally, as they are only obtained in an approximate manner. In particular we have assumed for the frequency calculations that only T moves, and as we have seen, relaxation energies of the other ions in the structure can be significant. However, it seems likely that tritium is localized at a distance of about 1 Å from an oxygen ion in both cases. For the substitutional defect the zero point energy is much less than the energy cost for tritium to move to other possible sites, so the classical picture will probably be fairly accurate. However, in the case of the interstitial defect, the zero-point energy is greater than the difference in energy between different possible orientations of the O—T bond. This suggests that T_i^+ may be able to move fairly freely round an oxygen ion, whilst still bound to a single oxygen ion. However, such motion will necessarily involve larger displacements than those considered here and relaxation of the surrounding lattice will become important. Hence it is not clear without more sophisticated calculation whether tritium might jump by thermally activated tunnelling between various localized sites around an oxygen or be fully delocalized around it.

5. Migration of interstitial through the crystal

There are many possible pathways by which the various defects may diffuse through the bulk. For simplicity we concentrate here just on the interstitial defect. A full dynamical simulation to obtain free energy barriers by, for example, thermodynamical integration [20] would be computationally expensive. Therefore we have instead performed a series of static calculations, looking for saddle points of the motion and obtaining activation energies. As

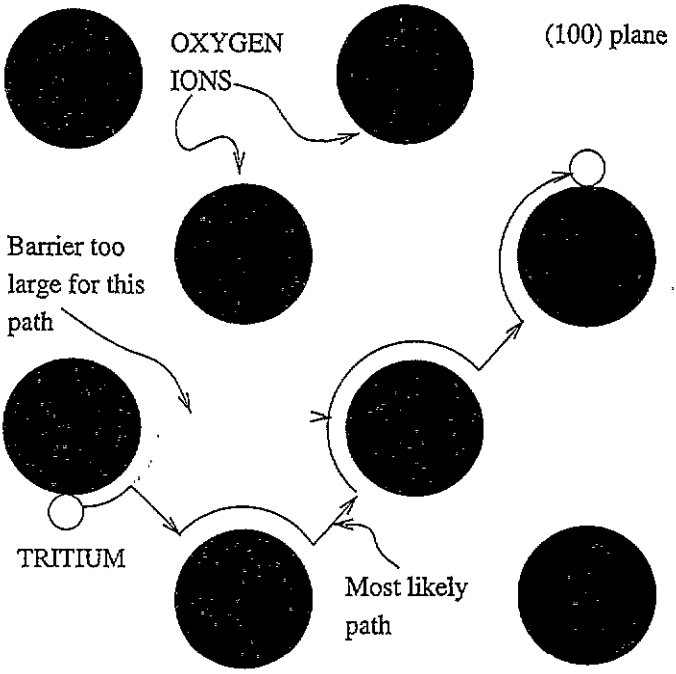

Figure 5. Schematic diagram to show what we have found to be the most likely interstitial migration mechanism.

in previous studies [10] we expect entropy contributions to the temperature dependence of the diffusion coefficient, and hence to the measured activation energy, to be small.

We have seen that the tritium interstitial may move fairly freely around a single oxygen, but to progress through the material it must jump from one oxygen to another. One might expect a jump along the ⟨100⟩ axis, i.e. via the vacant octahedral site, as this would minimize the cationic repulsion from surrounding Li^+ ions. However, it is found that due to the strong preference for tritium to remain bonded to an oxygen, the lowest barrier is for a jump along the ⟨110⟩ axis, between two nearest neighbour O^{2-} ions. This process is illustrated in figure 5. A calculation constraining tritium to lie on the plane midway between two nearest neighbour oxygens and allowing all other ions to fully relax gave the lowest energy when tritium lay on the line joining them. Furthermore this point was the only minimum found. Small displacements perpendicular to this plane decreased the energy, confirming that tritium midway along the line joining two neighbouring O^{2-} ions is the saddle point configuration for this path. The barrier is 1.8 eV in the rigid lattice, but just 0.45 eV when the other ions are allowed to fully relax at the saddle point. This low barrier is found because the two oxygen ions between which tritium is jumping move towards one another, reducing the O—T distance from the unrelaxed distance of 1.61 Å to 1.28 Å. This allows tritium to remain partially bonded to both at the saddle point, as can be clearly seen in figure 6, which shows the valence charge density for this configuration.

