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Mechanisms of tritium diffusion in Li_2O : quantum-chemical simulation

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Abstract. Using the intermediate neglect of differential overlap MO LCAO calculation procedure and the embedded molecular cluster model we have investigated atomic and electronic structure and key stages of diffusive transfer of T^+ and T^0 in Li_2O , containing cation vacancies and F^+ centres.

The activation energy for the cation vacancy diffusion in Li_2O is calculated to be 0.33 eV. Comparing different models of T^+ and T^0 atomic structures and the mechanisms of their diffusion, we have shown that the lowest activation energy (< 0.9 eV) requires the T^+ ion in the cation site to transfer by a vacancy mechanism. However, the T^0 diffusion activation energy is generally only slightly higher: if it occupies an interstitial position, it may jump via interstitial sites within an activation energy of about 1 eV; if it is trapped in the cation site, exchange with a nearest lattice cation will require an activation energy of about 1.1 eV. By analysing the driving forces for tritium diffusion we conclude that the isotopic effect cannot affect the results of our calculations.

1. Introduction

During the last decade Li_2O has attracted considerable attention due to its potential application as a blanket material for deuterium–tritium fusion reactors and also as a fast-ion conductor [1–3]. One of the features of this material is its relatively simple anti-fluorite atomic structure. Therefore, in addition to important technological applications, Li_2O may be considered as an interesting model system, which is useful in providing a deeper understanding of the mechanisms of irradiation-induced processes and of ionic conductivity in anti-fluorite structured crystals. Neutrons, being the main component of the fusion-reactor-produced radiation, effectively interact with Li-ion nuclei, causing the nuclear transformation ${}^6\text{Li}(n, \alpha)\text{-T}$. The initial energy of the triton is 2.7 MeV and before thermalization and stabilization in the lattice may cause significant radiation damage, including swelling and cracking of Li_2O [4, 5]. The final electronic state of thermalized tritium depends strongly on the temperature [6], but in Li_2O crystals heated above 570 K, 97% of the tritium is believed to be present as T^+ while the remaining 3% are T^0 atoms [6].

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One of the most important characteristics of any tritium breeding material in fusion reactors is the effectiveness of tritium release from a sample. In order to understand the mechanism of tritium release from Li_2O , investigations have been performed using Li_2O powder, sintered pellets and single crystals [2, 6–8]. The results of these studies have been briefly summarized in a recent article [2]. The tritium release is determined by its diffusion through the sample, which in turn depends on the preparation of the sample and on its chemical and phase composition. The most complete and reliable results concerning the tritium diffusion coefficient and its temperature dependence were obtained using high-purity Li_2O single crystals. The diffusivity of tritium was expressed in the temperature range 573–950 K by the usual Arrhenius activation law with a value of the activation energy equal to about 1 eV [7]. Comparison of the data on tritium release from Li_2O with those on ionic conductivity [3], nuclear magnetic resonance spectroscopy [10, 11] as well as tracer diffusion [12] in these crystals shows that the tritium release takes place near the temperatures at which the diffusivity of the lithium ions increases [13]. As is well established by experimental [10, 11] and theoretical [11, 14, 15] studies, the electrical conductivity of Li_2O is due to Li^+ ion migration proceeding by a vacancy mechanism. The approximately simultaneous increase of Li^+ and tritium diffusivity suggests a close relationship between lithium-ion (cation vacancy) diffusion and tritium diffusion in Li_2O [8].

Neutron irradiation of Li_2O produces radiation defects which may strongly affect ionic diffusion processes. In particular, the presence of F^+ centres (an electron localized in the doubly charged anion vacancy [16–19]) decreases the ionic conductivity of Li_2O by about 5–20%, depending on the irradiation dose [2, 8]. It is assumed that this happens because the lithium-ion vacancies, v_{Li}^- , are electrostatically attracted by the positively charged F^+ centres. Consequently, the mobility or the effective concentration of the vacancies may decrease, resulting in a decrease in ionic conductivity [2, 8]. If the diffusion of lithium ions is closely related to that of tritium it can be concluded that the diffusivity of tritium may also be reduced by the presence of F^+ centres, which are permanently generated by irradiation under reactor conditions.

