Effects of Self-Ionization of β-Active Elements in Nonmetals*

R. Smoluchowski
Princeton University, Princeton, New Jersey 08540
and
Sandia Laboratories, Livermore, California 94550
and
W. D. Wilson
Sandia Laboratories, Livermore, California 94550
(Received 4 May 1970)

A new mechanism is proposed for the formation of stable substitutional or interstitial diatomic molecules in nonmetallic crystals in which self-ionization of β-active ions occurs. In particular, the probability of self-ionization of tritium ions in LiT and LiH : LiT crystals due to "shake-off" following β decay is calculated. It is found that the probability of obtaining a He^{++} ion is 0.05, and for a He^{+} ion 0.32; and that the presence of these ions can lead directly to the formation of hydrogen molecules without diffusion. Using a model of LiH which includes noncentral forces, the energetics of this process, which is essentially temperature independent, and the rates of formation of hydrogen molecules are calculated. If, as experiments suggest, H^0 and H_2^- are indeed absent in irradiated LiH, then the formation of H_2 molecules (which accounts for the initial stage of swelling of LiH : LiT) is diffusion controlled above 200–300 °K but is due to the "shake-off" mode at lower temperatures.

I. INTRODUCTION

It is well known that a LiH crystal containing a large percentage of LiT shows a temperature-dependent volume increase as a result of the β decay of tritium into helium. Pretzel *et al.*[1,2] have attributed expansion of the lattice at liquid-nitrogen temperatures to the formation of interstitial helium and of F centers by primary and secondary ionization produced in the lattice by β radiation. Studies of irradiation of LiH crystals by Co^{60} γ rays[3] demonstrated that H_2 bubbles and Li metal colloids rather than helium are actually responsible for the initial stage of swelling.

In this paper it is shown that another cause of damage in any nonmetallic crystal containing a β^-- or β^+- active element can be the self-ionization of this element. The resulting excess positive charge, whether located on a cationic or anionic sublattice, may lead to the capture of electrons from neighboring ions and to the formation of stable substitutional or interstitial molecules. Since this process is temperature independent it is particularly important at low temperatures where other thermally activated processes are insignificant. The process, which should be observable in many crystals, is here analyzed in a quantitative manner for LiH:LiT. A recent comparison[4] of γ-irradiated and LiT-doped LiH crystals indicates that, for the same ionization dose, the volume increase at about 400 °K is essentially the same although in the early stages the self-irradiated crystals may swell a little more. Unfortunately, no experimental data taken at sufficiently low temperatures are available.

In the pioneering work of Feinberg and Migdal,[5] two primary mechanisms were proposed for the self-ionization of the K-shell electrons due to β^- decay. These are the "shake-off" mechanism – the ionization due to the sudden change in nuclear charge – and the direct-interaction mechanism (DIM) which is the direct collision process by which the β^- strips the orbital electrons from an inner shell of the atom. In the original work,[5] the DIM was regarded as negligible and the shake-off mechanism dominant. In the light of recent experimental results, however, Feinberg has reopened this question[6] and has shown that the probability of DIM in the K shell is of the order of the ratio of the K ionization potential to the energy of the β electron and could be significant. It turns out, however, that for T^- this ratio integrated over the β spectrum is so small that only the "shake-off" mechanism needs to be considered.

In Sec. II we calculate the probability of ionization due to the shake-off mechanism and in later sections discuss the ensuing damage events.

II. SHAKE-OFF PROBABILITY

The derivation of the probability of ionization due to shake-off given here follows closely that given by Levinger[7] except that the condition $Z \gg 1$, where Z is the nuclear charge, is eliminated. The probability of ionizing an electron in the $1s$ level

due to the rapid change of nuclear charge is

$$P(W)=\left|\langle\psi_W(Z+1,\ r)|\psi_0(Z,\ r)\rangle\right|^2, \tag{1}$$

where ψ_0 represents the bound-state wave function and ψ_W the continuum function for positive energy W. Since integration over angles gives the selection rule $\Delta l=0$, we consider only the $l=0$ radial functions. For convenience, we write a discrete state for $Z+1$, continuum for Z, and use screened hydrogenic wave functions. The radial function for the discrete state is thus

$$R_0(r)=2(Z+1)^{3/2}e^{-(Z+1)r}, \tag{2}$$

and that for the continuum, normalized per unit energy, is given by[7,8]

$$R_W(r)=(-2Z^{1/2}/2\pi)(2kr)^{-1}(1-e^{-2\pi n'})^{-1/2}$$
$$\times\oint e^{-2ikr\xi}(\xi+\tfrac{1}{2})^{-in'-1}(\xi-\tfrac{1}{2})^{in'-1}d\xi, \tag{3}$$

