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Low-Temperature Volume Expansion of LiH:LiT†

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Crystals of LiH:LiT undergo self-damage due to the β-decay of tritium. The low-temperature volume expansion associated with this damage has been investigated theoretically. Twenty-four defects relevant to the damage process have been studied. The results indicate that one of the various species of interstitial lithium is most likely responsible for the expansion, since these defects cause sufficiently large volume expansion to explain the experimental data. The calculations indicate that the Li_2^+ molecular ion is the favored interstitial species. In addition to the volume expansion, Li_2^+ can account for the observed NMR and ESR signals and it may well be the nucleus for subsequent lithium precipitation.

I. INTRODUCTION

THE production of defects in crystals exposed to external radiation has been studied for many substances.[1,2] Crystals of LiH experience self-damage when some of the H^- ions are replaced by tritium T^-. If the electrons remain on the nucleus during β^- decay, the T^- ions decay into He^0 atoms in accordance with

$$T^- \rightarrow He^0 + e^- . \qquad (1)$$

Tritium has a half-life of 12.4 yr and the β^- particles have a maximum energy of 18 keV and an average energy of 5.6 keV. The average recoil energy of the helium is 1 eV with a maximum of 3.3 eV.

Pretzel, Vier, Szklarz, and Lewis[3] found that at temperatures below 0°C (the low-temperature region), LiH crystals containing 40 mole % LiT expand by about 5% in 1000 days. The expansion is proportional to the number of T^- nuclei that decay. In heavily damaged samples, they found NMR signals that indicated the presence of metallic lithium (Knight shift), but not of hydrogen gas. The ESR signals of the body-centered-cubic form of metallic lithium were observed when the damaged samples were heated to room temperature. The volume expansion was found to be proportional to the growth of an optical absorption band at 5400 Å and a paramagnetic center. Pretzel *et al.* have attributed these to the *F* center, but Dvinyaninov and Gavrilov[4] have questioned this assignment. Pretzel interpreted the volume expansion by assuming that when the T^- decays, the resulting He^0 moves into an interstitial position. Pretzel's results for the high-temperature region (from 23 to 400°C) are more complicated. The volume expansion undergoes a rapid first stage followed by a lesser second growth stage. As the temperature increases, the volume expansion increases and at 400°C amounts to over 80% growth in 200 days. In this high-temperature region, several types of aggregations have been observed: (1) small precipitate particles of metallic lithium[3,5]; (2) bubbles of He and H_2 (hydrogen gas and its isotopes)[3,5]; and (3) cavities.[3,6] The crystals often fracture at high expansion. The types of defects found in neutron-irradiated LiF[7] are similar to those found in LiH:LiT.

Pretzel and Petty[8] exposed LiH crystals to *external* tritium β^- particles at −196°C. Using x-ray–diffraction techniques, they found no change in the lattice parameter of LiH, while alkali halides exposed under the same conditions showed a considerable increase in lattice parameter. They attribute the growth in the alkali halides to the formation of Frenkel pairs in the negative-ion sublattice.

Jones *et al.*[9] studied the high-temperature volume

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expansion of LiT, Li_2TD, and Li_3TD_2. The expansion of LiH with 40 mole % LiT observed by Pretzel *et al.* falls between the expansion of Li_2TD and Li_3TD_2 observed by Jones *et al.* at the same temperature. They fitted their high-temperature volume expansion to the form

$$V(t)=V(\infty)(1-e^{-dt}), \qquad (2)$$

where $V(t)$ is the percent volume increase at a time t, $V(\infty)$ is the final percent volume increase, and d is a constant. Pretzel's more comprehensive volume expansion data do not fit this form.

Souers, Jolly, and Cline[5] found that the volume growth of LiH containing 40 mole % LiT was proportional to the amount of H_2 gas and metallic lithium produced in the rapid first-stage growth for temperatures from 23 to 250°C. They propose that the less rapid second-stage growth is due to the He^0.

The main intent of this study is to investigate the role of a variety of defects which may be formed during the low-temperature irradiation of LiH:LiT crystals. In Sec. II, interactions between constituent ions and atoms used in the calculations are presented; in Sec. III, the method of defect calculations is described; in Sec. IV, the results of 24 defect calculations are presented; in Sec. V, the mechanism for radiation damage and subsequent low-temperature volume expansion is proposed; and in Sec. VI, a summary of the results is given.

II. QUANTUM-MECHANICAL INTERACTIONS

For the calculations of defect properties (discussed in IV), two-body repulsive interactions between the host ions, i.e., Li^+-H^-, H^--H^-, and Li^+-Li^+, as well as interactions with foreign atoms, i.e., He^0-H^- and He^0-Li^+, are required.

Empirical functions for the repulsive interactions in LiH have been investigated by Varshni and Shukla,[10] but their use in defect calculations has several drawbacks. The experimental evidence commonly employed in determining such interactions (cohesive energy, lattice parameter, compressibility, etc.) provides information in only a small region about the equilibrium internuclear separation. Thus, there is an uncertainty about the functional form of the repulsion, since several forms can fit the data reasonably well. Indeed, Dass and Saxena[11] found that they could fit the binding energy and interionic distance equally well with Born-Mayer or Hellman forms of the potential. In addition, in calculations of the relaxations of ions surrounding the defects, one needs to know the potential at positions considerably off the lattice sites and the interactions have to be extrapolated beyond the range of the data. Finally, to study the radiation damage of LiH:LiT, repulsive interactions involving foreign atoms must be considered. With only an empirical knowledge of the interactions between the host ions, a separate method would have to be developed to obtain the interactions with the foreign atoms.