In spite of the experimentally established qualitative correlations, the actual meaning of the relationship between the lithium and tritium diffusivity is still not clear. One of the suggested explanations is based on the idea that tritium release is mainly determined by T^+ diffusion in the sample. In its turn the migration of T^+ is assumed to occur by hopping from oxygen to oxygen on the oxygen sublattice of Li_2O . In such a migration process, T^+ must overcome the repulsive electrostatic barrier caused by the positive lithium ions. Since the lithium ions are considered to migrate via a vacancy mechanism, the Li^+ diffusion causes frequent replacement of one of the Li^+ sites of the barrier by a vacancy [8]. Consequently, the repulsive force decreases and the tritium can migrate.

On the other hand, it seems quite reasonable to assume the possibility of local compensation of the positive charge of the T^+ by a cation vacancy or, moreover, their association as a pair of charge-complementary defects $\text{T}^+ + v_{\text{Li}}^- = \text{T}_{\text{Li}}^+$. In particular, the model proposed in [20] relies on the idea that tritium migration is strongly correlated with lithium-ion vacancies by forming the triton/vacancy complex.

The mechanism of T^0 diffusion in Li_2O and its contribution to tritium release has not yet been discussed. However, it may be of fundamental as well as practical interest. Indeed, existing models of the tritium release have only qualitative meaning and are based on indirect experimental data. Therefore the real relationship between T^+ and T^0 contributions to tritium release is not clear.

To address these questions theoretically one has to begin with a microscopic study of the mechanisms of T^+ and T^0 behaviour in the bulk of Li_2O taking into account the presence of other lattice defects which can affect the process. The simplest of such defects are cation vacancies and F^+ centres. The next stage may be a Monte Carlo or molecular dynamics simulation, including all the different transfer processes. This can give a theoretical picture of different events contributing to tritium release as a function of temperature.

Quantum-mechanical methods have shown themselves to be a useful tool in theoretical studies of mechanisms of various hydrogen-transfer processes in solid materials [21, 22]. Their results may also be used for the further development of effective pair potentials, necessary to statistical simulations. Therefore, in the present study we have employed modern solid-state quantum-chemical simulation techniques for the investigation of atomic and electronic structure and key stages of diffusive transfer of T^+ and T^0 in Li_2O , containing cation vacancies and F^+ centres.

Comparing different models of T^+ and T^0 atomic structures and the mechanisms of their diffusion, we have shown that the lowest activation energy (< 0.9 eV) requires the T^+ ion in the cation site to transfer by a vacancy mechanism. However, the T^0 diffusion activation energy is generally only slightly higher: if it occupies an interstitial position, it may jump via interstitial sites within an activation energy of about 1 eV; if it is trapped in the cation site, exchange with a nearest lattice cation will require an activation energy of about 1.1 eV.

Our study of diffusion mechanisms has been performed in the framework of the adiabatic approximation. Therefore, the calculated adiabatic potential energy surfaces do not depend on the actual mass of the hydrogen isotope. However, the isotopic effect may strongly affect the kinetics and temperature dependence of the transfer processes [27, 28]. This point is considered in the discussion.

2. Method of calculation

For our purpose we need a method which will yield a reasonably accurate adiabatic potential energy surface and in addition allow the possibility of studying complicated systems, such as pairs of charged defects. Based on our previous experience of study of complicated multicomponent defects [29, 30] we have chosen to employ the intermediate neglect of differential overlap (INDO) MO LCAO calculation procedure [24, 25] and the embedded molecular cluster model [23, 31]. The same approach has been used in the study of electronic defects and self-trapped excitons in Li_2O [19] as well as proton conductivity mechanisms in a more complex oxide—hydronium perchlorate [22].

The method has been described in detail in our previous publications. Briefly, the procedure includes as a first stage (i) a perfect crystal electronic structure calculation within the framework of the large unit cell (LUC) model [26, 32]; (ii) the lattice constant optimization; and (iii) the analysis of the interband electronic transitions. In the next stage we choose a crystal cluster for the ensuing defect calculations. The cluster is not removed from the crystalline lattice, but remains embedded in a rigid lattice of non-point frozen ions. The atomic orbitals of these ions have the same populations as those in the perfect crystal. The matrix elements of the crystalline field produced by all the ions in the lattice are explicitly evaluated by the Ewald summation procedure on the atomic orbitals of the cluster ions [25, 26]. In this way only the Coulomb part

of the interaction of the cluster ions with the ions in the rest of the crystal is taken into account. At the same time, within the cluster all the interactions between ions are included (in the INDO approximation). The difference in the interaction between cluster ions and those between cluster and the non-point embedding ions, results in a relaxed cluster configuration in which the boundary ions are slightly displaced inwards (about 3% of the interionic distance) from their positions in the perfect lattice [19]. The parametrization of the INDO semi-empirical calculation scheme and the set of parameters employed in the present work are discussed in [24, 25].

