Ab-initio study on interaction of hydrogen isotopes with charged defects in lithium oxide

Hisashi Tanigawa [*], Satoru Tanaka

Department of Quantum Engineering and Systems Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Abstract

The interaction of hydrogen isotopes with defects in Li_2O was studied by ab-initio quantum chemical calculations. Three kinds of F-centers and the lithium vacancy were considered. The relaxation of ions around the vacancy and the stable position of a proton were calculated when the vacancy was produced in the Li_2O crystal. From the obtained energies and the electronic charge density maps for each configuration, the effects of the vacancies on the proton were discussed.
© 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The tritium release behaviour from the blanket materials is an important subject for the design of the fusion reactor fuel cycle. The breeding material is planned to be exposed to a high radiation dose. In the case of solid breeding materials, this neutron irradiation leads to the formation of various defects. It is reported that these defects could increase the tritium inventory. This has been explained by trapping of tritium at the defects. However, little is known about the interaction of tritium with the defects. In our previous infrared studies, multiple peaks were observed in lithium oxide which was subjected to the thermal absorption of D_2, and these peaks were assigned to O–D stretching vibrations that were affected or not affected by defects [1,2]. The purpose of the present study is to elucidate how the defects interact with hydrogen isotopes in Li_2O using ab-initio quantum chemical calculations. It is well known that there exist three varieties of oxygen vacancies in the neutron irradiated Li_2O: F^{2+}, F^+ and F^0 centers. Adding a lithium vacancy to them, four kinds of defects were considered.
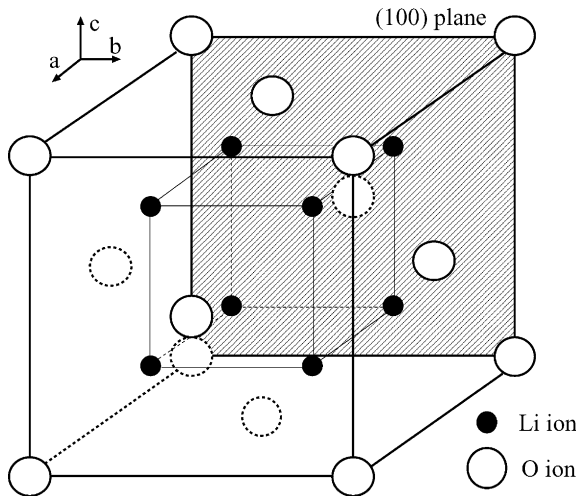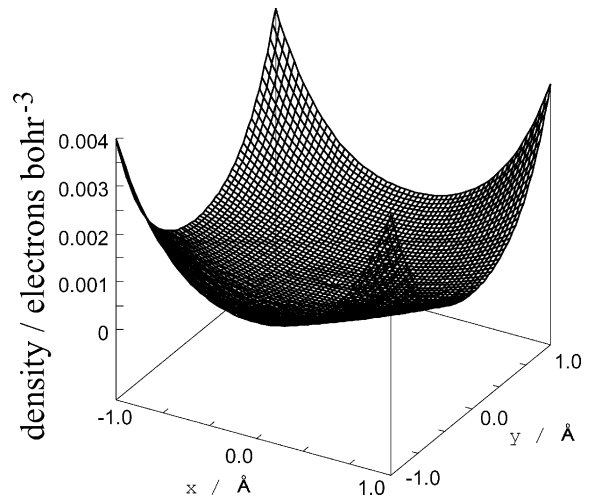
2. Calculation details

2.1. Computational methods

Two calculation codes were used for the investigation: the CRYSTAL95 code [3] with all-electron Gaussian-type basis sets and the CASTEP code with pseudopotentials and plane wave basis sets. In CRYSTAL, it is a great advantage to have reported basis sets that are optimized to Li_2O [4]. The calculations using CRYSTAL were performed at the Hartree–Fock level. CASTEP enables us to get a relaxed configuration, which CRYSTAL could not. In the density functional theory calculations using CASTEP, the generalized gradient approximation (GGA) was used and GGA is one of the most popular functionals. No other exchange-correlation functionals were adopted in this stage. Comparison of the results from these two codes would make the ab-initio analysis more reliable.