where $n'=Z/k$ and $W=\frac{1}{2}k^2$ in atomic units. Following Levinger let

$$\langle R_0|R_W\rangle=NJ \tag{4}$$

with

$$N=-Z^{1/2}(Z+1)^{3/2}(1-e^{-2\pi n'})^{-1/2} \tag{5}$$

and

$$J=\frac{2}{\pi}\int\oint e^{-(Z+1)r}e^{-2ikr\xi}(2kr)^{-1}(\xi+\tfrac{1}{2})^{-in'-1}$$
$$\times(\xi-\tfrac{1}{2})^{in'-1}d\xi\, r^2\,dr, \tag{6}$$

but without using his approximation $Z\gg1$. Evaluating J by first integrating over r and then calculating the residue at the resulting double pole gives

$$J=\frac{8}{k^4}\left(n'^2+\frac{1}{k^2}+\frac{2n'}{k}+1\right)^{-2}\exp[-2n'\cot^{-1}(n'+1/k)], \tag{7}$$

where the relation

$$\cot^{-1}X=\tfrac{1}{2}\ln\left(\frac{iX+1}{iX-1}\right)$$

was utilized. Note that Eq. (7) reduces to the expression for J given by Levinger in the $Z\gg1$ limit. Collecting terms and substituting into Eq. (1) gives, finally,

$$P(W)=\frac{4(Z+1)^3Z}{W^4}\left[1-\exp\left(\frac{-2\pi Z}{\sqrt{(2W)}}\right)\right]^{-1}\left(\frac{(Z+1)^2}{2W}+1\right)^{-4}$$
$$\times\exp\left[\frac{-4Z}{\sqrt{(2W)}}\cot^{-1}\left(\frac{Z+1}{\sqrt{(2W)}}\right)\right]. \tag{8}$$

Since $P(W)$ is the probability of ionizing each electron of the T^- independently of the other, the probability of ionizing only one of the two electrons is $2P(W)[1-P(W)]$ and the probability of double ionization is $[P(W)]^2$.

In Fig. 1 the probability $P(W)$ is plotted against W using Eq. (8) for various values of Z, where Z is now the "effective" or "screened" nuclear charge characteristic of the particular crystal. It is clear that the ionization probability appreciably increases with decreasing effective nuclear charge and that a significant probability still exists at continuum energies and above the LiH band-gap energy E_g = 6.5 eV. Using the relation $P=\int_{E_g}^{\infty}P(W)dW$, the total probabilityof independent ionization was determined numerically and is given in Table I. The first column gives the effective Z values, the second column gives the probability of independently ionizing a T^- electron to the continuum, the third column gives the independent ionization probability to the conduction band of LiH. The last columns give the single-ionization probability P_+ $=2P(1-P)$ and the double-ionization probability P_{++} $=P^2$. As shown in Sec. III, the best values for the screening parameters δ for the H^- ion in LiH for the first and second neighbors are 0.9500 and 0.6875, respectively, giving a weighted average of 0.77. The second-neighbor value compares favorably with Lundquist's[9] early values 0.6875 and 0.7208 for a free H^- ion. Assuming $Z=0.8$, the

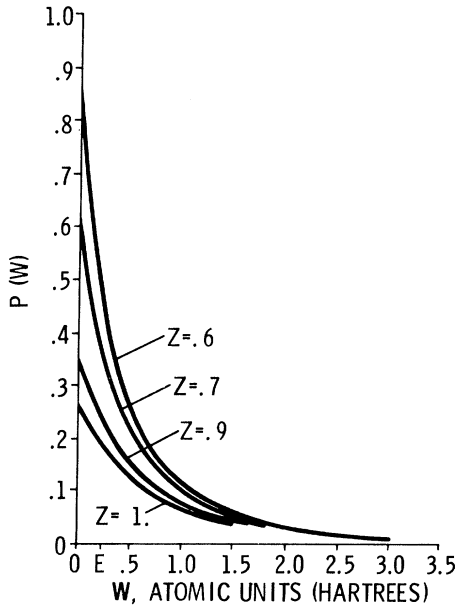

FIG. 1. Probability $P(W)$ of independent ionization of a T^- electron to continuum energy W for various effective charges Z.

probability of T^- decay leaving a He^{++} ion or a He^+ ion is 0.052 and 0.321, respectively. As shown below, the presence of these ions can lead to the formation of a large amount of hydrogen molecules without diffusion independently of any other defect-forming ionization processes.

III. IONIZATION OF HYDROGEN IONS AND LOCAL LATTICE CONFIGURATION

In order to analyze the situation in the lattice immediately after the β decay has taken place it is necessary to estimate first the lifetime τ of the positive helium ions. These ions can either (a) capture electrons from the neighboring negative hydrogen ions, or (b) recapture electrons which were ejected, or, finally, (c) capture electrons liberated in the lattice by the ejected electrons. The rate of the first process, case (a), can be estimated to an accuracy better than an order of magnitude by putting $\tau^{-1} \simeq \Delta E h^{-1} S$, where ΔE is the energy of the transition and S is the overlap integral between the He^+ and T^- electronic wave functions. Rosen[10] has calculated such overlap integrals for two screened hydrogenic wave functions with screening parameters α and β. After some manipulation his expression reduces to