All the electronic structure and adiabatic potential energy surface (APES) calculations were carried out for embedded clusters of $(\text{Li}_{36}\text{O}_{18})$ and $(\text{Li}_{41}\text{O}_{20})^+$, where one or several ions were replaced by cation vacancies, F^+ centres, the hydrogen atoms or ions as appropriate. Due to the large cluster size and the low symmetry of the defect pairs, the calculations of their electronic structure at each APES point are complex and time-consuming. To keep the calculations practicable we did not take account of the polarization of the crystal outside the cluster. In some cases this may cause changes in the shape of the APES but, keeping in mind that most of the defect pairs are electrically neutral relative to the lattice, we believe that neglect of the lattice polarization does not change the qualitative conclusions of this work.

The results of our calculations may only be quantitatively compared with the experimental data on the diffusion activation energies of v_c^- and tritium in Li_2O [7, 11]. Therefore we have focused our attention principally on the calculation of the lattice deformation around the defects and also on the evaluation of the relative energies in the extremum points on the APES, corresponding to the adiabatic motion of the defects in the crystalline lattice.

We will begin with the results on the atomic structure of the cation vacancy and its interaction with the F^+ centre. Then we shall analyse the results of the simulation of the tritium atom in the perfect lattice and its interaction with the v_c^- defect in addition to two models of tritium atom diffusion in Li_2O . We shall conclude our study with an analysis of the tritium diffusion model.

3. Results of calculations

3.1. v_c^- and $v_c^- - \text{F}^+$ -centre pair

According to the experimental data [14] and the results of the theoretical calculations [15], the energy of formation of Frenkel defects in the cation sublattice of Li_2O is about 2.55 eV, and is significantly smaller than the corresponding theoretical values for Schottky defects (5.8 eV [15]) and Frenkel defects in the anion sublattice (8.31 eV [15]). Diffusion of the v_c^- defect causes the relatively high ionic conductivity of Li_2O [11]. The values of the v_c^- diffusion activation energy obtained experimentally differ depending on the manner of sample preparation and actual experimental conditions [9–11]. Recent results obtained for pure single crystalline samples show that at low temperatures the diffusion activation energy for v_c^- is about 0.43–0.49 eV [11, 14]. The theoretical values, derived from the Mott–Littleton calculation [33], are much smaller—0.26 [15] and 0.21 [14] eV.

We have calculated the static lattice deformation around the cation vacancy (see figure 1). The inward displacements of the six nearest cations are $0.09 a_0$ (a_0 is the distance between nearest cation sites in the perfect lattice; $a_0 = 2.3 \text{ \AA}$) and the

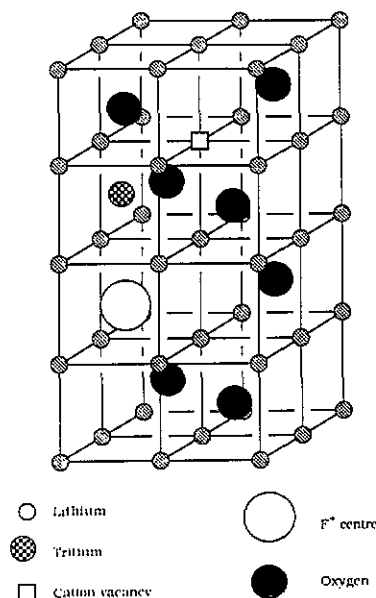


Figure 1. A fragment of the Li_2O lattice with the F^+ -centre cation vacancy pair and the tritium atom in the interstitial position.

outward displacements of the four nearest anions are equal to $0.03\sqrt{3} a_0$ (i.e. $0.03 a_0$ along each Cartesian axis).