2.2. The system for calculations

Fig. 1 shows the anti-fluorite structure of Li_2O. Both the codes, CRYSTAL and CASTEP, can deal with an infinite system such as crystal environment by considering a series of consecutive supercells. Supercells are made up of several unit cells. In the present work, two kinds of supercells were used, the supercell which con-
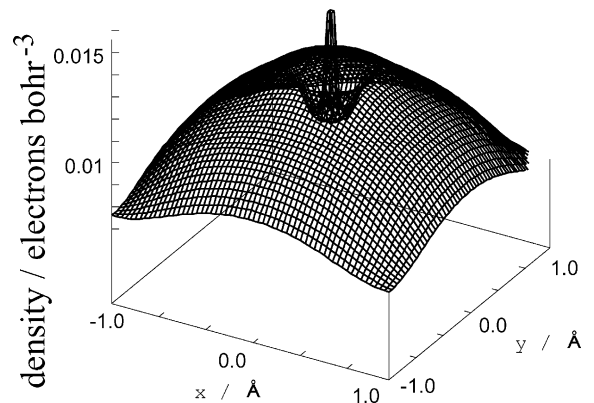
---

[*] Corresponding author. Tel.: +81-3 3812 2111/5841 6970; fax: +81-3 3818 3455.

E-mail address: hisashi@flanker.q.t.u-tokyo.ac.jp (H. Tanigawa).

Fig. 1. Conventional cell of Li_2O.

Fig. 2. Electronic charge density map around the F^{2+} center.

Fig. 3. Electronic charge density map around the F^0 center.

sisted of 27 Li_2O for CRYSTAL and that of 16 Li_2O for CASTEP. In the calculation, a hydrogen ion was used, not deuterium or tritium ions. The results of the present calculation, for instance, the stable position of the proton and the electronic charge density map, correspond to those of deuterium or tritium ions.

3. Results and discussion

3.1. Electronic states of F-centers

In the first step of this study, the electronic states of F-centers were checked. In order to treat the defects that trap electrons in CRYSTAL, the proper basis sets should be considered. In the present study, the basis sets for oxygen ion in Li_2O was used for F-centers. It was reported that the formation energy of an oxygen vacancy in the MgO crystal was estimated accurately using the optimized basis sets for the oxygen ion in MgO [5]. In the case of CASTEP, it is not necessary to input the basis sets for the vacancy. The electronic structure around the vacancy is built from the expanding wave functions of adjacent ions. In both the codes, the most stable electronic configuration is found for the inputted geometrical structure. The electronic charge density maps around the F^{2+} and F^0 centers calculated by CRYSTAL are shown in Figs. 2 and 3, respectively. The centers of the figures are the vacancy sites and charge density maps are plotted in the square area 2×2 $Å^2$. Note that corners of the figures are not lattice points. The nearest four oxygen ions are at points (± 2.31, ± 2.31). In the case of the F^0 center, it was confirmed that electrons were trapped by the defect. The results from CASTEP were almost the same. The more detailed

comparison of the results from the two codes will be made later emphasizing the relaxation of ions.

3.2. Relaxation of ions around F-centers

When an oxygen ion site becomes vacant in Li_2O, ions around the vacancy are displaced to the more stable configuration. This relaxation is important to estimate the interaction of a proton with F-centers. Each oxygen ion in Li_2O has eight lithium ions and twelve oxygen ions at the nearest position. The displacement of these twenty ions was calculated when the oxygen site became vacant. CASTEP enables us to obtain the optimized geometrical structure. In CRYSTAL, lithium and oxygen ions were put on various positions in the input data and the most stable configuration was searched. Table 1 shows the calculated relaxation of ions. In the column, 'in' means the inward displacement to the defects and 'out' means the outward one.