$$S = \frac{\alpha^{3/2}\beta^{3/2}R^3 e^{-C}}{2CD} \sinh D \left(\frac{2}{C^2}(1 + C + \tfrac{1}{2}C^2) - 1 + \frac{2}{D^2}(D \coth D - 1) \right),$$

where R is the internuclear separation and

$$C = \tfrac{1}{2}R(\alpha + \beta), \quad D = \tfrac{1}{2}R(\alpha - \beta).$$

For $R = 5.46$ bohr (the second-nearest-neighbor distance in LiH), $\alpha = 2(He^+)$, and $\beta = 0.6875(T^-)$, one finds that $S = 0.042$, which with $\Delta E \sim 25$ eV (for He^+) gives τ about 6×10^{-16} sec.

Case (b) concerns the recapture of those ejected electrons which can be scattered by phonons but cannot ionize the lattice ($E < E_g = 6.5$ eV). While no pertinent experimental data on LiH exist, one can use recent measurements[11] of energy losses of electrons of $E \sim 1$ eV in LiI and CsI and extrapolate them to LiH at liquid-nitrogen temperature. The result is a loss of 2–5 eV per 100-Å path, which gives a range up to 10 000 Å for kinetic energy up to 20 eV. It turns out that only electrons with energy up to a few tenths of an electron volt can be recaptured in a time comparable to 6×10^{-16} sec. The calculation of the self-ionization process made in Sec. II indicates that only about 1% of all the ejected electrons fall in this range. Thus this mechanism is not significant.

Finally, in order to estimate the rate of the third process, case (c), one has to consider those ejected electrons which have enough energy to ionize the lattice ($E > E_g = 6.5$ eV). With an ionization cross section of the negative hydrogen ions about 10^{-16} cm^2 one obtains a mean path of about 100 Å, and thus the less efficient process of scattering of these electrons by phonons does not need to be considered separately. The mean time for capture by a Coulomb trap (He^+ or He^{++}) of an electron from a distance of 100 Å in LiH is of the order of $10^{-12} - 10^{-13}$ sec. There are no electrons produced by Auger processes because both the lithium and the hydrogen ions have a $(1s)^2$ configuration. Therefore, the capture of electrons from neighboring negative hydrogen ions (i.e., formation of neutral hydrogen atoms) is by far the most important mechanism of neutralization of the helium ions even in a trap-free crystal.

It is clear that the sudden formation of a $2e$ (or $3e$) anomaly of charge on a lattice site will produce drastic local perturbations. In particular, a strong low-frequency "optical" breathing mode of negative hydrogen ions towards the helium ion and of positive lithium ions away from it is generated. This is analogous to what happens in alkali halides under x-ray irradiation.[12] Close to the charge anomaly (whether located on one or two sites) the amplitude of these displacements may be of the order of a few percent of the interionic distance, but it will decrease roughly as r^{-2} and thus further out it will be small compared to normal lattice vibrations. Nevertheless, the resulting vibrational excitation and loosening of the first two or three shells of neighbors will greatly facilitate the defect formation discussed below. It should be stressed that this multiple-charge anomaly produces exceedingly high local electric fields which can lead to unreasonably high polarization energies and even to "polarization catastrophes" well known[13] in theories of alkali halide defect calculations.

Before evaluating (in Sec. IV) certain simple idealized configurations it is interesting to consider the motion and fate of the helium ion itself. To be-

TABLE I. Probability (in %) of independent ionization of T^- to all continuum states ($E_g = 0$) and to the conduction band ($E_g = 6.5$ eV) and probabilities of the formation of singly and doubly charged ions.

Z	$P(E_g = 0)$	$P(E_g = 6.5$ eV)	P_+	P_{++}
0.6	43.5	29.0	41.2	8.41
0.7	36.8	25.6	38.1	6.55
0.8	31.4	22.7	35.1	5.15
0.9	27.0	20.2	32.2	4.08
1.0	23.4	18.0	29.5	3.24