To calculate the cation vacancy diffusion activation energy we assumed that a jump of one of the nearest cations into the vacancy takes place along the $\langle 100 \rangle$ crystalline axis. The calculated activation energy is equal to 0.33 eV, which is markedly smaller than the experimental values, but close to the results of Mott-Littleton calculations. The explanation of this result may consist in the approximate character of our calculation. There is, however, another possible explanation, namely that the experimentally observed activation energies are related to temperatures higher than 300 K [9-11], where the v_c^- are mobile. As noted in [8], experimental samples usually contain fairly large concentrations of two- and three-valent metal impurities, attracting cation vacancies to compensate locally for their surplus charge [34]. For example, the binding energy for $\text{Mg}^{2+}-v_c^-$ in Li_2O was found to be about 0.94 eV [15]. If one supposes that the experimentally observed diffusion activation energy also includes the dissociation energy of some fraction of the v_c^- from different impurities, the experimental value of the activation energy will be larger than the theoretical estimate. This point, however, requires more detailed analysis on the basis of a thermodynamic approach.

The electronic structure of the F^+ centre and other electronic centres in Li_2O has been considered in our previous article [19]. Creation of positively charged F^+ centres under irradiation may not be accompanied by the simultaneous appearance of a cation vacancy in its immediate vicinity. But, as was suggested in [35], the Coulomb attraction may result in the creation of $F^+-v_c^-$ pairs at temperatures, where the v_c^- defects are mobile in the lattice. We have studied the atomic and electronic structure of such pairs.

When studying charged defects one has to include fewer than three or four spheres of surrounding ions in the lattice distortion calculation. In view of the relatively small

size of our largest cluster ($\text{Li}_{41}\text{O}_{20}$), a proper comparison of the configuration energies was possible only for two cases: namely v_c^- location in the nearest-neighbour (NN) and the next-nearest-neighbour (NNN) positions relative to the F^+ centre (see figure 1). To model the F^+ centre, we extended our basis set of atomic orbitals (AOs) to include 2s and 2p Slater-type AOs centred at the vacancy. The exponent of each function was optimized to fit the experimentally observed optical absorption energy and the EPR isotropic hyperfine interaction with neighbouring cations [16, 17, 19]. The values of the exponents thus determined were 1.24 Bohr^{-1} for the 2s AO and 1.15 Bohr^{-1} for the 2p AO [19].

Putting v_c^- in the NN and NNN vicinity of the F^+ centre, we have therefore calculated the deformation of the surrounding lattice, minimizing the total crystal energy with respect to the positions of the cluster ions. In both configurations the resulting ionic displacements are close to the vector sums of those for the separate defects. Such lattice deformation behaviour is peculiar to ionic crystals, where the pair approximation for inter-ionic interactions works well (see, for example, [30]). The total crystal energy was approximately 0.7 eV lower in the case of the NNN configuration (see figure 1). The presence of the cation vacancy, however, somewhat distorts the symmetry of the F^+ centre; although the values of the unpaired electron spin density on the neighbouring Li^+ -ions nuclei are close to those obtained for the single F^+ centre [19] ($0.9\text{--}1.2 \times 10^{-2} \text{ Bohr}^{-3}$) and agree with the experimental value of $1.5 \times 10^{-2} \text{ Bohr}^{-3}$ [16]. The energy of the optical transition, calculated using the ΔSCF procedure, is equal to 3.97 eV and did not change substantially compared with the single F^+ centre (3.93 eV [19]), in spite of the strong simultaneous shift of the ground and excited one-electron states in the Coulomb field of the cation vacancy. The experimental value of the energy, corresponding to the maximum of the F^+ centre optical absorption band is equal to 4.13 eV [17]. When the v_c^- is situated in the immediate vicinity of the F^+ centre the distortion of the spin density distribution is much stronger, whereas the optical transition energy only changes slightly.

Due to the limited size of the cluster we could not extend our study to larger $\text{F}^+ - v_c^-$ distances with a view to calculating the centre's binding energy. The comparison with the F^+ centre EPR parameters is prevented by the absence of information concerning the relative concentrations of F^+ centres and v_c^- defects in the experimental samples [16] and the small distortion of the hyperfine interaction in the NNN configuration.

It is interesting to note that there is a certain analogy between NNN $\text{F}^+ - v_c^-$ pairs and the $\text{Me}^{2+} - v_c^-$ dipoles in alkali halides (Me indicates a divalent metal, for example Mg, Ca, Pb, etc) in the case when the impurity radius is close to or smaller than that of the host cation [34]. The compensating cation vacancy is situated in the NN position to the impurity cation site only if the impurity radius is so large that it creates considerable strain [30, 34]. In the case of the $\text{F}^+ - v_c^-$ pair there is an additional strong effect, competing with the Coulombic interaction between the centres and the interference of their lattice distortions. This is the shift of the unpaired electron's occupied one-electron state, which increases the crystal energy much more strongly when v_c^- is in the NN position to the F^+ centre. Therefore, the NNN atomic configuration of the $\text{F}^+ - v_c^-$ pair can be readily understood.