Table 1
Displacement of ions around F-centers

		CRYSTAL95 (Å)	CASTEP (Å)
F^{2+} center	O	In : 0.06	In : 0.07
	Li	Out : 0.29	Out : 0.30
F^+ center	O	In : 0.01	In : 0.06
	Li	Out : 0.17	Out: 0.15
F^0 center	O	Out : 0.01	In : 0.03
	Li	Out : 0.05	Out : 0.07

Both results from the two codes showed a good agreement. The largest difference between the results from the two codes was 0.05 Å. Only for the oxygen ions around the F^0 center, the directions of relaxation were opposite, however, it could be considered that these relaxations were too small to estimate the accuracy of the present calculation. In every case, lithium ions moved larger than oxygen ions. The fact that lithium ions exist more closely to F-centers than oxygen ions is given as the reason. The displacements were the largest in the F^{2+} center. The different displacements could be understood by considering the various charges of the F-centers. In the perfect crystal, lithium ions are attracted by Coulomb's force from adjacent oxygen ions. When an F^{2+} center is produced, lithium ions are considered to lose the attractive force and then move outward. In the case of F^0 center, this effect becomes small because of its neutral charge.

3.3. Interaction of –OH with F-centers

Based on these results, the interaction of –OH with F-centers was studied. As described above, there are twelve nearest oxygen sites for an oxygen ion. Putting a proton as forming O–H in the stable point of the perfect crystal which was determined in our previous study [1], we can categorize the twelve sites into three configurations: p1, p2 and p3. As shown in Fig. 4, angles for H_{ion}–O_{ion}–$O_{vacancy}$ are 45° (p1), 90° (p2) and 135° (p3), respectively, before relaxation. Suppose that oxygen in these sites becomes vacant, the interaction of –OH and F-centers should be different in each configuration. The stable position of the proton was calculated when an oxygen site in these three configurations became vacant.

In order to pay attention to the difference in the charge of defects, O–H distances, angles and total energies of the stable structure with F^{2+} and F^0 centers are summarized in Table 2. The results for the F^+ center stand almost middle of the two values for F^{2+} and F^0 centers. The total energies are displayed as the difference from that of p1 in each F-center. In the following parts, the presented results are all from CRYSTAL, because the optimized basis sets are able to be used and the results are considered to be more accurate. Every result
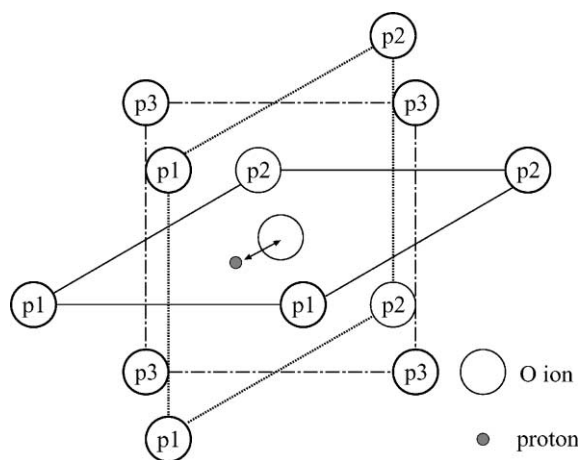

Fig. 4. –OH and the nearest O sites in Li_2O.

Table 2
Stable O–H length, angle, and difference of energy

		Difference of energy (eV)	O–H distance (Å)	Angle (°)
Perfect crystal		–	0.939	–
p1	F^{2+}	–	0.943	49
	F^0	–	0.956	37
p2	F^{2+}	−0.20	0.935	137
	F^0	+0.31	0.939	135
p3	F^{2+}	+0.22	0.930	103
	F^0	+0.31	0.936	89

was also confirmed by comparison with that from CASTEP.