gin with, during its lifetime τ the positive helium ion may travel a distance $\tau(2E/M)^{1/2}$, where E is the recoil energy of the helium nucleus and M its mass. With E having its maximum value 3.2 eV one obtains a maximum distance of 0.05 Å which is about one-third of the zero-point amplitude of T (or He^3). For a He^{++} ion the lifetime and the displacement are smaller by about a factor of 2. It follows that the neutralization of the helium ions and the ionization of the neighboring ions occurs "instantaneously" so that all of them are close to their normal sites. It follows also that the direction of the subsequent collision between the recoiling helium atom and the neighboring lithium or hydrogen ions (or hydrogen atoms) is not influenced by the location of the hydrogen atoms. There are at present no adequate procedures available for calculating the threshold energies for displacement of ions in an ionic lattice, but by analogy with experimental data for alkali halides[14] one can conclude that they should be of the order of a few eV. Since the maximum available kinetic energy is not greater than something over 3 eV and the mean energy is about 1 eV, it is unlikely that the recoil of the helium atom would displace a large number of lattice ions. Nevertheless, one would expect that the Li^+ ions which are smaller than the H^- ions (approximately 0.41 and 0.59 of the interionic distance) will be easily pushed into interstitial positions and, at temperatures which permit diffusion, will form lithium clusters as observed experimentally. It is interesting, however, to inquire into the possibility that the recoiling helium atom itself will leave its initial site and end up in an interstitial position. Wilson and Johnson[15] have obtained a value of 0.69 eV for the energy necessary for a helium atom to move from a cube-center to a face-center position in LiH. It remains to calculate the energy necessary for the helium atom to leave its initial lattice site and reach the cube center. Using the formalism and the interaction parameters described in Sec. IV, this energy appears to be about 1 eV, giving a total of about 1.7 eV. The β spectrum of T indicates that about one-third of the helium atoms receive a recoil energy in excess of this value and of those nearly one-half move in a direction suitable for reaching nearby cube centers. Thus a total of about one-sixth of all tritium decays lead to the formation of a vacancy in the hydrogen sublattice and to a nearby interstitial helium atom. As long as the temperature is low enough this configuration can be assumed to have sufficient stability so that a reverse diffusive motion of the helium atom does not take place. These results will play a role in the discussion of the formation of hydrogen molecules later on.

Turning now to the process of ionization of hydrogen ions following the β decay, one has to distinguish between the case when the initial He^{++} leads to the formation of two hydrogen atoms and the case when a He^+ leads to the formation of only one hydrogen atom among the neighbors. In the first case there are four possible relative positions of the hydrogen atoms as illustrated in Fig. 2: If one hydrogen atom is formed on site 1 then the other one can be located either on (a) one of the four sites (2, 3, 4, 5) at a distance $r_0\sqrt{2}$, or (b) one of the two sites (10, 11) at a distance $2r_0$, or (c) one of the four sites (6, 7, 8, 9) at a distance $r_0\sqrt{6}$, or (d) on a site (12) $2r_0\sqrt{2}$ away where r_0 is the interionic distance. In the second case there is the possibility that besides the hydrogen ion which lost its electron to the He^+ ion there is another hydrogen atom in its proximity which became formed either (e) by the emerging β electron from the initial T^- decay or (f) by an ionization sequence associated with another nearby T^- decay. (Another mechanism, involving dissociation of H_2^- into H_2 and an electron, will be discussed later.)

Clearly, the probability of cases (a)–(d) is 0.052 $\frac{4}{11}$ = 0.02, 0.052 $\frac{2}{11}$ = 0.01, 0.052 $\frac{4}{11}$ = 0.02, and 0.052 $\frac{1}{11}$ = 0.005, respectively. In order to evaluate the probability of case (e), the probability that the emerging β electron will ionize a T^- ion, the ionization cross section of T^- has to be integrated over the spectrum of the β electrons. The cross section can be estimated by assuming in the usual way[16] that at an energy 3–5 times greater than the ionization energy the cross section reaches its maximum value, which is of the order 10^{-16} cm^2, and that it drops as $E^{-1}\ln E$ for higher energies. The

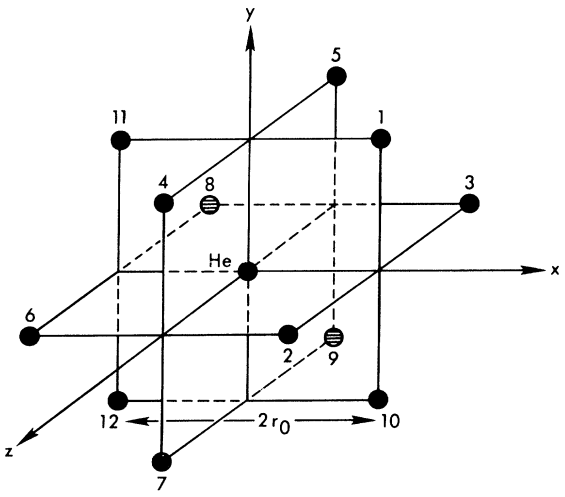

FIG. 2. H^- ions surrounding a He ion immediately after β^- decay; Li^+ ions are located along x, y, and z axes one unit distance away from the origin.

spectrum of the β electrons can be approximated by a distribution which reaches a maximum value at about one-third of the maximum energy of the β spectrum (18 keV) and drops linearly on both sides. The resulting ionization probability of a T^- ion turns out to be of the order 10^{-4}. Since the initial neutral T^0 atom has 11 neighboring T^- ions (the 12th one being now a He atom), the total probability of the formation of a T^0 atom in its neighborhood is of the order 10^{-3}. Thus the net probability of case (e) is $0.32\times10^{-3}=3.2\times10^{-4}$. In order to calculate the probability of case (f) one has to know the average number of hydrogen ions which become ionized either directly by each β electron or by the secondary, tertiary, etc., electrons which the β electrons produce by ionizing other ions (hydrogen 0.72 eV, lithium 75 eV). It is well known from the work of Itoh[17] that such ionization sequences can reach very high numbers. A rough estimate of this number can be made by dividing the average energy 5.7 keV of a β particle by the average energy loss of about 75 eV per ion pair formed. (The situation here is simple because the Li^+ and the H^- ions have the same electron configuration.) The result is nearly 100 ionizations per β particle. Application of the usual recombination kinetics[18] in a trap-free pure LiT crystal leads to an entirely negligible probability of case (f). One concludes that the existence of He^{++} ions is the major factor in simultaneous formation of neutral hydrogen atoms within a few interionic spacings of each other. As shown below, this effect can lead to the formation of a substantial number of hydrogen molecules even in the absence of diffusion.