3.2. T^0 in the Li_2O crystalline lattice

As there are no experimental data concerning the atomic structure of T^0 in Li_2O we must postulate plausible models. In particular, one can assume that T^0 may be localized in the lattice interstitial position, for example at the cubic interstitial site,

surrounded by eight lithium ions (see figure 1). Placing T^0 in this position, we have calculated the deformation of three spheres of neighbouring ions. Since T^0 is relatively small and neutral, it causes only a small lattice deformation. In particular, the inwards displacements of the eight NN Li^+ -ions are about $0.01\sqrt{3} a_0$. The effective charge of the T^0 remains close to zero, reflecting the absence of any chemical bonding with the lattice ions. The study of T^0 stability in the interstitial position has shown that the T_i^0 centre APES in fact has a deep minimum in the centre of the cube. If one may assume that T^0 diffusion is slow and is accompanied by adiabatic lattice distortion at each point of the T^0 classical trajectory, then the lowest calculated barrier for T^0 transfer is situated on the $\langle 110 \rangle$ crystalline axis between two equivalent cubic interstitial positions. The height of the barrier is equal to 1.0 eV. It is of interest to evaluate the height of the barrier for the same process, but for an energetic non-thermalized T^0 , when the effective time of its transfer is much shorter than the period of the characteristic lattice vibrations. Moving in the rigid lattice along the $\langle 110 \rangle$ axis from one interstitial site to another the T^0 then has to surmount a barrier of 2.7 eV.

These two energies give the limits within which the T^0 transfer barrier height may change depending upon the real dynamics of the process. The actual transfer mechanism may turn out to be much more complicated due to non-adiabaticity at high temperatures and T^0 tunnelling near the top of the barrier at low temperatures.

The interstitial position is most certainly not the only way in which T^0 can be localized in Li_2O . For example, the interaction of the T_i^0 centre with a mobile cation vacancy may result in its capture in a cation site with the formation of a $(\text{T}^0)_c^-$ centre. The same centre may be generated after electron trapping by a T^+ , already localized in some cation site. Since both processes seem possible, we have studied the $(\text{T}^0)_c^-$ centre formation mechanism and its diffusion in more detail.

We considered the electronic and atomic structure of the T^0 - v_c^- centre pairs at different distances, taking into account the lattice distortion. The comparison of the total crystal energies reveals that

(i) T^0 localization in the cation site is energetically much more favourable than in the interstitial position;

(ii) T^0 capture by the vacancy from the nearest interstitial position takes place as a barrierless jump with the energy gain of 1 eV; and

(iii) cation vacancies farther away than the nearest neighbours to the T_i^0 centre do not affect its activation energy for diffusive jumps. The last result is caused mainly by the short-range character of the defect's interaction.

Both in the interstitial position and in the cation site the spin density of the unpaired electron is strongly localized on the tritium, being slightly more delocalized in the $(\text{T}^0)_c^-$ centre. However, even in this case the values of the spin density on the nuclei of eight surrounding Li^+ -ions do not exceed 10^{-4} Bohr $^{-3}$. The lattice deformation around $(\text{T}^0)_c^-$ is close to that for the v_c^- defect and causes the appearance of quasi-local electronic states in the valence band as well as in the conduction band of the crystal. The wavefunctions of the quasi-local states in the valence band are formed from linear combinations of AOs centred on the T^0 and on the anions nearest to it. We have employed the restricted configuration interaction technique [36] to calculate the electronic transition energies between occupied quasi-local states and the unoccupied state, localized on the tritium atom. The minimal energy, corresponding to the non-forbidden transition, is 8.7 eV.

The $(\text{T}^0)_c^-$ centre repels the negatively charged cation vacancy. Therefore the

only way for it to diffuse is to exchange places with one of the nearest cations (site mechanism). The optimal classical trajectories of both the T^0 and Li^+ pass through the opposite interstitial positions and the minimum activation energy of this process, obtained in our calculations, is about 1.1 eV, close to the activation energy of the T_i^0 centre diffusion.

