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Theoretical Research on Radiation
Induced Defects in LIH

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THEORETICAL RESEARCH ON RADIATION INDUCED DEFECTS IN LiH

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INTRODUCTION

The original contract called for work to be done on three phases of the general problem of radiation defects in LiH:

- (1) The calculation of interaction energies between the separate ions
- (2) The development of suitable methods for calculating the properties of defects in crystals.
- (3) The application to specific defects in LiH.

The three sections to follow describe work that has been done along these lines.

In section I, the cohesive energy, lattice parameter, compressibility and elastic constants have been obtained for the LiH crystal employing a point ion model with repulsive two - body interactions calculated in the Heitler - London approximation. A method for obtaining a better approximation to the interactions is considered involving a quantum mechanical calculation involving three or seven ions instead of just two. For defects in LiH, for example, interstitial He, the interactions He-Li^+ , He-H^- are also required. These were calculated and are given in an attached paper where the He-Li^+ interactions were compared with the results on atomic scattering of these ions. The presence of Li^+ as a defect in alkali halide crystals was studied last year; we now append two papers on this work. Our capabilities with respect to the quantum mechanical calculation of interactions is indicated in part (e) while in the final part preliminary results on the frequency distribution of LiH are reported.

In section II, our new method for computing the polarization energy in defect problems is outlined. In this method the dipoles induced on the separate ions are evaluated taking into account the electric field on the ions due to relaxation of nearby ions as well as due to the induced dipoles on the nearby ions. Previous methods could not ascertain the induced dipoles accurately. This method is tested on several cases where the experimental results are well-known, for example the energy of a Schottky pair in K Cl. This calculation is outlined here as well as that for the activation energy for an interstitial Cl^- in K Cl. Since our new method implies several things about the dielectric constant of a crystal, a study is reported of the effects of adding a small charge to a lattice to examine the response of the lattice in terms of the relaxation of the ions.

In section III calculations using the new methods and interactions are reported on for LiH. The energy of a Schottky pair and the relaxation around positive and negative ion vacancies in LiH is given first. Then the relaxation around an interstitial He atom is

discussed and the activation energy for motion is calculated. In addition several other calculations on LiH and closely related substances are mentioned.

In each of the sections, equations, tables and references are numbered from the beginning of that part.

Future work on LiH is indicated throughout the report. Here we summarize some of the main lines of research to be undertaken in the near future.

1. Interactions between the ions will be obtained by means of a program involving 3 or 7 ions treated at the same time to improve the basic model.

2. Calculations on H interstitials will be continued, and the nature of the hydrogen migration will be established.

3. A study will be made of the migration in LiH to form clusters of ions or bubbles of gas, and the possibility of slowing down or stopping this process by the introduction of impurity ions.

4. Calculations on Li and Li^+ interstitials will be performed.

5. The properties of the pure crystal i.e. infrared absorption, specific heat, equation of state, eigenvectors and other connected quantities will be studied to obtain a good model for LiH.

6. A study will be made to involve covalency into the model.

7. Other defects will be examined as they appear to be important, (for example the H_2 molecule at the ion site.)

8. To study the information that can be obtained from NQR measurements on LiH containing defects.

9. To study the dielectric properties of a crystal when electric fields are present, and to ascertain what value of the dielectric constant to use in defect work.

The work appearing in the following was done by C. Rutherford Fischer, Robert D. Hatchett, Jacob Neuberger and William Wilson of the Queens College Faculty and Andrew Blum and Shirley Harrison, graduate students at Queens College. One other faculty member Ian Boswarva, a visiting Assistant Professor has now joined in the work and as well three other graduate students, Conrad Goldberg, Morris Samberg and Theodore Dellin. In addition we have the benefit of consultation with Arthur C. Damask of the Queens College Physics department, G. J. Dienes of Brookhaven and Roman Smoluchowski of Princeton.

The actual work on this contract was carried out at Queens College, Brookhaven National Lab and the Lawrence Radiation Labs, Livermore, California. Machine calculations were carried out at Brookhaven and Livermore on CDC 6600 computers. At the Lawrence Radiation Labs during the month of August the basic method for treating the polarization energy in defect problems was developed and tested.

I. Interactions and model for LiH.

(a). Pairwise interaction model of LiH from diatomic LCAO calculations

A number of quantum mechanical calculations of Lithium Hydride crystal parameters have been reported in the literature.¹ Hylleraas² and Lundquist³ used screened hydrogenic wave functions for Li^+ and H^- in a single determinant ionic configuration calculation of the cohesive energy of the crystal. Morita and Takahashi⁴ extended Lundquist's calculation by adding electron pair or covalent bonding. Hurst⁵ used a two-electron function for both H^- and Li^+ and calculated the crystal energy by optimizing wave function parameters in the field of positive and negative point charges arranged to simulate the crystalline field. It should be noted that neither Hurst nor Morita and Takahashi determined what lattice parameter was predicted by their models.