Fischer *et al.*[12] have determined quantum-mechanical two-body interactions for LiH suitable for defect calculations. They used determinantal wave functions made up of various one-electron functions. With the use of determinants made up of screened hydrogenic wave functions, they calculated the cohesive energy, lattice parameter, and compressibility for various values of the screening parameter δ of the negative hydrogen ion.

The interactions corresponding to a hydrogen screening parameter of 0.90 (in a.u.) gave the best simultaneous fit to cohesive energy, lattice parameter, and compressibility and were used in the present study. This is a considerably more contracted hydrogen ion than the free ion which has a screening parameter of 0.6875. The value of the cohesive energy predicted by this model is -9.69 eV per ion pair, which is within 2.5% of Gunn and Green's[13] experimental value of -9.44 eV per ion pair. The lattice constant is 2.216 Å compared with the experimental value of 2.0415 Å.[14] The theoretical compressibility is 2.22×10^{-12} cm^2/dyn compared with experimental values which range from 2.5×10^{-12} to 4.38×10^{-12} cm^2/dyn.[15-18] These results are summarized in Table I. It should be noted that Subhadra and Sirdeshmuka,[19] in a recent paper, carried out an analysis of the compressibility data. They concluded that the experimental values are in doubt and suggested an upper limit of 2.15×10^{-12} cm^2/dyn for the compressibility.

The repulsive interactions calculated above were fitted very closely (within 1.5%) by the exponential Born-Mayer form, $A\exp(-Br)$. The values of A and B are listed in Table II. The exponential form for the repulsive interactions was used in the present study.

Fischer *et al.*[12] generalized the semiclassical interaction method developed by Wedepohl[20] and this method was employed to obtain the interactions between the host ions and He^0 and Li^0. These repulsive interactions were also found to be of the Born-Mayer form and the corresponding A and B values are also listed in Table II. The interaction between the con-

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TABLE I. Properties of LiH.

	Theoretical	Experimental	Reference
Cohesive Energy (eV/ion pair)	−9.69	−9.44	13
Lattice Constant (Å)	2.216	2.0415	14
Compressibility (10^{-12} cm^2/dyn)	2.22	2.5	15
		2.88	16
		3.7	17
		4.38	18

stituents of the Li_2^+ molecule was taken from the work of Fischer and Kemmey.[21]

Despite the simplicity of the model, the interactions developed give a reasonable simulation of the LiH crystal. Because these interactions were obtained from quantum-mechanical results, it is felt that they give the interactions over a wide range of internuclear distances and give a reasonably accurate description of the forces between the defects and the host ions.

III. METHOD OF DEFECT CALCULATIONS

The energy of a defect crystal relative to the energy of the perfect crystal and the displacements of the ions surrounding the defect were calculated using an extension of the method of Hatcher and Dienes.[22] In the model employed, the crystal is made up of polarizable point ions. For purposes of calculation, the crystal is divided into two regions. Region I contains the defect and a number of surrounding ions that are allowed to displace and polarize. Region II begins at the boundary of Region I and contains additional ions that are allowed to polarize, but not to relax. The energy of formation of a defect is written as the sum of the electrostatic, repulsive, and polarization contributions

$$E_{\text{def}}=E_{\text{stat}}+E_{\text{rep}}+E_{\text{pol}}\,, \tag{3}$$

each relative to the perfect crystal. The energy is minimized with respect to the displacements of the ions in Region I.

The electrostatic energy is given by

$$E_{\text{stat}}=\sum_{ij}{}'\left(\frac{e_ie_j}{r_{ij}'}-\frac{e_ie_j}{r_{ij}}\right), \tag{4}$$

TABLE II. Repulsive interactions in LiH.

Interaction[a]	A (in eV)	B (in Å^{-1})
Li^+-H^-	257	3.24
H^--H^-	29.3	1.88
Li^+-Li^+	1610	7.29
He^0-H^-	151	2.94
He^0-Li^+	616	5.07
Li^0-H^-	11.2	1.52
Li^0-Li^+	63.4	1.94

[a] Interactions are of the Born-Mayer form $A\exp(-Br)$.

where the sum is over all ions in the crystal, e_i and e_j are the charges on ions i and j, r_{ij}' is the distance between ions i and j in the defect crystal, and r_{ij} is that in the perfect crystal. The prime on the summation indicates that the sum is not to be taken for $i=j$.

The repulsive interactions are made up of two-body central forces of the Born-Mayer form $A_{ij}\exp(-B_{ij}r_{ij})$, with the parameters listed in Table II. The repulsive energy is given by

$$E_{\text{rep}}=\sum_{ij}{}'\left[A_{ij}\exp(-B_{ij}r_{ij}')-A_{ij}\exp(-B_{ij}r_{ij})\right], \tag{5}$$

where the sum is over all ions in the crystal excluding $i=j$.

The polarization energy is given by

$$E_{\text{pol}}=-\tfrac{1}{2}\sum_i \mathbf{p}_i\cdot\mathbf{E}_i^{\text{chg}}\,, \tag{6}$$

where the sum is over all the polarizable ions, $\mathbf{p}_i$ is the induced electronic dipole ion i due to the field of the charges and dipoles external to it, and $\mathbf{E}_i^{\text{chg}}$ is the monopole electric field at ion i due to the asymmetrical distribution of point charges around it. The total field at ion i is the field due to monopoles and dipoles external to ion i:

$$\mathbf{E}_i^{\text{tot}}=\mathbf{E}_i^{\text{chg}}+\mathbf{E}_i^{\text{dip}}\,. \tag{7}$$

The induced electronic dipole on ion i is given by

$$\begin{aligned}\mathbf{p}_i&=\alpha_i\mathbf{E}_i^{\text{tot}}\\ &=\alpha_i\mathbf{E}_i^{\text{chg}}+\alpha_i\mathbf{E}_i^{\text{dip}}\\ &=\alpha_i\mathbf{E}_i^{\text{chg}}+\alpha_i\sum_j\left\{\left[3\mathbf{r}_{ij}(\mathbf{p}_j\cdot\mathbf{r}_{ij}')/r_{ij}'^5\right]-(\mathbf{p}_j/r_{ij}'^3)\right\},\end{aligned} \tag{8}$$

where α_i is the polarizability of ion i and the sum over j is over all dipoles but i. Equation (8) holds for all dipoles and this set of simultaneous equations may be solved for the individual dipoles which can then be used in Eq. (6) to obtain the polarization energy.