The barrier calculated for this migration process is low, and similar to that for v_{Li} diffusion [18]. This similarity may have affected previous experimental reports of a correlation between Li and T diffusion [21], which may simply have been coincidence.

As previously mentioned, it is seen experimentally that the activation energy for T diffusion in irradiated samples of Li_2O is 0.7–1.0 eV. Indeed, as we have seen, in

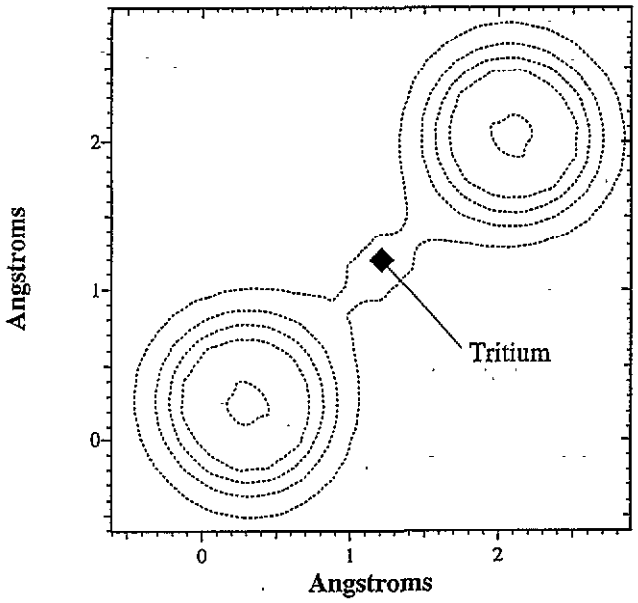

Figure 6. Valence charge density at the saddle point of the interstitial migration process, in a (110) plane containing T and the two oxygens between which it is jumping. Note that T is partially bonded to both oxygens at this point. Contours as for figure 2.

such samples tritium is likely to be bound to a lithium vacancy, so such a difference is unsurprising. It was, however, reported by Kudo and Okuno [5] that the activation energy for bulk T diffusion when tritium was simply dissolved in the material was about 0.5 eV. In such a situation one might expect tritium to simply exist as an interstitial, and this does therefore provide experimental support for our results.

6. Conclusions

We have found that for both the interstitial and substitutional tritium defects in Li_2O tritium is bound close to a single oxygen ion, at a distance of about 1 Å. The bonding pattern leads us to conclude that formation of an OT^- species occurs in both cases. In the case of the substitutional defect the O—T bond is strongly constrained to point in the direction of the vacant Li site, but for the interstitial defect the bond may, in effect, point freely in any direction. The binding energy of tritium to a lithium vacancy is found to be 1.3 eV. In all these systems lattice relaxation effects were found to be important, but zero-point quantum effects were estimated to be not very significant. These results show that although the tritium ions may recoil a significant distance from the lithium vacancies it is likely that in thermal equilibrium almost all the tritium will be bound to lithium vacancies forming substitutional defects.

To reach this equilibrium configuration the defects must diffuse through the material. The most likely mechanism for diffusion of the tritium interstitial has been found to consist of hopping from one oxygen to another, with an activation energy of 0.45 eV. This appears to correspond to the mechanism involved when tritium is simply dissolved in the crystal, as one might expect. These results, together with those found before for lithium vacancy diffusion [18] suggest a picture of thermally assisted diffusion of tritium interstitials and

lithium vacancies along the anion and cation sublattices respectively, with the eventual trapping of the two defects into substitutional complexes.

It is likely that a different mechanism is involved for the diffusion observed when tritium is extracted from irradiated samples, probably because of the presence of lithium vacancies associated with the tritium defect. There are a large number of possibilities for such a diffusion mechanism—work is in progress to investigate them, and will be published in a forthcoming paper [22].

Acknowledgments

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