It was shown that p1 was the most stable when the F^0 center was produced around –OH and p2 for F^{2+} center. Besides this result, it was found that the direction of angle relaxation differed between F^0 (45–37°) and F^{2+} (45–49°) centers in p1. It is considered that a proton in Li_2O is repulsively forced by adjacent lithium ions, and the stable position of the proton is also affected by lithium ions. For the results of the F^{2+} center, the motion of the proton was understood by taking into consideration the relaxation of the nearest lithium ions. When the F^{2+} center is produced, lithium ions move outward and then the proton moves also outward. However, the motion of the proton could not be explained by this effect for the F^0 center. The calculated electronic charge density maps are shown for F^{2+} and F^0 centers in Figs. 5 and 6, respectively. In Fig. 5, –OH is relaxed outward from the vacancy as described before. Fig. 6 shows that electrons trapped by the F^0 center interact with –OH. In the case of the F^0 center, the proton is considered to move inward because of the at-
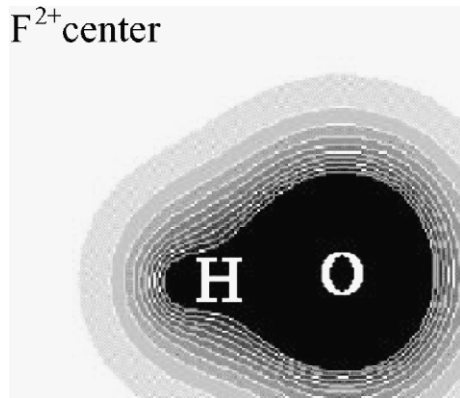
Fig. 5. Electronic charge density map of –OH and F^{2+} center on the Li_2O (1 0 0) plane.
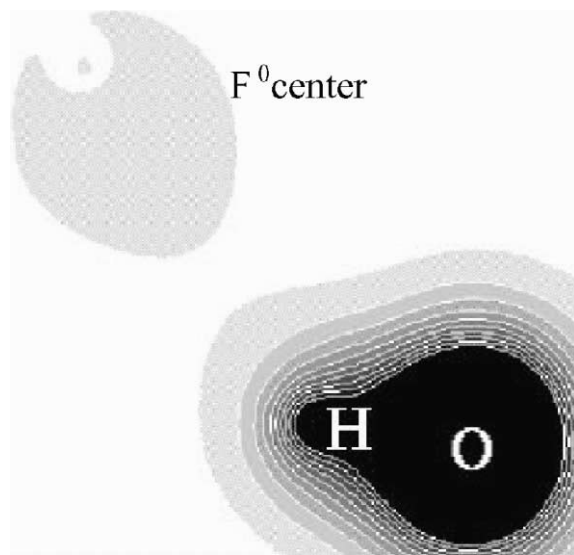

Fig. 6. Electronic charge density map of –OH and F^0 center on the Li_2O (1 0 0) plane.

tractive force from the F^0 center despite outward displacement of the nearest lithium ions.

3.4. Trapping of a proton by F^0 center

In Fig. 7, 'A' is the most stable position of –OH when the F^0 center exists and named as p1 in the last section. In the analysis discussed before, the O–H length was maintained about 1 Å, in order to keep O–H bonding. When this limitation was removed and all possible positions for the proton were searched, it was found that the proton could be trapped by the F^0 center. 'C' is the most stable position of the proton with the O–H distance of 2.75 Å, where O–H bonding is very week or almost broken. 'B' is the position on the straight line
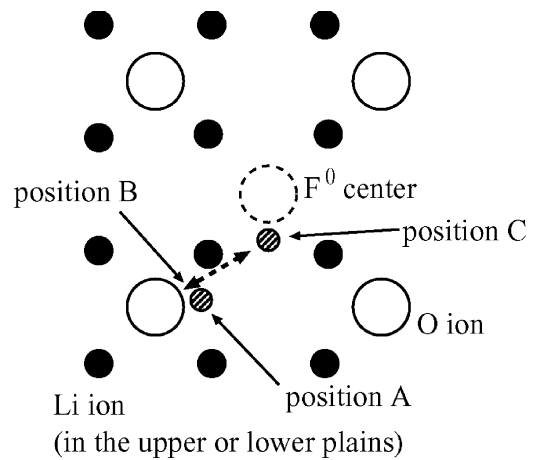

Fig. 7. –OH and F^0 center on the Li_2O (1 0 0) plane.

which connects the oxygen ion and 'C'. At 'B', the O–H distance is 0.956 Å, which is the same as the length from the oxygen ion to the proton at 'A'. Between 'B' and 'C', several points were calculated. The energy of the system is shown in Fig. 8.