Pauling[23] has shown that the polarizability of two-electron screened hydrogenic wave functions is proportional to the inverse fourth power of the screening parameter. The polarizability of the Li^+, α_{Li^+}, is 0.029 Å^3. There is a large uncertainty in the value of the free H^- polarizability—many widely varying (7–20 Å^3) values are reported in the literature.[10] The crystalline polarizability of the H^-, α_{H^-}, applicable to LiH was determined from the Lorentz-Lorenz relation

$$(n^2-1)/(n^2+2)=(2\pi/3r_0^3)(\alpha_{Li^+}+\alpha_{H^-})\,, \tag{9}$$

where r_0 is the interionic distance and n is the refractive index (=1.984) taken from Pretzel *et al.*[3] The resulting value of α_{H^-} is 1.90 Å^3. Using Pauling's formula for the hydrogen ion with the screening parameter employed

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in determining the interactions ($\delta = 0.90$), the polarizability obtained is 2.03 Å^3, in excellent agreement with the experimental value deduced via the Lorentz-Lorenz relation. The free H$^-$ ($\delta = 0.6875$), using Pauling's formula, has a polarizability of 6 Å^3.

It is found in certain cases that, if the polarizability is held constant, the defect calculations can yield unphysical results as the ions come very close together. This "polarization catastrophe" is a result of the polarization energy overcoming the Born-Mayer repulsion between the ions at small separations. This type of difficulty has been observed for other ionic crystals. Scholz[24] has found this type of instability for defects in lithium halides, and Quigley and Das[25] have encountered this problem with off-center Li$^+$ in KCl. Yamashita and Kurosowa[26] had to reduce arbitrarily the value of the anion polarizability in the alkaline earth oxides in order to obtain agreement with experimental values of the Schottky-pair energy. In a recent review article, Barr and Lidiard[27] have noted that in defect calculations with constant polarizabilities, the results are usually below the experimental values indicating that the polarization is too great. They point out that it is reasonable for the polarizability to decrease as the ions overlap and, indeed, this is what Quigley and Das did to correct the polarization energy.

The variation of the polarizability as a function of the separation between the ions is a complicated problem. Some simplified systems can be investigated. Consider a model of an ion in which a nuclear charge $+Ze$ is surrounded by a spherical charge distribution of radius a_0 and total negative change $-Qe$. Classically the polarization of such an ion is given by[28]

$$\alpha = a_0^3 Q/Z\,. \tag{10}$$

The polarizabilities of two such ions, A and B, with radii a_0 and b_0 are given by Eq. (10) when their internuclear separation r is such that $r > (a_0 + b_0)$. The point-dipole model implies, as far as calculating the polarization is concerned, that the electron distributions do not overlap. Therefore, when $r < (a_0 + b_0)$, it may be assumed that the ions still contain uniform spherical charge distributions of total charge Q but that the radii contract to a and b, respectively, such that $a + b = r$ and that a and b are in the same ratio as a_0 and b_0. This means

$$a = [a_0/(a_0 + b_0)]r\,. \tag{11}$$

When this radius is used in (10), the polarizability decreases as r^3 when $r < (a_0 + b_0)$. A similar calculation was carried out with exponentially decreasing charge densities instead of constant charge densities. This is the functional form of the charge distributions for the screened hydrogenic wave functions used in the model of repulsive interactions. The polarizabilities are still constant when $r > (a_0 + b_0)$. For $0 < r < (a_0 + b_0)$, polarizability depends on a convergent power series starting with terms in r^3, r^4, and r^5.

Accordingly, in the present investigation, the polarizability of an H$^-$ ion was treated as a function of the positions of the ions surrounding it. When the nearest ion to an H$^-$ is at the equilibrium separation r_0 or greater, the polarizability has the constant value given by the Lorentz-Lorenz relation, Eq. (9). When an ion comes closer to the H$^-$ than r_0, it is assumed that the polarizability decreases as r^4, such that at $r = 0$, $\alpha = 0$, and at $r = r_0$, $\alpha = 1.90$ Å^3. The results are not sensitive to the particular choice of the functional dependence (see Sec. IV).

Depending on the symmetry of the defect, the ions may be grouped into shells in which the ions have similar displacements and dipoles. This greatly simplifies finding the minimum energy configuration and reduces the computer time needed to solve the set of linear equations in (8). The general method discussed here enables large regions of the crystal to be treated atomistically. The dipoles are solved for exactly in the region allowed to polarize, and there is no need to use a polarizable continuum, if relative energies alone are needed. The relaxations are not constrained to be radial but have the symmetry of the LiH crystal.

In practice, 50–60 ions were allowed to relax and polarize (Region I). For charged defects, an additional 50–60 ions were allowed to polarize to better account for long-range polarization effects (Region II). Defects of eight symmetry types were investigated: vacancy, divacancy, dinegative-vacancy, quadrivacancy, body-center–interstitial, face-center–interstitial, [111] saddle-point for interstitialcy migration, and [110] saddle-point for interstitialcy migration.