IV. DIFFUSIONLESS MECHANISMS OF FORMATION OF HYDROGEN MOLECULES

Experimental evidence[19] suggests that hydrogens in LiH (LiT) are present only as negative ions or in diatomic form, and therefore it is of interest to consider the possible diffusionless mechanisms of formation of hydrogen molecules. Direct ionization by β electrons could ionize two neighboring H^- ions simultaneously but the probability of this process is quite low. When only one H^- is ionized it could attach itself to a neighboring H^- ion thus forming an H_2^- molecular ion occupying two lattice sites. Davidson[20] and Taylor[21] have shown that in the free state this molecule is unstable relative to the formation of an H_2 molecule and a free electron. Although it remains to be shown that crystalline fields do not alter this result, it is felt that the process of H_2^- formation and subsequent dissociation into H_2 and an electron (perhaps later trapped at an F center) is a possible mechanism of hydrogen-molecule formation in LiH without diffusion. Its probability per initial ionization event has not been evaluated.

In order to investigate the process of H_2 formation following shake-off in a reasonably quantitative manner, a model of LiH recently developed by Wilson and Johnson[15] was employed. The nonelectrostatic part of the potential between host ions i and j in the lattice is assumed to have the form

$$V(\bar{r}_{ij})=\phi(|\bar{r}_{ij}|)\left[1+k\left(\frac{x_{ij}^4+y_{ij}^4+z_{ij}^4}{\bar{r}_{ij}^4}-\frac{3}{5}\right)\right],$$

where $\bar{r}_{ij}$ is the vector distance between ions i and j – x_{ij}, y_{ij}, and z_{ij} being its Cartesian components. $\phi(\bar{r}_{ij})$ is the central repulsive part of the potential and was taken to have the Born-Mayer form

$$\phi(|\bar{r}_{ij}|)=A_{ij}(\delta)\exp[-B_{ij}(\delta)|\bar{r}_{ij}|],$$

in which δ is the screening parameter for the H^- orbital and the coefficients A_{ij} and B_{ij} are obtained by comparing $\phi(|\bar{r}_{ij}|)$ with the quantum-mechanical results of Fischer *et al.*[22] These results were obtained for internuclear separations $\gtrsim$1.5 Å and so, strictly speaking, the Born-Mayer form only holds for such "large" separations. It is well known that inert-gas interactions behave more like A/r^n for small separations and therefore one might expect the same behavior here. As discussed below, the "polarization catastrophe" necessitated a modification of the potential by assuming $\phi=A/r^n$ for separations $\leq r_s$ and then obtaining A and n from the continuity of the potential and of its first derivative at r_s. The value of r_s was taken as 1.5 Å, but variations in this value were found not to influence the results significantly. The noncentral-force parameter k is introduced because of the known deviation from the Cauchy relations in LiH.[23] The functional form of $V(r_{ij})$ will be recognized as the lowest-order linear combination of spherical harmonics having cubic symmetry.

The four adjustable parameters in the model are the two screening parameters δ_{+-} and δ_{--} for the H^- wave function and the two noncentral force parameters k_{+-} and k_{--} in the Li^+-H^- and H^--H^- interactions. These parameters were determined by fitting the calculated elastic constants, binding energy, and interionic distance to the experimental data. Using an effective charge 0.875 e as indicated by various studies,[23] one obtains $\delta_{+-}=0.95$, $\delta_{--}=0.6875$, $k_{+-}=-0.50$, and $k_{--}=+1.00$. Table II shows the degree of agreement between the calculated and experimental values.

Besides the potential describing the normal LiH lattice it is necessary to know the following interactions: He^0-Li^+, He^0-H^-, H^0-Li^+, H^0-H^-, H^0-He^0, and H^0-H^0. The first four of these have been ob-

TABLE II. Crystal parameters.

	Expt. [a]	Theor.
$C_{11}-C_{12}$ [b,c]	0.412	0.436
C_{44} [c]	0.419	0.424
B [d]	0.351	0.355
U_0	−9.50	−8.50
r_0	2.035	1.951

[a]These values are actually for ^{7}LiD which is assumed to have the same electronic structure as LiH. The shear elastic constants C_{11}-C_{12}, C_{44}, and the bulk modules are in units of 10^{12} dyn/cm^2; the binding energy is in eV/mol and the interionic distance is in Å.

