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Mechanism of tritium diffusion in lithium oxide

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Lithium oxide is a possible candidate for a breeder blanket material in fusion reactors. Tritium is generated in the material, which can be extracted and fed into the fusion reactor to help sustain the fusion reaction. Experimental studies have shown the extraction rate is controlled by diffusion of tritium in the bulk, but the exact mechanism is not clear. Here we present *ab initio* density functional calculations of the various diffusion pathways which have been suggested, including the diffusion of tritium as an interstitial and various vacancy assisted mechanisms. The activation energy has been calculated for each pathway, and by comparison with experimental results we have deduced which mechanism is most likely. This is shown to be a simple two-stage swapping of a lithium and tritium ion.

I. INTRODUCTION

Lithium oxide, Li_2O, is an ionic material with the antifluorite structure. It can be thought of as an fcc lattice of O^{2-} ions, with tetrahedral holes filled with Li^+ ions, and vacant octahedral holes (see Fig. 1). Among its suggested uses, lithium oxide is a leading candidate as breeder blanket material for proposed deuterium-tritium fusion reactors.[1] This is because when irradiated with neutrons a nuclear reaction converts lithium ions to tritium ions, thus creating equal numbers of tritium ions and lithium vacancies. Tritium extracted from the material may be fed into the reactor to help sustain the fusion reaction. In principle many factors can influence the kinetics of tritium release from irradiated Li_2O, including bulk diffusion through the grains, diffusion along the grain boundaries, release at the surface, etc.

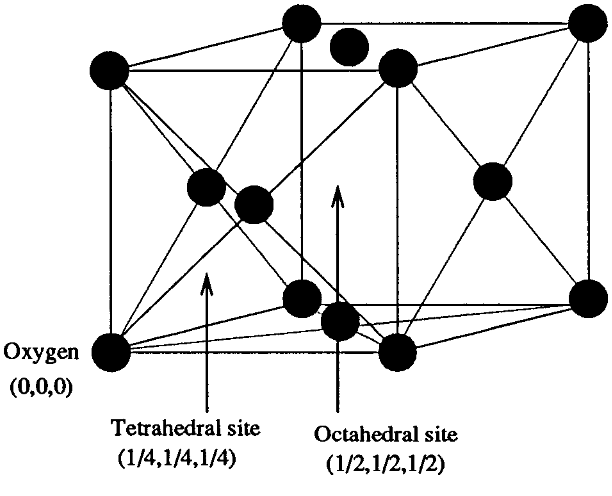

FIG. 1. The antifluorite structure of Li_2O, showing the fcc lattice of oxygen ions. The lithium ions have been omitted for clarity, but occupy the tetrahedral sites of the form $(\pm 1/4, \pm 1/4, \pm 1/4)$. The octahedral sites are vacant.

Many experiments have been performed to measure the kinetics of tritium release from Li_2O, for example the work of Kudo and Okuno[2–4] and of Tanifuji *et al.*[5]—a more comprehensive list may be found in the references cited in Refs. 1,6. Much work has gone into modeling this process, as reviewed by Federici *et al.*[7] An analysis of the observed kinetics suggests they are generally controlled by bulk diffusion, and experimental values have been obtained for the tritium bulk diffusion coefficient, D_T. Plots of $\log D_T$ vs $1/T$ suggest that at temperatures above about 600 K the diffusion coefficient may be expressed in the familiar Arrhenius form, $D_T = D_0 \exp(-E_a/k_B T)$ with an activation energy E_a, generally found to be about 1.0 eV, although different authors have found large variations in values for the prefactor D_0. In the work by Kudo *et al.*[8] results were also obtained for samples of Li_2O which were not irradiated, but in which HT gas was dissolved, where a lower activation energy of about 0.5 eV was found.