IV. DEFECTS IN LiH:LiT

In order to investigate atomistic mechanisms of low-temperature volume expansion of LiH:LiT crystals, 24 defect calculations were carried out. A compilation of the cases studied and their energies relative to the perfect crystal is contained in Table III. Table IV gives the activation energies for diffusion of several atoms and ions using the results in Table III. [100] migration is from the center of a cube through a face to the center of an adjacent cube. Interstitialcy migration along [111] ([110]) involves the interstitial moving from the body (face) of the cube along [111] ([110]) towards an on-site ion of the same species which is pushed into the body (face) of a diagonally adjacent cube while the original interstitial occupies the vacated lattice site. Table IV also contains an estimate of the temperature at which the species is mobile using the

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TABLE III. Energy of defects relative to the perfect crystals.

	eV
1. Li^+ Body-Center Interstitial	−3.8
2. Li^+ Face-Center Interstitial	−3.3
3. Li^+ (111) Split Configuration	−3.5
4. Li^+ (110) Split Configuration	−3.2
5. H^- Body-Center Interstitial	−2.4
6. H^- Face-Center Interstitial	−1.2
7. H^- (111) Split Configuration	−2.9
8. H^- (110) Split Configuration	−2.2
9. Positive Vacancy	6.3
10. Negative Vacancy	5.3
11. Divacancy	9.0
12. Dinegative Vacancy	13.2
13. Quadrivacancy	16.6
14. Saddle Point for Li^+ Vacancy Migration	6.2
15. Saddle Point for H^- Vacancy Migration	5.4
16. He^0 Body-Center Interstitial	0.2
17. He^0 Face-Center Interstitial	0.8
18. He^0 on a Negative Vacancy	5.6
19. He^0 on a Dinegative Vacancy	13.5
20. He^0 on a Divancy	6.3
21. He^0 on a Quadrivacancy	16.7
22. Li^0 Body-Center Interstitial	3.7
23. Li^0 Face-Center Interstitial	4.9
24. $Li_2{}^+$ on a Cation Site Oriented Along [111]	1.4

simple relation

$$p=\nu e^{-Q/kT}, \qquad (12)$$

with p (=1) the probability of a jump, ν the reststrahlen frequency[29] ($=8.39/2\pi\times10^{13}$ sec^{-1}), Q the activation energy determined in this work, and kT has its usual meaning.

It is to be noted from Table IV that Li^+ interstitials have the lowest activation energy of all the interstitial species studied, regardless of the mechanism of migration. This is not surprising as the Li^+ ion has a very tightly bound charge distribution, that is, it is a small ion, and, hence, is more free to move about. Similar results for cation diffusion in the alkali halides were found by Tharmalingam.[30] Although the migration along [110] gives the lowest activation energy, 0.5 eV is required to bring the Li^+ initially into a face-center position (from its minimum energy configuration in the center of a cube) and, hence, this process is unlikely to occur in diffusion. The Li^+ ions are quite free to move about by many modes of migration at temperatures well below 0°C.

TABLE IV. Activation energy for migration in LiH.

Species	Direction	Activation energy (eV)	T (°K)
Li^+ Interstitial	[100]	0.5	191
	[111]	0.3	115
	[110]	0.1	38
H^- Interstitial	[100]	0.7	269
	[111]	0.5	191
	[110]	1.0	383
He^0 Interstitial	[100]	0.6	230
Li^0 Interstitial	[100]	1.2	460
Li^+ Vacancy	[110]	0.1	38
H^- Vacancy	[110]	0.1	38

The energy of a crystal with a Li^+ interstitial is less than the energy of a perfect crystal and a free Li^+ at infinite separation. The increased electrostatic attraction and polarization due to the charged interstitial is greater than the additional repulsive interaction. To form an interstitial Li^+ in a perfect crystal, a positive vacancy must also be formed. The formation energy of the Frenkel pair is 2.5 eV (sum of the energy of a positive vacancy, +6.3 eV, and the energy of the Li^+ body-center interstitial, −3.8 eV). Therefore, LiH will not spontaneously form Li^+ interstitials.

From Table III, it is seen that the H^- ion has a lower energy in the split interstitial [111] configuration than in the cube-center configuration. Tharmalingam[30] found similar results for Cl^- in NaCl using Born-Mayer interactions. The H^- ion has a relatively more diffuse charge distribution and has more "room" in the split configuration. The split interstitial has four equivalent orientations about a given lattice site and the activation energy for reorientation ([111]−[110] saddle-point energies) is 0.7 eV. Since the activation energy for diffusion via the body centered configuration is 0.5 eV, the H^- will migrate away before it reorients itself. Below room temperature, diffusion is only possible along a ⟨111⟩ direction.

The Schottky-pair energy (sum of the formation energy of a positive vacancy, 6.3 eV, and a negative vacancy, +5.3 eV, minus the binding energy per ion pair, −9.69 eV) is 1.9 eV. The migration of either vacancy along a [110] has an activation energy of 0.1 eV. From conductivity data, Pretzel *et al.*[3] determined the experimental values of 2.4±0.2 eV for the Schottky-pair energy and 0.53±0.5 eV for the activation energy of the cation vacancy. The formation energy of a Schottky pair in LiH is less than the formation energy of either Frenkel pair indicating that the conductivity will be due primarily to vacancy migration in agreement with Pretzel's experimental results. The Li^+ vacancy has a lower energy in the configuration that would normally be the saddle point for vacancy migration. The increased repulsion of placing an Li^+ ion in the center of the face is offset by decrease in the electrostatic and polarization energies.