3.3. T^+ -ion diffusion mechanism in Li_2O

There is no experimental information concerning the atomic structure of defects containing T^+ in Li_2O . Therefore we have started our study with the same assumptions as for T^0 , namely that after thermalization a T^+ -ion may find itself in a lattice interstitial position. We have found that, in contrast to the T_i^0 centre, the triton ion immediately makes a very strong chemical bond with one of the nearest oxygen ions. The length of this bond is about 0.98 Å, which is very close to the equilibrium distance in the OT^- molecular ion (0.97 Å). The energy gain relative to the T^+ state in the unrelaxed lattice due to chemical bond formation and lattice relaxation was about 5 eV. The structure of the defect is shown schematically in figure 2. The oxygen ion which makes the bond with T^+ moves from its site towards the triton by $0.06 a_0$. We should stress the difference between the free OT^- molecular ion and the solid state defect under study. In the latter case the triton forms a bond with the oxygen ion which has a charge in the lattice of about $-1.75 e$ (Lowdin population analysis). The bond formation is accompanied by electronic density redistribution from the oxygen ion onto the T^+ and the triton effective charge becomes 0.55 e instead of 1.0 e .

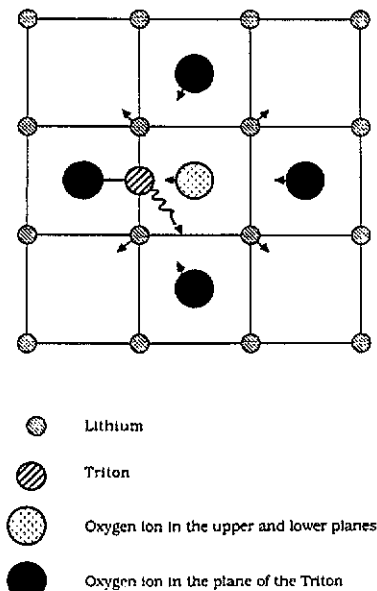


Figure 2. Schematic representation of the atomic structure of Li_2O with triton in the interstitial position. Arrows show the directions and relative magnitudes of the displacements of the surrounding ions and triton diffusion mechanism.

The relatively small distance (about 1.5 Å) between equivalent positions of T^+ (see figure 2) in the cubic cage, formed by six oxygens, suggests that jumps between

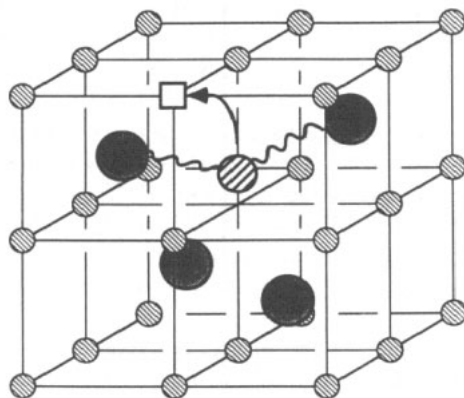


Figure 3. Schematic representation of the atomic structure of the $(T_c^+)^0$ centre in Li_2O . The arrow shows the possible mechanism for tritium diffusion via a vacancy mechanism. For ion types see figures 1 and 2.

these positions may be easily made. We have calculated an activation energy for such a jump within the adiabatic approximation. In other words, we have assumed that the tritium moves slowly enough and the remaining lattice follows its motion at any point of the classical trajectory. Such an approach gives us a lower limit of activation energy, which in our calculation was determined to be 1.6 eV, much higher than the experimental value ascribed to T^+ diffusion in Li_2O [7]. This result indirectly confirms the assumption made in [8, 20] that the Coulomb repulsion between the tritium and surrounding cations, which causes the large value of the activation energy, requires for its reduction the participation of the cation vacancy in the tritium transfer process.

We have studied this vacancy-assisted model, by choosing different positions for the cation vacancy and then calculating the lattice distortion. The total crystal energy is least when the vacancy occupies a site in the plane of the four cations which lie nearest to the tritium (see figure 2). The atomic structure of this defect in its relaxed configuration is shown in figure 3. The tritium ion occupies one of the six equivalent off-centre positions in the cation site, making chemical bonds with two oxygens. The tritium's displacement along the $\langle 100 \rangle$ axis is $0.25 a_0$ and the length of two shortest $T^+-O^=$ chemical bonds is 1.2 Å. The effective charge of the tritium is $0.6 e$, while the effective charges of all four nearest oxygens are approximately equal to $-1.57 e$. The energy barrier for the tritium transfer between equivalent positions in the cation site is less than 0.1 eV. Thus, the tritium-cation vacancy complex has qualitatively the same atomic structure as the off-centre Li^+ -ion, substituting for K^+ in KCl [34], and we will refer to it as $(T^+)_c^0$ centre, where 'o' notation shows that it is neutral relative to the lattice.