The interpretation of data obtained for tritium release at lower temperatures differs widely. The work of Tanifuji *et al.* [5] simply notes the lower values of the diffusion coefficient obtained in this region, and suggests this could be due to retardation of tritium motion by radiation defects such as F^+ centers. This is supported by experiments[9] showing that such centers are annealed out at temperatures above about 570 K. Kudo and Okuno[3] found that there is still an Arrhenius-type behavior below about 570 K but with an increased activation energy of about 1.4 eV, comparable with the activation energy for the decomposition of LiOH to Li_2O and water. They therefore suggest that the rate controlling step at lower temperatures is the surface release of tritium by the reaction $LiOT.LiOH \rightleftharpoons Li_2O + HTO$. They also found that the activation energy for tritium release from sintered pellets (rather than the crystalline powder used for most of their work) of Li_2O is about 1.4 eV, which could support the theory that some sort of surface/boundary effect becomes important in the lower temperature region. The review of Johnson and Hollenberg[1] suggests a change to an activation energy of about 1.3 eV at temperatures below 700 K, with an intermediate, non-Arrhenius behavior between 700 and 800 K. They offer yet another possible explanation, namely that the diffusing species is a lithium vacancy/tritium interstitial complex at low temperatures, which dissociates at higher temperatures and the diffusing species becomes just the tritium interstitial.

In addition to the lithium vacancies created by the nuclear reactions, there will also be additional vacancies due to impurities. (Even in the "high purity" samples of Tanifuji *et al.*[5] the metallic impurity concentration is 10 ppm, of the same order as the tritium concentration.) There has been some suggestion of a link between lithium (vacancy) diffusion and tritium diffusion, e.g., by Ohno *et al.*[10] Their data seems to suggest in the case of single crystal samples of Li_2O little evidence of a link between activation energies for these processes, although there may be some link for polycrystalline samples. It does appear, however, that processes such as ionic conductivity, etc., become more rapid at temperatures above about 600 K, and as noted above there seems to be a lower activation energy for tritium diffusion above this temperature than below. This may suggest some link, such as a vacancy-assisted diffusion mechanism.

Hence it is seen that experimentally there is much uncertainty about the actual mechanism by which tritium diffuses through Li_2O, with a variety of inferences being drawn from the available data. The subject has been studied theoretically by Schluger *et al.*[11] using semiempirical calculations. They support the hypothesis of a vacancy assisted pathway, concluding that tritium diffusion takes place by tritium jumping between two adjacent vacancies, with an activation energy between 0.5–0.8 eV.

In a previous study[12] we have successfully applied *ab initio* quantum mechanical methods to the study of tritium defects in lithium oxide, identifying the stable form of these defects. These methods are reviewed briefly in Sec. II. This paper extends our work to focus on the mechanism of tritium diffusion. Although our previous work showed that the stable form of such defects is for tritium to be bound to a lithium vacancy forming a substitutional defect, we note that the recoil from the nuclear reaction can initially separate tritium from the associated vacancy by a large distance.[13] Also there is the possibility mentioned above of defects being associated with additional lithium vacancies which may exist. We have therefore considered in Sec. III possible pathways for diffusion of tritium ions alone (interstitials), tritium bound to a lithium vacancy (substitutionals), and tritium associated with two lithium vacancies. These results are discussed in Sec. IV, and Sec. V summarizes our conclusions.

II. TOTAL ENERGY CALCULATION METHODS

The system is modeled by a 48 atom supercell and periodic boundary conditions, and the Schrodinger equation is solved for the whole system, to correctly obtain all the bonding and polarization effects. The detailed method is described in a previous paper.[12] To summarize here, the ionic cores are represented by norm-conserving pseudopotentials and the valence electron pseudo wave functions are expanded in terms of plane waves. The total energy is calculated by density functional theory, with the local density approximation for the exchange-correlation energy, and minimized by a conjugate-gradients technique.[14] The calculations are performed on a parallel computer using the CETEP code.[15] A full dynamical simulation of the diffusion process would be computationally expensive, and therefore we have opted to examine a number of possible static configurations, searching for the stable structures and transition states. From the energy differences between them activation barriers can then be obtained. Using the *ab initio* Hellman-Feynman forces on the ions and a simple steepest descent technique, the ionic configurations have been relaxed to equilibrium, subject to appropriate constraints in the case of transition states.