The clustering of vacancies into neutral pairs tends to reduce the electrical singularity of the isolated vacancies and is energetically favorable. The binding energy of a divacancy is 2.6 eV (the energy of the divacancy compared to the energy of separated positive and negative vacancies). The binding energy of the quadrivacancy is 1.4 eV (compared to two isolated

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divacancies). However, the dinegative vacancy, a charged configuration, is not bound and it is energetically favorable for it to dissociate into two isolated negative vacancies.

As far as distortions in the neighborhood of a vacancy are concerned, ions of the same sign as the missing ion move away from the defect, while ions of opposite sign move toward the defect.

He^0 interstitials have a lower energy in the body center than in the face-center configuration. The theoretical activation energy for migration of He^0 along a $\langle 100 \rangle$ is 0.6 eV. Based on the size and separation of He bubbles formed in damaged LiT crystals, Jones[9] estimated the activation energy is of the order of 0.4 eV. The addition of a He^0 to a negative vacancy, a dinegative vacancy, and a quadrivacancy raises the energy of these defects because of the increase repulsion between the host ions and the He^0. However, He^0 is bound to a divacancy.

Li^0 atoms migrate with an activation energy of 1.2 eV. From Table III, it is seen that the interstitial Li^0 is at a lower energy when it joins with an onsite Li^+ ion to form an Li_2^+ molecule ion oriented along a $\langle 111 \rangle$.

The sensitivity of the results to a change in the model of LiH used was investigated and the results are summarized in Table V. Case A is the model used in the present study. In cases B and C, the anion polarizability varied as R^3 and R^5 instead of R^4. In cases D and E, the repulsive interactions, determined by Fischer *et al.*[12] for H^- screening parameters of 0.95 and 0.82, were used. Data are given in Table V for the formation energy relative to the perfect crystal of Li^+ body- and face-center interstitials and the activation energy for migration along a $\langle 100 \rangle$. The formation energies of the Li^+ interstitials shift up and down in each case, but the activation energy for migration is not very sensitive to a change in the variation of the polarizability or to the use of quantum-mechanical interactions for different screening parameters of the H^- ions. Similarly, the distortions were found to be rather insensitive to these changes in the parameters. Cases A, D, and E predict binding energies of −9.69, −9.99, and −9.22 eV/ion pair and lattice parameters of 2.216, 2.160, and 2.303 Å, respectively. It is noted from Table V that the lower the binding energy of the crystal, the lower the formation energy of the defect. Furthermore, since the activation energy and the distortions are not very sensitive to the lattice parameter, the 9% error in the theoretical r_0 does not affect the validity of the results.

The activation energies given in Table III assume that the crystal is in equilibrium at all times during the diffusion. When the ion or atom is diffusing rapidly, i.e., under any kind of impact condition, the crystal will not be in equilibrium and calculating the activation energy is very complicated. Consider the case of the motion of an Li^+ ion along [110] with no ions relaxing except those directly involved in the diffusion. The activation energy is 0.5 eV compared to 0.1 eV in the equilibrium case.

V. RADIATION DAMAGE IN LiH:LiT

The experimental work of Pretzel and Petty[8] demonstrated that the β particles alone were not responsible for the low-temperature expansion. Pretzel[8] interpreted the low-temperature expansion by assuming that the He^0 formed in the β decay of the T^- goes into the body-center interstitial position. An approximate calculation (a more detailed one is given below) of the volume expansion, based on the outward displacements for the interstitial's first nearest neighbors, gave a value of 7 Å^3. From the experimental volume expansion data and the half-life of the T^-, Pretzel and Petty determined that an expansion of 12.4 Å^3 per β decay was needed to agree with experiment. Therefore, interstitial helium is probably not the defect responsible for the volume expansion.

Following Eshelby,[31] the volume expansion may be calculated from continuum-elastic theory. In a continuous isotropic medium, the relaxations around a spherically symmetric defect are given by

$$\mathbf{d} = C\mathbf{r}/r^3, \tag{13}$$

where $\mathbf{d}$ is the radial displacement at a point a distance $\mathbf{r}$ from the defect and C is a constant measuring the "elastic strength" of the defect. The volume expansion in an infinite medium caused by this displacement field is

$$V = 4\pi C. \tag{14}$$

For a finite medium, surface effects must be taken into

TABLE V. Different models of LiH.

Case	H^- screening parameter (a_0^{-1})	Polarizability varies as	Formation energy Li^+ Body center (eV)	 Li^+ Face center (eV)	[100] Activation energy (eV)
A	0.9	R^4	−3.8	−3.3	0.5
B	0.9	R^3	−4.1	−3.7	0.4
C	0.9	R^5	−3.7	−3.2	0.5
D	0.95	R^4	−4.2	−3.7	0.5
E	0.82	R^4	−3.2	−2.8	0.4

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[31] J. D. Eshelby, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 3.

account and the volume expansion for a finite spherical medium containing the defect is

$$V=4\pi C[3(1-\sigma)/(1+\sigma)], \qquad (15)$$

where σ is Poisson's ratio ($=0.4$ using the elastic constants[32] $C_{11}=0.626\times10^{12}$ and $C_{12}=C_{44}=0.419\times10^{12}$ dyn/cm^2).

The relaxations for 136 ions around a body center interstitial He^0 are listed in Table VI. For each shell, the radial displacement was calculated and a value of C was determined using Eq. (13). The C's for all the shells were averaged taking the multiplicity of the shells into account and the value $C=0.047$ in units of r_0^3 obtained. The resulting volume expansion using Eq. (15) is 8 Å^3, which is not sufficient to explain the observed volume expansion.

When the T$^-$ decays and emits the β particle, the He^0 recoils. The average recoil energy is 1.04 eV and the maximum recoil energy is 3.25 eV. It is possible that in recoiling the He^0 might collide with one of the surrounding Li$^+$ of H$^-$ ions and transfer some of its energy. In Table VII, the maximum energy transferable in an elastic collision between the recoiling He^0 atom and the hot ions is presented. The initial β particle can also transfer energies to the nearest-neighbor ions of the same order of magnitude as listed in Table VII.