[b]There is no available experimental value of C_{12} and therefore the relation $B=1/3(C_{11}+2C_{12})$ was used to obtain this quantity.

[c]S. P. Marsh, as reported by Verble *et al.* (Ref. 23).

[d]D. R. Stephens and E. M. Lilley, J. Appl. Phys. 39, 177 (1967).

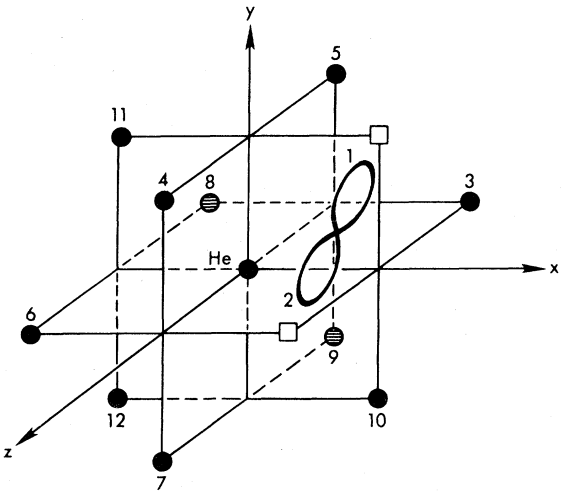

FIG. 3. Hydrogen molecule formation following the neutralization of the He^{++} ion.

tained by Fischer in the single-determinantal approximation.[24] The H^0-He^0 interaction has been determined by Fischer and Kemmy[25] and agrees very well with the experimental results of Amdur and Mason.[26] These repulsive interactions were fitted to the Born-Mayer form, Ae^{-Br}, and the appropriate values of A and B are given in Table III. The H^0-H^0 molecular interaction was calculated by Kolos and Wolniewicz.[27] We found their results to be well represented in the region of the minimum by a Morse potential

$$V(r)=4.7464\{\exp[-4.548(r-0.7414)] - 2\exp[-2.274(r-0.7414)]\}.$$

As in the model of Wilson and Johnson,[15] the polarizabilities of the Li^+ and H^- ions were taken to be 0.029 and 1.90 Å^3 and were allowed to vary linearly with the closest distance of approach to a neighboring ion. Such a variable polarizability, which was proposed by many authors,[13,28–30] was found to be sufficient to avoid a "polarization catastrophe" in the He-migration calculation of Ref. 15. In the present calculation, however, which contains a charge anomaly due to three adjacent H^- vacancies, a "runaway" of the ions still occurred. It was for this reason that the harder form of central potential, $\phi=A/r^n$ discussed above, was used for small internuclear separations.

TABLE III. Born-Mayer coefficients for defect-atom interactions. The A coefficient is in units of eV/mol; B is in Å^{-1}.

	A	B
He^0-Li^+	615.99	5.0680
He^0-H^-	119.72	2.8320
H^0-Li^+	87.84	2.9827
H^0-He^0	37.19	2.8302
H^0-H^-	30.27	2.1428

We shall consider first the situation when the neutral helium atom remains on its lattice site: In configuration (a), as denoted in Sec. III (see Fig. 3), symmetry considerations demand that 45 displacement parameters be assigned to the first three nearest-neighbor shells of ions surrounding the He, a total of only 27 atoms. The formation energy of this defect is therefore an upper limit of the true formation energy and the relaxations of outer-region ions are not well described because of the restricted motion of their neighbors. Relaxations of first-neighbor Li^+ ions, however, should be reasonably well determined. In Table IV are listed the coordinates of the He, H^0, and first-neighbor Li^+ ions and the parameters assigned to their motion. Table V gives the calculated energies relative to the perfect lattice (E_s, E_{el}, E_P, and E_r being the electrostatic, electronic, polarization, and repulsive contributions to the total E_t) and the displacement parameters. From the table one can see that the He atom moves only 2% toward the H_2 molecule. The separation of the H^0 nuclei in this molecule is 0.745 Å as compared to 0.741 Å in the free H_2 molecule. As mentioned earlier, the H_2^- molecule is unstable and so the H_2 molecule formed here does not trap electrons. The first-nearest-neighbor Li^+ ions generally move away from the defect region. The Li^+ ion at (1, 0, 0) is pushed 0.27 $\sqrt{2}r_0$(= 0.74 Å) in the yz plane away from the H_2 molecule. Such an enormous relaxation may lead to a complete displacement and to the formation of the observed Li

TABLE IV. Coordinates and displacement parameters p_i for configuration (a) (all $p_i = 0$ in the initial state). In Fig. 2 the Li^+ ions are located on the x, y, and z axes one unit distance away from the origin.