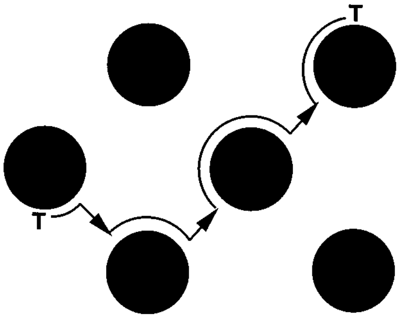

FIG. 2. The migration path found for the tritium interstitial to move through the material. (100) plane of oxygen ions, denoted by black circles, tritium denoted by T.

III. POSSIBLE DIFFUSION PATHWAYS

A. Diffusion of tritium alone

Tritium alone in the lattice forms an interstitial defect, T_i. This is the easiest diffusion mechanism to consider conceptually, only involving movement of a single species, a tritium ion. It was discussed in detail in our previous work.[12] The stable form of this defect was found to have tritium close to a single oxygen ion, forming an O—T bond at a distance of about 1 Å. Although we have shown that this interstitial can move freely around this single oxygen, to progress through the material it must jump from one oxygen to another. The lowest barrier path for this jump was shown to be between nearest neighbor oxygens, with a barrier of 0.45 eV, which we suggest is controlled by O—T bond breaking. An examination of the charge density of the saddle point of this motion shows tritium to be partially bonded to the two oxygen ions between which it is jumping.[12] This diffusion process is illustrated in Fig. 2.

B. Diffusion of tritium with a lithium vacancy

Our previous work showed that tritium and a lithium vacancy bind to form a substitutional defect, T_{Li}, with a binding energy of 1.3 eV. The most stable form of this defect is, like the interstitial, for tritium to be close to an oxygen ion, forming an O—T bond, of length 1 Å. However, in this case the O—T bond is constrained quite strongly to point in the direction of the vacant Li site with which it is associated. The

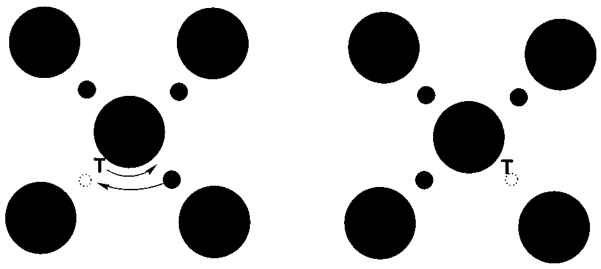

FIG. 3. Diffusion of substitutional defect, before (left) and after (right) the jump. Effectively the tritium has changed places with the Li ion. Small black circles are Li ions, and the (100) plane of oxygen ions below are shown as large black circles. Tritium is shown as T, and the Li vacancy as small open circle.

picture of this defect is therefore of it being associated with a vacant Li site, and with one of the four equivalent oxygens around that site.

Tritium may jump between these four equivalent sites, and we have found an energy barrier of 0.58 eV for this process. This again seems to be controlled by O—T bond breaking, with the saddle point having T midway between two oxygen ions, and well off center from the vacant site (only 0.2 Å out of the ⟨100⟩ plane of oxygen ions), reducing the O—T distance to 1.3 Å. Displacement away from the energetically favorable direction of the vacant site accounts for this barrier being higher than for the similar process of the interstitial defect.