A possible mechanism for the low-temperature volume expansion is suggested in Fig. 1. In (A), a T$^-$ ion is about to undergo β decay. In (B), the decay has just occurred and the recoiling He^0 atom collides with one of its 6 nearest-neighbor Li$^+$ ions transferring some of its energy. (Alternatively, the energy comes from the β particle). From Table VII, it is seen that for a He^0 atom with average recoil energy, the Li$^+$ could receive up to 0.85 eV of energy. Because of the low-activation energy for Li$^+$ migration (for example, 0.1 eV along the [110] with relaxations, 0.5 eV without) it is probable that in many of the collisions the Li$^+$ will be displaced away from its site and become a body-center interstitial as shown in (C). The immediate result of the β decay is to have an He^0 on a negative ion site with no relaxation of the surrounding ions which raises the energy of the crystal by 7.8 eV. After the production of an interstitial Li$^+$, the energy of the resultant He^0 in a divacancy (6.3 eV) and the body-center interstitial Li$^+$ (-3.8 eV) is 2.5 eV and, therefore, the reaction is energetically favorable. The relaxations of the ions surrounding a body-centered Li$^+$ interstitial are given in Table VIII. The volume expansion using Eq. (15) is 12 Å^3. The interstitial Li$^+$ comes close to explaining the observed volume expansion.

It was shown in Sec. IV that the Li$^+$ vacancies are very mobile. If free positive vacancies exist, they

TABLE VI. Displacements around a body-center interstitial He^0.[a]

		Typical ion					
		Position			Displacement		
Shell	Multiplicity	x	y	z	x	y	z
1	1	0	0	0	0	0	0
2	4	0.5	0.5	0.5	0.11	0.11	0.11
3	4	0.5	−0.5	0.5	0.08	−0.08	0.08
4	12	1.5	0.5	0.5	−0.01	0.03	0.03
5	12	1.5	0.5	−0.5	−0.04	0.10	−0.10
6	12	1.5	1.5	−0.5	0.01	0.01	−0.025
7	12	1.5	0.5	0.5	−0.06	−0.06	−0.06
8	4	1.5	1.5	1.5	−0.005	−0.005	−0.005
9	4	1.5	1.5	−1.5	−0.01	−0.01	0.01
10	12	2.5	0.5	−0.5	0.005	0.01	−0.01
11	12	2.5	0.5	−0.5	0.01	0.02	0.02
12	24	2.5	1.5	0.5	0.01	−0.01	0.005
13	24	2.5	1.5	−0.5	0.04	−0.02	0.015

[a] Shell 1 is the interstitial. The displacement gives the components of the displacement vector of the typical ion about its normal lattice site. The ion at (0.5,0.5,0.5) is a Li$^+$.

TABLE VII. Maximum energy transferable in an elastic collision with an He^0.[a]

		He^0 Energy	
Ion	Mass	1.04 eV	3.28 eV
H$^-$	1	0.78	2.46
T$^-$	3	1.04	3.28
Li$^+$	6	0.93	2.92
Li$^+$	7	0.85	2.76

[a] When a T$^-$ β decays into He^0, the He^0 acquires an average of 1.04 eV and a maximum of 3.28 eV of recoil energy. When the He^0 with mass m_{He} and energy E_{He} collides with an ion of mass m_i at rest, the maximum energy transferable to the ion E_i is given by $E_i=[4m_{\mathrm{He}}m_i/(m_{\mathrm{He}}+m_i)^2]E_{\mathrm{He}}$.

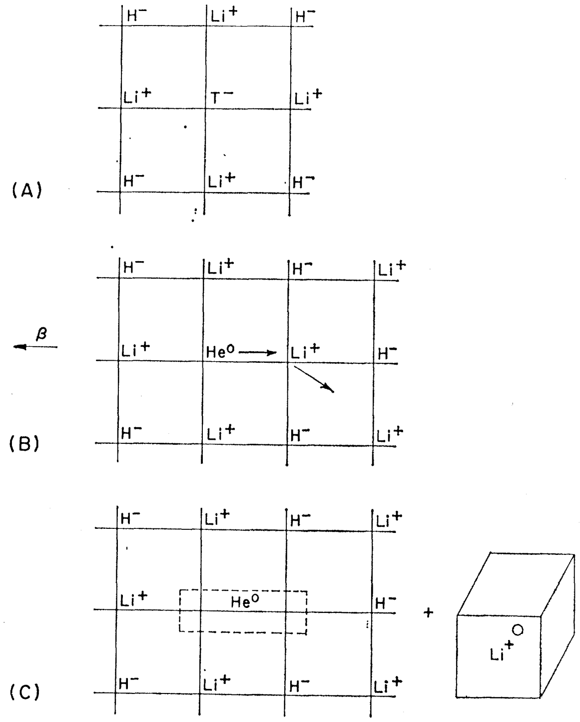

FIG. 1. The suggested steps for the formation of interstitial Li$^+$.

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[32] S. P. Marsh quoted by J. L. Verble, J. L. Warrn, and J. L. Yarnell, Phys. Rev. 168, 980 (1968).

TABLE VIII. Displacements around a body-center interstitial Li^+.