Fig. 8 shows that the proton is strongly trapped by the F^0 center. The energy difference between 'A' and 'C' is larger than 5 eV. The potential barrier is about 1 eV higher than 'A'. At the transition state, the O–H distance is about 1.3 Å. This is caused by the repulsive force from lithium ions and the barrier probably becomes small when the relaxation of the lithium ions, which is neglected in the present calculation, is taken into account. In the model study of tritium diffusion in the neutron irradiated Li_2O, two reactions are proposed for diffusion in the grain [6].

$$LiOT + F^0 \rightarrow LiT, \quad LiT + 1/2\,O_2 \rightarrow LiOT.$$
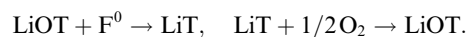
After a number of conversions between LiT and LiOT, tritium diffuses to the grain surface. In the scheme, the
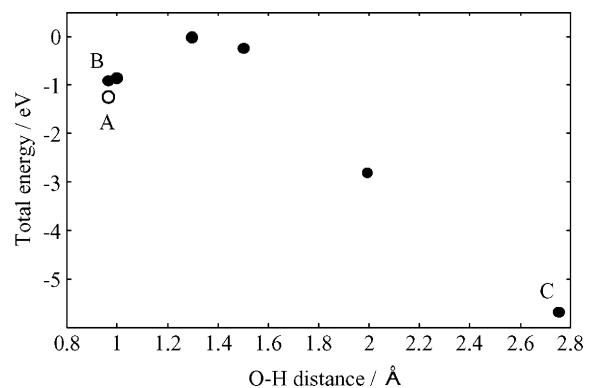

Fig. 8. Energy of the system with the F^0 center as a function of the O–H distance.

Table 3
Stability of a proton with defects

		E_{rem} (eV)	O–H distance (Å)
F^{2+} center, p2		–	0.935
F^{+} center, p1		0.00	0.950
F^{0} center	p1	+0.27	0.956
	C	+4.73	2.750
Perfect crystal		−0.01	0.939
Li vacancy		+3.65	0.971

reduction of the proton by the F^{0} center is considered to be necessary. The present result confirms the model of tritium diffusion from the quantum chemical view point.

3.5. Stability of a proton in Li_2O with defects

At the end of this work, the stability of the proton will be discussed. In the way described above, the stable position of the proton was calculated when the F^{2+}, F^{+} and F^{0} centers were produced around –OH. In addition to F-centers, the lithium vacancy was also considered. The stable position of the proton in Li_2O with the lithium vacancy was reported by Shah et al. [7]. As mentioned in their paper, the proton moves to the lithium vacancy site when the nearest lithium site becomes vacant because the relaxation to this direction decreases the repulsive force from the other lithium ions. In the present study, only the O–H distance was optimized in the case of a lithium vacancy. The effect of relaxation of adjoining ions to the lithium vacancy was considered to be very small, therefore, it was neglected. The energies which are needed to remove the proton from the system, E_{rem}, and the O–H distance are shown in Table 3. For F centers, the most stable configurations among p1, p2, and p3 are presented. The energy E_{rem} is displayed as the difference from that of p2 for F^{2+} center.

From the results, it was found that the proton was much more stable in the cases of the lithium vacancy and the F^{0} center than the other cases. In the former, the decrease of repulsive force considerably contributes to the increase of the stability and the interaction of the electrons trapped by the F^{0} center in the latter. Among the F centers, the order of the O–H length corresponds to the charge of the defects. This suggests that the interaction of the proton with the electrons becomes strong when the number of the trapped electrons increases.

4. Conclusions

The interaction of hydrogen isotopes with defects in Li_2O was studied by ab-initio quantum chemical calculations. The analysis of the stable position of the proton and the electronic charge density map showed that the relaxation of the proton was explained by taking into account two effects: the replacement of the lithium ion caused by production of the defects and the interaction with the electrons trapped by F centers. As regards the F^{0} center, it was shown that the proton could be trapped and reduced by the defect.

References

[1] H. Tanigawa, M. Taniguchi, S. Tanaka, Fus. Technol. 34 (1998) 872.
[2] H. Tanigawa, S. Tanaka, Fus. Eng. Des. 51&52 (2000) 193.
[3] R. Dovesi et al., CRYSTAL95 code, 1996.
[4] R. Dovesi, Solid State Commun. 54 (1985) 183.
[5] A. De Vita et al., Phys. Rev. B 46 (1992) 12964.
[6] H. Moriyama, T. Kurasawa, J. Nucl. Mater. 212&215 (1994) 932.
[7] R. Shah et al., Phys. Rev. B 53 (1996) 8257.