Diffusion of this species requires both the tritium ion and the lithium vacancy to move, since a lithium ion and a tritium ion must swap places (Fig. 3). The presence of two moving species and the need for some correlation between their motion makes the parameter space for modeling their motion more complex than for the interstitial. We can consider this formally as a six-dimensional (6D) coordinate space consisting of three coordinates for each moving ion. Consider the two sites between which the ions are being exchanged to be separated along the z axis, with the same x and y coordinates—we can then define the z coordinate of one of the moving ions, say Li, as our diffusion coordinate z_{Li}. Each value of this coordinate then corresponds to a 5D hyperplane. If we denote the minimum energy on a given hyperplane by $E_{\mathrm{min}}(z_{\mathrm{Li}})$, the activation barrier for this process is then

$$E_a = \max_{z_{\mathrm{Li}}}\{E_{\mathrm{min}}(z_{\mathrm{Li}})\}. \tag{1}$$

Unfortunately an exhaustive search through this 6D space is well beyond the computing resources available, so we have studied particular regions of the phase space that intuitively might be expected to include the saddle point of the motion.

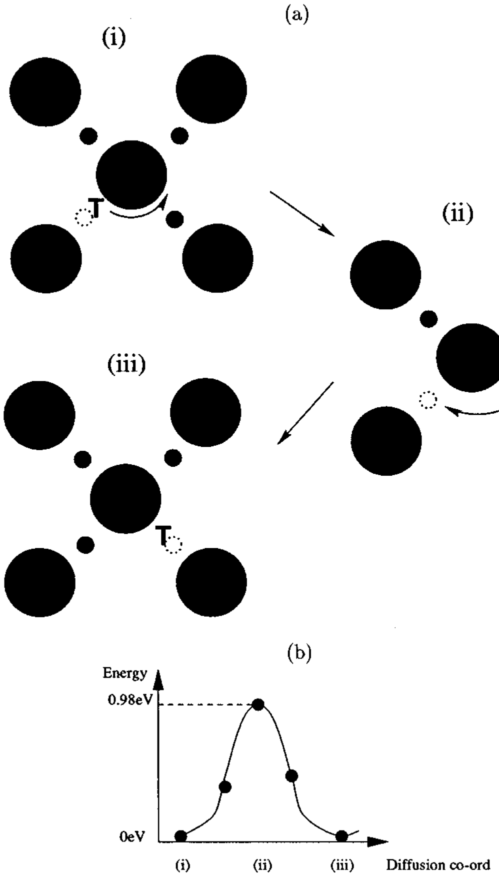

FIG. 4. (a) Possible pathway for substitutional migration, with tritium moving first, then lithium moving. Symbols as in Fig. 3. (b) Schematic energy profile along this path. Dots indicate points actually calculated.

(i) The simplest possibility is a coordinated motion of Li and T moving at the same time. This would give the saddle point when both ions lie on the plane midway between these two cation sites. The results above showing the importance of the O—T bond suggest that the tritium will probably remain close to the oxygen ion shared by the two sites during this motion. However, due to Coulombic repulsion we would expect the Li and T to be separated as much as possible, and hence expect one of them to go via the vacant octahedral site. Our calculations show that the barrier is lowest in energy if tritium goes via the octahedral site (i.e., the O—T bond points towards the cube center), and lithium lies almost along the straight line between the cation sites. In this case we find the energy of the fully relaxed structure constrained to have T and Li on the plane midway between the two sites to be 1.32 eV higher in energy than the equilibrium structure, i.e., for this path the activation energy barrier is estimated as 1.32 eV.

(ii) One could also consider the opposite extreme, where as Li moves between the two sites, tritium moves off to a third site as an interstitial. However the binding energy of the substitutional is 1.3 eV,[12] and the energy barrier for Li (vacancy) and tritium interstitial diffusion are 0.33 (Ref. 16) and 0.45 eV, respectively, making the barrier for this path higher, at about 1.75 eV (1.3 eV + 0.45 eV).

(iii) A third possibility is first lithium moves across, then tritium moves to the new vacant Li site. (Of course one could argue that tritium moves first, and then lithium, but this is the identical process time reversed, so will have the same barrier as defined above.) Our realization of this pathway is illustrated in Fig. 4. The maximum energy found along this path is 0.98 eV higher than the relaxed equilibrium structure.

The lowest barrier of these, 0.98 eV, represents an upper bound on the activation energy for the substitutional diffusion. Although there always exists the possibility that a lower barrier path exists in some region of the parameter space we have not been able to explore, we believe that there is unlikely to be any path with a significantly lower barrier than this.