Atom	Coords. and displacement parameters	Atom	Coords. and displacement parameters	Atom	Coords. and displacement parameters
He	p_1, p_2, p_2	Li^+	$1+p_6$, p_7, p_7	Li^+	p_{11}, p_{12}, $-1+p_{13}$
H^0	$1+p_3$, $1+p_4$, p_5	Li^+	p_8, $1+p_9$, p_{10}	Li^+	p_{11}, $-1+p_{13}$, p_{12}
H^0	$1+p_3$, p_5, $1+p_4$	Li^+	p_8, p_{10}, $1+p_9$	Li^+	$-1+p_{14}$, p_{15}, p_{15}

metal clusters at higher temperatures.[31]

The hydrogen atoms in configurations (b) and (c) described in Sec. III are initially very far from each other and are, furthermore, hampered by the presence of the He atom from froming an H_2 molecule. If the He atom were to go into a nearby interstitial position due to recoil leaving a negative ion vacancy, the efficiency of H_2 formation would clearly be greatly increased. In fact, it is quite likely that such vacant sites are the nuclei for the subsequent formation of the observed H_2 bubbles at higher temperatures when diffusion becomes significant. In configuration (d) the attractive H^0-H^0 interaction is too weak to affect its stability. In any case, H_2 molecules could be formed in configurations (b)–(d) by the $H^0 + H^- \rightarrow H_2^- \rightarrow H_2 + e^-$ process described earlier if the latter is permitted.

V. RATE OF FORMATION OF HYDROGEN MOLECULES

Most of the experimental studies on the effect of T decay on crystals were made on LiH crystals containing around 40 mole% of LiT, and thus the estimates given below are made for this composition. In such a crystal the rate of T decay is 5×10^{13} $sec^{-1}\,cm^{-3}$ leading to the formation of an equal number of β electrons, of 1.6×10^{13} $sec^{-1}\,cm^{-3}$ He^+ ions, of 2.5×10^{12} sec^{-1} cm^{-3} He^{++} ions, and of 5×10^{15} $sec^{-1}\,cm^{-3}$ neutral hydrogen atoms by the β electrons. With a Coulomb-capture cross section at liquid-nitrogen temperature equal to 3×10^{-12} cm^{-2} one obtains for the mean lifetime and steady-state concentration of neutral hydrogen atoms on lattice sites 10^{-5} sec and 10^{10} cm^{-3}, respectively. Using the results of previous sections one concludes that the presence of He^{++} ions leads to the formation of not less than 10^{12} $sec^{-1}\,cm^{-3}$ hydrogen molecules. This number could be bigger by a factor of 3 or so if the other mechanisms besides the one based on configuration (a) were operative. The presence of He^+ ions leads to the formation of only 10^{10} sec^{-1} cm^{-3} molecules through mechanism (e). Mechanism (f) is entirely negligible as long as the hydrogen atoms cannot diffuse away within 10^{-5} sec to interstitial positions where they would not act as Coulombic traps for free electrons. However, if the $H^0 + H^- \rightarrow H_2^- \rightarrow H_2 + e^-$ mechanism were operative, then each He^+ would lead to a H_2 molecule and the rate of formation could be comparable to that of He^+.

TABLE V. Energies relative to the perfect lattice (in eV) and displacement parameters (in units of interionic distance r_0) for configuration (a).

p_1	+0.02	p_9	+0.05	$E_s = 30.34$
p_2	0	p_{10}	−0.07	$E_{el} = -77.18$
p_3	−0.130	p_{11}	−0.13	$E_p = -4.28$
p_4	−0.380	p_{12}	−0.07	$E_r = 2.77$
p_5	+0.350	p_{13}	0	$E_t = -48.37$
p_6	+0.100	p_{14}	0	
p_7	−0.270	p_{15}	−0.05	
p_8	−0.180			

It remains to compare the rate of hydrogen-molecule formation through the shake-off self-ionization process of T^- ions with the more familar formation by the emitted β rays or incident γ rays. This process could be based on one of the mechanisms[32,33] which have been proposed for alkali halides or on the process involving the intermediate formation of H_2^-. As mentioned earlier,[4] the volume swelling of a LiH or LiH:LiT crystal is essentially the same for β and γ irradiations when the ionization dose is the same. This result combined with the recent data of Souers *et al.*[3] permits the conclusion that at 150 °C the rate of formation of free hydrogen is somewhat less than 0.5 at.% per day or about 2×10^{15} $sec^{-1}\,cm^{-3}$ of hydrogen atoms. This number is in satisfactory agreement with the number of hydrogen atoms formed by β electrons calculated in the previous paragraph. Were it not for the experimental suggestion[19] that H^0 atoms do not exist in LiH one could interpret the rapid formation of H_2 molecules at higher temperatures as the result of increased diffusion of H^0 atoms in the lattice. In any case the H^0 atoms would have to leave their H^- lattice sites in a time which is short compared to 10^{-5} sec in order not to trap electrons as discussed above.

A theoretical estimate of the activation energy for interstitial diffusion of an H_2 molecule[34] in LiH yields a value of about 0.7 eV. This result and the observed rates[3] at high temperatures show that the diffusion-controlled process is essentially frozen at 80 °K and that somewhere between 200 and 300 °K

its efficiency would begin to be comparable to the efficiency of the self-ionization mechanism.