		Typical ion					
		Position			Displacement		
Shell	Multiplicity	x	y	z	x	y	z
1	1	0	0	0	0	0	0
2	4	0.5	0.5	0.5	0.15	0.15	0.15
3	4	0.5	−0.5	0.5	−0.01	−0.01	−0.01
4	12	1.5	0.5	0.5	0	0.03	0.03
5	12	1.5	0.5	−0.5	−0.01	0.05	−0.05
6	12	1.5	1.5	−0.5	−0.02	−0.02	−0.01
7	12	1.5	1.5	0.5	0.01	0.01	0.04
8	4	1.5	1.5	1.5	0.01	0.01	0.01
9	4	1.5	1.5	−1.5	0	0	0
10	12	2.5	0.5	−0.5	0	0.01	−0.01
11	12	2.5	0.5	0.5	0.03	0.055	0.055
12	24	2.5	1.5	0.5	0.005	−0.005	0.01
13	24	2.5	1.5	−0.5	0.035	−0.035	−0.035

could trap the Li^+ interstitials formed during the β decay. However, the positive vacancies formed in the proposed damage mechanism are bound in divacancies and will not dissociate below room temperature.

The possibility of the interstitial Li^+ capturing the electron from the β decay was investigated. The ionization energy of the Li^0 atom in the LiH crystal can be obtained by considering a cycle similar to the one used by Dienes and Smoluchowski[33] to estimate the electron affinity of Cl^0 in NaCl:

$$
\begin{array}{llll}
\text{(a)} & \mathrm{Li}^0\ \text{(crystal)} \to \mathrm{Li}^0\ \text{(free)} & & \Delta U = -3.7\ \text{eV} \\
\text{(b)} & \mathrm{Li}^0\ \text{(free)} \to \mathrm{Li}^+\ \text{(free)} & +e^-\ \text{(free)} & \Delta U = 5.36 \\
\text{(c)} & \mathrm{Li}^+\ \text{(free)} \to \mathrm{Li}^+\ \text{(crystal)} & & \Delta U = -3.8 \\
\text{(d)} & e^-\ \text{(free)} \to e^-\ \text{(crystal)} & & \Delta U = 0 \\
\text{(e)} & \mathrm{Li}^+\ \text{(crystal)} + e^-\ \text{(crystal)} \to & \mathrm{Li}^0\ \text{(crystal)} & \Delta U = X \\
 & & & \sum \Delta U = 0.
\end{array}
$$

In (a), a Li^0 body-center interstitial is removed from the crystal with an energy change of −3.7 eV. In (b), the free Li^0 is ionized and the change in energy is the normal ionization energy. In (c), the Li^+ is put back in the body-center interstitial position with a gain in energy of 3.8 eV. In (d), the electron is brought back from infinity to the bottom of the conduction band. This energy change will be small and is taken as zero. In (e), the Li^+ in the crystal and the electron in the conduction band join and the change in energy X is the negative of the ionization energy in the crystal. The cycle is now complete and the net energy change is zero. The ionization energy calculated from this cycle is −2.2 eV, indicating that the Li^0 is unstable against dissociation into an interstitial Li^+ ion and an e^- in the conduction band. The Li^0 may still be metastable, however. In Table IX are presented the relaxations for 136 ions surrounding a body-center Li^0. The expansion using Eq. (15) is 19 Å^3.

The interstitial Li^+, the e^- from the β decay, and an on-site Li^+ could form a Li_2^+ molecular ion on a cation site. From the data of Table III and from the electron affinity determined above, we can calculate the energy change for the reaction

$$\mathrm{Li}_2^+\ \text{(site)} \to \mathrm{Li}^+\ \text{(interstitial)} + e^- + \mathrm{Li}^+\ \text{(site)} \qquad \Delta U = 0.1\ \text{eV},$$

indicating that Li_2^+ is stable by 0.1 eV toward this decomposition.

The volume expansion of a sphere drawn through the first nearest neighbors of the Li_2^+ is 12 Å^3, using the relaxations given in Table X. The Li_2^+ is not a spherically symmetric defect and the calculation of the volume expansion by continuum elastic theory is more complicated. Townsend[34] has solved the problem of the relaxations around a linear defect in an isotropic medium. The displacement field is given by

$$\mathbf{d} = (C\mathbf{r}/3r^3) + (D\mathbf{r}/r^3)(3\cos^2\theta - 1) - (C/r^2)\mathbf{r}_\theta \sin\theta\cos\theta, \qquad (16)$$

where $\mathbf{d}$ is the displacement at a distance $\mathbf{r}$ from the center of the defect and making an angle θ with the axis of the defect, $\mathbf{r}_\theta$ is a unit vector in the θ direction, and $D = (C/2C_{44})[C_{44} + (1/K)]$, where K is the compressibility. Only the first term on the left-hand side of Eq. (16), the purely radial term, contributes to the volume expansion and the total expansion including surface effects is given by Eq. (15). The displacements around the Li_2^+ were resolved into radial and angular components and the value of C was determined for each shell. The average value of C is 0.084 in units of r_0^3. The expansion, as calculated from Eq. (15), is 14 Å^3, which is sufficient to explain the observed volume expansion.

The formation of the Li_2^+ would explain the paramagnetic resonance observed in expanded crystals.

TABLE IX. Displacements around a body-center interstitial Li^0.

		Typical ion					
		Position			Displacement		
Shell	Multiplicity	x	y	z	x	y	z
1	1	0	0	0	0	0	0
2	4	0.5	0.5	0.5	0.21	0.21	0.21
3	4	0.5	−0.5	0.5	0.10	−0.10	0.10
4	12	1.5	0.5	0.5	0.02	0.05	0.05
5	12	1.5	0.5	−0.5	−0.04	0.09	−0.09
6	12	1.5	1.5	−0.5	0.03	0.03	−0.02
7	12	1.5	1.5	0.5	0.02	0.02	0.04
8	4	1.5	1.5	1.5	0.02	0.02	0.02
9	4	1.5	1.5	−1.5	0.02	0.02	−0.02
10	12	2.5	0.5	−0.5	0.005	0	0
11	12	2.5	0.5	0.5	0.02	−0.005	−0.005
12	24	2.5	1.5	0.5	0.005	0.005	0
13	24	2.5	1.5	−0.5	0.015	0.005	−0.015

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[33] G. J. Dienes and R. Smoluchowski, J. Phys. Chem. Solids **27**, 611 (1966).