C. Vacancy assisted tritium diffusion

It has been suggested by various authors[10,11] that tritium diffusion in lithium oxide is associated with additional Li vacancies beyond those produced in association with tritium. Such vacancies may be present due to, for example, impurities in the material and other radiation damage. Therefore we consider a defect complex consisting of two Li vacancies and a tritium ion, which we denote by T_{2Li}.

To begin with we examine the stable form of such a complex. This is found to be when the two vacancies are on nearest neighbor sites, with an energy 0.17 eV lower than a separate substitutional defect and isolated lithium vacancy, i.e.,

$$T_{2Li} \rightarrow T_{Li} + v_{Li}, \Delta E = +0.17 \text{ eV} \qquad (2)$$

and the complex is bound.

Tritium is, as before, bound to an oxygen ion. This oxygen ion forms one of the tetrahedral corners on both vacant sites, the O—T bond pointing midway between these two vacancies. This can be understood as minimizing the Coulomb repulsion from the occupied cation sites.

The movement of T_{2Li} is potentially very complex to analyze, with the motion of three atoms forming a 9D parameter space. In the work of Schluger *et al.* on this process[11] they considered the saddle point of the motion to simply be when tritium was in the middle of the two vacancies. However, here we find this state is actually a local energy minimum, so cannot be the transition state. We have identified one possible path for this diffusion mechanism, illustrated in Fig. 5, and investigated this. The barrier for this path is estimated as 0.50 eV, which can be considered an upper bound on the actual barrier. However any pathway must involve an O—T bond breaking and remaking step, of the kind shown by (iii)→(iv) in Fig. 5. From the results above it is likely that any step of this form will have an energy barrier of at least 0.45 eV, thus the activation energy for diffusion of the tritium and two vacancies complex is expected to be 0.45–0.50 eV.

IV. DISCUSSION

Table I summarizes the results of the previous section. How can we relate these to the experimental observation at temperatures above 600 K of an activation barrier for tritium diffusion of around 1.0 eV? We have calculated internal energy barriers E_a, and experimental results will involve the free energy barrier, $G_a = E_a - TS_a$. The entropy of diffusion, S_a consists of a configurational entropy component and a phonon entropy component.[17] (Note that when the jump requires correlation between different ions, this is likely to make the configurational entropy negative.) The normal mode frequencies that determine the phonon entropy can in principle be determined by harmonic analysis[17] or thermodynamic integration,[18] although either would be extremely computationally expensive. We assume both these and the configurational entropy do not vary significantly with temperature. Therefore in the Arrhenius form $D = D_0 \exp(-G_a/k_B T)$ the entropy is absorbed into the prefactor, and will not affect the measured activation energy.