There are two possible mechanisms of the $(T^+)_c^0$ centre diffusion in the lattice: (i) correlated exchange of tritium with one of the nearest cations; and (ii) a vacancy

mechanism, characteristic of Li^+ -ions in Li_2O . The strong repulsion with surrounding cations in the compact cation sublattice of Li_2O makes the exchange mechanism of the $(\text{T}^+)_c^0$ centre diffusion improbable. The activation energy for this transfer was found to be at least 2.7 eV.

For the mechanism of triton hopping via a vacancy one more cation vacancy must come into the immediate (NN) or the next nearest (NNN) vicinity of the $(\text{T}^+)_c^0$ centre. Our calculations show that when the cation vacancy is in an NN position to the $(\text{T}^+)_c^0$ centre the crystal energy is lower by 0.15 eV than when it occupies the NNN position, shown in figure 3. The activation energy for the triton jump into the nearest vacancy was calculated to be 0.2 eV, whereas the jump into the NNN vacancy requires the activation energy of 0.5 eV.

The measured activation energy for the tritium release from Li_2O corresponds to the temperature range below 1000 K, where ionic conductivity is controlled by the diffusion of already existing cation vacancies [2, 7, 8]. Therefore, the total activation energy for $(\text{T}^+)_c^0$ centre diffusion may be roughly estimated as the sum of

- (i) the activation energies for the cation vacancy diffusion (0.33 eV in our calculations, 0.43–0.49 eV measured experimentally);
- (ii) the binding energy of the cation vacancy to the $(\text{T}^+)_c^0$ centre (i.e. the cation vacancy activation energy change in the vicinity of the centre); and
- (iii) the activation energy for triton jumps between the vacancies (0.2 and 0.5 eV for NN and NNN vacancy positions).

Since the $(\text{T}^+)_c^0$ centre is neutral, we believe that the energy contribution (ii) is negative and does not exceed 0.1 eV, that is the cation vacancy is attractive at small distances. Taking, for the cation vacancy activation energy, the average of the experimentally observed values, -0.46 eV, we receive our estimation for the $(\text{T}^+)_c^0$ centre diffusion activation energy, E_a , $0.56 < E_a < 0.86$ eV.

To make more accurate predictions we need to employ not only a static approach, but also a more sophisticated statistical analysis of the different mutually dependent mechanisms for T^+ and v_c^- diffusion and thermally activated v_c^- production in the lattice. For instance, from a purely geometrical point of view it is clear that the probability for the cation vacancy to be bound in the NNN vicinity of the $(\text{T}^+)_c^0$ centre is twice as great as that in the NN position. The statistical simulation requires us to develop new pair potentials for the triton/tritium–oxygen interactions in the lattice of Li_2O . This work is now in progress.

4. Discussion and conclusion

In summary, we can conclude that the majority of the tritium release from Li_2O is determined by the triton ion's diffusion by a vacancy mechanism. The activation energies for the T_i^0 and $(\text{T}^0)_c^-$ centre diffusion are not much higher than that for the $(\text{T}^+)_c^0$ centre. Thus, it is also possible for T_i^0 and $(\text{T}^0)_c^-$ to take part in the tritium transfer, especially at high temperatures. However, their contribution would be comparatively small due to low concentration of T^0 .

By analysing the driving forces for tritium diffusion we can conclude how the isotopic effect may affect the results of our calculations. In fact, the isotope replacement in hydrogen-containing crystals mainly changes the frequencies of the anion-hydrogen vibrations. When these vibrations determine the structural transformations, the isotopic effect may produce drastic changes in the temperature dependence of the process

(for instance, the phase transitions, as in the case of KDP and other ferroelectrics [27, 28]). In the present study the energy barriers for tritium diffusion are determined mainly by the lattice vibrations rather than by O-T vibrations. Therefore isotope replacement will definitely change the frequency of the hydrogen-ion's jumps inside the cation vacancy. Its influence on the activation energies of the tritium diffusion will presumably be negligible.