Clearly, the relative importance of the self-ionization and of the direct-ionization mechanisms depends in a crucial manner upon two factors: One of them is the validity of the Lewis-Pretzel[19] interpretation of their data, and the other, related to it, is the question of the stability of the H_2^- molecule occupying a H^- lattice site. Further analysis of these phenomena and in particular detailed experimental studies, over a wide temperature range, of LiH:LiT or γ-irradiated LiH would be of great interest.

Note added in proof. Calculations by T. A. Dellin, G. J. Dienes, C. R. Fischer, R. D. Hatcher, and W. D. Wilson, Phys. Rev. B 1, 1745 (1970) and also S. S. Jaswal and M. E. Striefler, Phys. Rev. B 1, 4118 (1970) give activation energies of He migration of 0.60 and 0.65 eV, respectively, in good agreement with the value 0.69 eV used herein.

ACKNOWLEDGMENTS

The authors wish to thank Professor C. R. Fischer for making available his quantum-mechanical studies prior to publication, and also for many helpful discussions. They are also grateful to Dr. Herman Leider and Professor J. J. Hopfield for several fruitful discussions.

---

*Work supported by the U.S. Atomic Energy Commission, under Contract No. AT-(29-1)-789.

[1]F. E. Pretzel and R. L. Petty, Phys. Rev. 127, 777 (1962).

[2]F. E. Pretzel, G. V. Gritton, C. C. Rushing, R. J. Friauf, W. B. Lewis, and P. Waldstein, J. Phys. Chem. Solids 23, 325 (1962).

[3]P. C. Souers, T. S. Blake, R. M. Penpraze, and C. F. Cline, J. Phys. Chem. Solids 30, 2649 (1969).

[4]H. Leider (private communication).

[5]E. L. Feinberg, J. Phys. (USSR) 4, 423 (1941); A. Migdal, *ibid.* 4, 449 (1941).

[6]E. L. Feinberg, Yad. Fiz. 1, 612 (1965) [Soviet J. Nucl. Phys. 1, 438 (1965)].

[7]J. S. Levinger, Phys. Rev. 90, 11 (1953).

[8]H. A. Bethe and E. E. Salpeter, in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1957), Vol. 35.

[9]S. O. Lundquist, Arkiv Fysik 8, 177 (1954).

[10]N. Rosen, Phys. Rev. 38, 255 (1931).

[11]W. E. Spicer (private communication).

[12]R. Smoluchowski, Ann. Braz. Acad. Sci. 37, 415 (1965).

[13]L. W. Barr and A. B. Lidiard, *Physical Chemistry, an Advanced Treatise* (Academic, New York, 1969), Vol. 10.

[14]See, e.g., J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon, New York, 1962).

[15]W. D. Wilson and R. A. Johnson, Phys. Rev. B 1, 3510 (1970).

[16]H. W. S. Massey and E. H. S. Burhop, *Electronic and Impact Phenomena* (Clarendon, Oxford, 1952).

[17]N. Itoh, Phys. Status Solidi 30, 199 (1968).

[18]A. Rose, *Concepts in Photoconductivity and Allied Problems* (Interscience, New York, 1963).

[19]W. Burton Lewis and F. E. Pretzel, J. Phys. Chem. Solids 19, 139 (1961); see also, H. R. Leider, Lawrence Radiation Laboratory Report No. UCRL-50698, 1969 (unpublished).

[20]E. R. Davidson, J. Chem. Phys. 36, 1080 (1962).

[21]H. S. Taylor, J. Chem. Phys. 39, 1012 (1963).

[22]C. R. Fischer, T. A. Dellin, S. W. Harrison, R. D. Hatcher, and W. D. Wilson, Phys. Rev. B 1, 876 (1970).

[23]J. L. Verble, J. L. Warren, and J. L. Yarnell, Phys. Rev. 168, 980 (1968); and references there cited.

[24]C. R. Fischer (private communication).

[25]C. R. Fischer and P. Kemmy, Phys. Rev. 186, 272 (1969).

[26]I. Amdur and E. A. Mason, J. Chem. Phys. 25, 630 (1956).

[27]W. Kolos and L. Wolniewicz, J. Chem. Phys. 41, 3663 (1964).

[28]R. J. Quigley and T. P. Das, Solid State Commun. 5, 487 (1967).

[29]A. Scholz, Phys. Status Solidi 25, 285 (1968).

[30]J. Yamashita and T. Kurosawa, J. Phys. Soc. Japan 9, 944 (1954).

[31]F. E. Pretzel, D. T. Vier, E. G. Syklarz, and W. B. Lewis, LASL Report No. La-2463, 1961 (unpublished).

[32]R. E. Howard, S. Vosko, and R. Smoluchowski, Phys. Rev. 122, 1405 (1961).

[33]D. Pooley, Proc. Phys. Soc. (London) 87, 245 (1966).

[34]W. D. Wilson (unpublished).