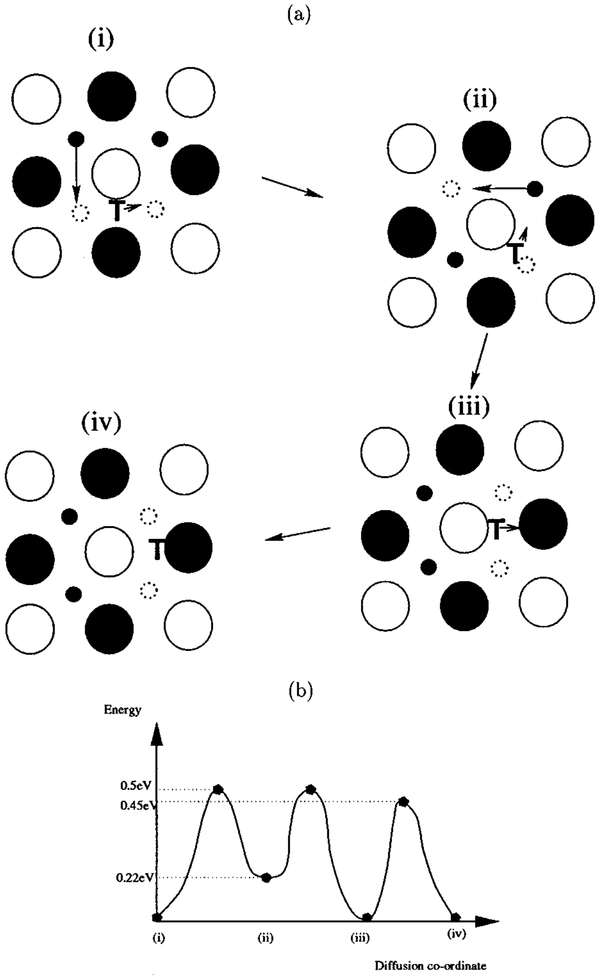

FIG. 5. (a) Possible pathway for migration of defect complex of two lithium vacancies and tritium ion. Large open circles denote the (100) plane of oxygen ions below the Li ion plane, and large open circles the plane of oxygen ions above. Other symbols as in Fig. 3. (b) Schematic energy profile along this path. Dots indicate points actually calculated.

The overall diffusion constant for tritium will be the average of the diffusion coefficients for each defect species, weighted by their respective concentrations. Note that the energy difference between the tritium interstitial defect, T_i,

TABLE I. Summary of results of Sec. III. Zero of energy arbitrarily taken as energy of isolated interstitial.

Defect species	Energy (eV)	Upper limit to diffusion barrier (eV)
T_i	0.00	0.45
T_{Li}	-1.32	0.98
T_{2Li}	-1.49	0.50

and the other defect forms is much greater than $k_B T$ at the temperatures in question (<1000 K), and that there will be at least as many lithium vacancies as tritium atoms in the material due to the stoichiometry of the nuclear reaction producing the latter. Therefore, in thermal equilibrium the T_i concentration should be negligible, and hence their contribution to the diffusion coefficient should be similarly negligible. The binding energy of the tritium and two lithium vacancies complex, $\mathrm{T}_{2\mathrm{Li}}$, at 0.17 eV, is also much greater than $k_B T$, so as much tritium as possible will be in this form—if we write the concentration of lithium vacancies as $n_v = n_T + \Delta n_v$, the concentration of $\mathrm{T}_{2\mathrm{Li}}$ will be approximately Δn_v. Since the experimental data do not agree with the results for $\mathrm{T}_{2\mathrm{Li}}$ diffusion, we suggest that this mechanism is inhibited, either by Δn_v being small, or a large negative configurational entropy term due to the complicated nature of such a mechanism, or a combination of both.

Thus by comparing the experimental and theoretical results, we propose that the observed mechanism is that of diffusion of the substitutional defect. Our calculations suggest this takes place by a two-stage swapping process. It seems likely that the experimental reports of a link between lithium vacancy diffusion and tritium diffusion[10] are probably not significant. While we cannot directly suggest an explanation for the lower temperature data, we note that the previously mentioned hypothesis of Johnson and Hollenberg[1] is not supported by our data. The explanation is probably due to surface release becoming the limiting factor,[3] or retardation by radiation defects.[5] We note that our results suggest that additional Li vacancies introduced into the material could speed up the rate of tritium diffusion. However, if these extra vacancies are created by introduction of impurities then it is possible these impurities could inhibit diffusion, negating the benefit. Nonetheless this could be a suggestion for further experimental work in this area.

V. CONCLUSIONS

We have performed *ab initio* density functional calculations to elucidate the mechanism of tritium diffusion in lithium oxide. By comparison between our results and experimental data we have shown that at temperatures above 600 K this consists of diffusion of a substitutional tritium defect by a simple two stage mechanism of tritium swapping places with lithium. Our results do not support previously proposed theories that the mechanism actually observed is assisted by additional lithium vacancies. However, we do confirm that more rapid diffusion may be obtained by increasing the number of lithium vacancies in the material, although other factors may affect the benefits gained from this. Further work is needed to investigate this, and also to elucidate the rate controlling factors at lower temperatures.

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