[34] J. R. Townsend, Acta Met. **13**, 325 (1965).

TABLE X. Displacements around a Li_2^+.

		Typical ion					
		Position			Displacement		
Shell	Multiplicity	x	y	z	x	y	z
1	2	0.2	0.2	0.2	0.06	0.06	0.06
2	6	1	0	0	0.08	0	0
3	6	1	1	0	0.14	0.14	−0.06
4	6	1	0	−1	−0.06	0	0.06
5	2	1	1	1	0	0	0
6	2	1	1	−1	0.04	0.04	0.03
7	6	2	0	0	−0.01	−0.011	−0.011
8	12	2	1	0	0	0.04	−0.005
9	12	2	0	−1	0.03	−0.035	−0.01
10	6	2	1	1	−0.035	0.045	0.045
11	12	2	1	−1	−0.02	0.06	0.005
12	6	2	−1	−1	0.07	−0.035	−0.035
13	6	2	2	0	−0.02	−0.02	−0.01
14	6	2	−2	0	0.025	−0.025	0
15	6	3	0	0	0	0.005	0.005
16	6	2	2	1	−0.005	−0.005	0.02
17	6	2	2	−1	0.01	0.01	−0.015

The Li_2^+ may also serve as the nucleus for precipitation of Li metal in heavily damaged samples that are raised to room temperature.

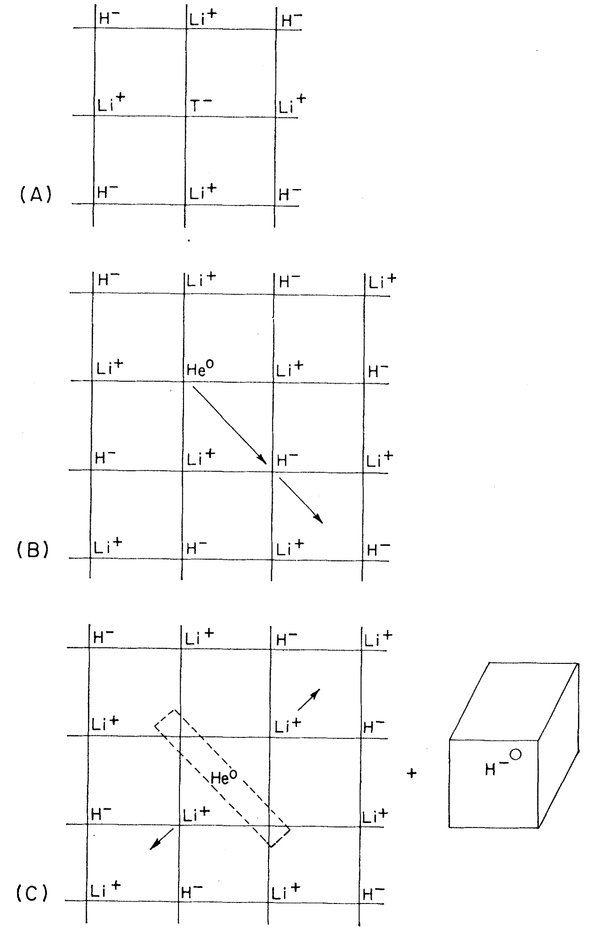

FIG. 2. The suggested steps for the formation of interstitial H^-.

It is difficult to estimate the fraction of disintegration that will result in interstitial lithium. The possibility of other mechanisms being present cannot be excluded. More than one Li^+ may be displaced by a recoiling He^0 atom; a Li^+ may be displaced even though the He^0 goes into an interstitial position; or the ions displaced by the He^0 may not be those adjacent to the site where it was created.

A similar low-temperature mechanism involving the H^- has been considered as illustrated in Fig. 2. The T^- in (A) undergoes β decay and in (B) it collides with one of its 12 next-nearest-neighbor H^- ions and transfers some of its energy. It is less probable for the H^- to be displaced in a collision with the He^0 than the Li^+ because of its higher activation energy for migration. In (C), the resulting He^0 located in a dinegative vacancy (13.5 eV) and the interstitial H^- (−2.9 eV) are shown. The final energy is 10.6 eV, which is considerably higher than the 7.8 eV of the He^0 on the negative ion site which started this mechanism. Pretzel and Petty[8] have presented arguments to show that if an interstitial H^- were formed it would join with an on-site anion to form H_2. Since no hydrogen gas is observed at low temperature, this adds support to the theoretical prediction that no interstitial H^- ions are formed, because the displacement sequence is energetically unfavorable at low temperatures.

VI. SUMMARY

The low-temperature volume expansion of LiH:LiT has been theoretically investigated within the framework of a polarizable point ion model of LiH. Twenty-four defect calculations on LiH were performed and the results interpreted. The theoretical model of the low-temperature volume expansion of Pretzel, involving an interstitial He^0 atom, was shown to be inadequate in expnaining the observed expansion. An alternative mechanism involving the formation of interstitial lithium is suggested since the various species of interstitial lithium cause a sufficiently large volume expansion to explain the experimental results. The calculations indicate that the Li_2^+ molecular ion is the favored interstitial species. Its presence can account for the observed NMR and ESR signals and it may well be the nucleus for subsequent lithium precipitation. A similar mechanism for the low-temperature formation of H_2 was investigated and found to be energetically unfavorable.

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