Acknowledgments

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References

- [1] Tone T, Fujisawa N, Seki Y *et al* 1983 *Nucl. Tech./Fus.* **4** 573
- [2] Noda K, Ishii Y, Ohno H, Watanabe H and Matsui H 1989 *Adv. Ceram.* **25** 155
- [3] Salamon M G (ed) 1979 *Physics of Superionic Conductors* (Berlin: Springer)
- [4] Hollenberg G W 1984 *J. Nucl. Mater.* **122-3** 896
- [5] Hollenberg G W and Baldwin D L 1985 *J. Nucl. Mater.* **133-4** 242
- [6] Kudo H and Okuno K 1985 *J. Nucl. Mater.* **133-4** 192
- [7] Tanifuji T, Noda K, Takahashi T and Watanabe H 1987 *J. Nucl. Mater.* **149** 227
- [8] Noda K, Ishii Y, Matsui H, Ohno H and Watanabe H 1989 *Fus. Engrg. Design* **8** 329
- [9] Ohno H, Konishi S, Noda K, Takeshita H, Yoshida H and Watanabe H 1983 *J. Nucl. Mater.* **118** 242
- [10] Matsuo T, Ohno H, Noda K, Konishi S, Yoshida H and Watanabe H 1983 *J. Chem. Soc. Faraday Trans. II* **79** 1205
- [11] Strange J H, Rageb S M, Chadwick A V, Flack K W and Harding J H 1990 *J. Chem. Soc. Faraday Trans.* **86** 1239
- [12] Akiyama M, Ando K and Oishi Y 1981 *Solid State Ionics* **3-4** 469
- [13] Ohno H, Konishi S, Nagasaki T, Kurasawa T, Katsuta H and Watanabe H 1985 *J. Nucl. Mater.* **133-4** 181
- [14] Chadwick A V, Flack K, Strange J H and Harding J H 1988 *Solid State Ionics* **28-30** 185
- [15] Jacobs P W M and Vernon M. L 1990 *J. Chem. Soc. Faraday Trans.* **86** 1233
- [16] Noda K, Uchida K, Tanifuji T and Nasu S 1981 *Phys. Rev. B* **24** 3736
- [17] Uchida K, Noda K, Tanifuji T, Nasu S, Kirihara T and Kikuchi A 1980 *Phys. Status Solidi a* **58** 557
- [18] Ong C K 1983 *J. Phys. C: Solid State Phys.* **16** 4081
- [19] Shluger A and Itoh N 1990 *J. Phys.: Condens. Matter* **2** 4119
- [20] Tam S W, Wright J, Curtiss L A and Johnson C E 1991 *J. Nucl. Mater.* **179-81** 859
- [21] Flynn C P and Stoneham A M 1970 *Phys. Rev. B* **1** 3966
- [22] Angyán J, Allavena M, Picard M, Potier A and Tapia O 1982 *J. Chem. Phys.* **77** 4723
- [23] Shluger A L, Kotomin E A and Kantorovich L N 1986 *J. Phys. C: Solid State Phys.* **19** 4183
- [24] Shluger A L 1985 *Theor. Chim. Acta* **66** 355
- [25] Stefanovich E V, Shidlovskaya E K, Shluger A L and Zakharov M A 1990 *Phys. Status Solidi b* **160** 529
- [26] Shluger A L and Stefanovich E V 1990 *Phys. Rev. B* **42** 9646
- [27] Sokolov N D, Vener M V and Savel'ev V A 1988 *J. Mol. Struct.* **177** 93
- [28] Colomban Ph and Novak A 1988 *J. Mol. Struct.* **177** 277
- [29] Shluger A L, Mysovsky S N and Nepomnyaschikh A I 1988 *J. Phys. Chem. Solids* **49** 1043
- [30] Gavartin J L, Shidlovskaya E K, Shluger A L and Varaksin A N 1991 *J. Phys.: Condens. Matter* **3** 2237

- [31] Kantorovich L N 1988 *J. Phys. C: Solid State Phys.* **21** 5041
- [32] Evarestov R A and Lovchikov V A 1977 *Phys. Status Solidi* **b 80** 743
- [33] Catlow C R A and Mackrodt W C 1982 *Computational Solid State Physics* ed C R A Catlow and W C Mackrodt (Berlin: Springer) p 3
- [34] Agullo-Lopez P, Catlow C R A and Townsend P D 1988 *Point Defects in Materials* (London: Academic)
- [35] Noda K, Ishii Y, Matsui H, Ohno H, Hirano S and Watanabe H 1988 *J. Nucl. Mater.* **155-7** 568
- [36] Hehre W J, Radom L, Shleyer P v R and Popl J A 1986 *Ab initio Molecular Orbital Theory* (New York: Wiley)