For the calculation of the properties of defects in LiH, e.g., interstitial atoms or ions, it is useful to use a point ion model together with two-body repulsive interactions.^{6,7} We have found these interactions and determined the Born-Mayer parameters by the Heitler-London method for some of the wave functions used in the papers referenced above, in particular for screened hydrogenic functions and for the two-electron open shell configuration. In addition, a calculation was performed employing the free-ion Hartree-Fock wave functions.

It should be noted that the pairwise quantum mechanical calculation of repulsive forces described below does omit the many body effects which Lowdin¹ and Lundquist³ have considered. Westin, Waller and Lundquist⁸ point out that the crystal charge distribution calculated from Lundquist's screened hydrogenic wave functions does differ from a superposition of the free ion charge distribution due to the overlap terms arising from the antisymmetry of the wave function. Hurst's calculation⁵ does not include any overlap effects but does include the effect of the crystal field on the H^- ion, while the present calculation includes overlap between Li^+-H^- and H^--H^- pairs. Our calculation indicates that the overlap terms in the case of Lithium Hydride affect the position of the minimum in the binding energy vs. interionic distance curve for the crystal more seriously than they affect the value of the binding energy. This conclusion is in agreement with Lundquist's result that second and sixth order calculations gave the same binding energy while only the sixth order calculation yielded a value for interionic distance in agreement with experiment.

The importance of including the crystal field is harder to determine since Hurst's work does not include a binding energy vs. interionic distance curve. For this reason it also may be the case that the binding energy given by his calculation is not the minimum obtainable from his model.

The repulsive two-body interactions were found by calculating the net interaction energy of a pair of ions, $E_{\text{int}} = E(r) - E(\infty)$, and then subtracting the point ion energy, $e_1 e_2 / r$. Here $E(r)$ and $E(\infty)$ are the total energies of a pair of ions at distances r and at infinite separation calculated using the same wave function parameters. The energy is calculated from

$$E = \int \psi^* H \psi d\tau \quad (1)$$

with

$$H = -1/2 \sum_i \nabla_i^2 - \sum_{i,a} \frac{Z_a}{r_{ia}} + \sum_{i>j} \frac{1}{r_{ij}} + \frac{Z_a Z_b}{r_{ab}}$$

Here ψ is a single determinant wave function except in the open shell case where a linear combination of four determinants is required in order that ψ be an eigenfunction of the square of the total spin operator for the four electron system.^{5,9} For the single determinant case the energy was calculated using Lowdin's formula¹⁰ for non-orthogonal orbitals. In the open shell case, the energy formula was worked out by the authors.

The use of an open shell wave function is important for H^- in the free-ion case as it is the only wave function tried which provides enough correlation energy to yield a bound state for a free H^- ion.¹¹ Neither the screened hydrogenic function used in most calculations including this one, nor the Hartree-Fock free ion function yields a bound state for H^- .

The necessary one- and two-center integrals over Slater functions were calculated using the Harwell Laboratory version of the Corbato-Switendick program¹² DIATOM further modified for the CDC 6600 at Brookhaven National Laboratory.

The cohesive energy per molecule of the crystal, U , at each value of the lattice parameter, r , was calculated from the expression

$$U = 6Ae^{-Br} + 6Ce^{-Dr} - \alpha |e|^2 / r \quad (2)$$

where α is the Madelung constant (1.747558 for a f. c. c. structure), A and B are the Born-Mayer parameters appropriate to the $Li^+ - H^-$ interaction, C and D those for the $H^- - H^-$ interaction and e the electronic charge. The $Li^+ - Li^+$ interaction was calculated and found to be effectively zero at the second nearest neighbor internuclear distance in LiH and is therefore neglected. The interionic separation is obtained by minimizing Eq. 2 with respect to r .

The compressibility, K , is obtained from the well-known relation¹³

$$\frac{1}{K} = \frac{1}{18r_0} \left(\frac{d^2 U}{dr^2} \right)_{r=r_0} \quad (3)$$

where r_0 is the interionic distance obtained from 2.

Using a method developed by Fuchs¹⁴ for monovalent metals and applied by Price¹⁵ to some of the alkali halides, we calculated the shear elastic constants c_{11} , c_{12} and c_{44} for LiH.

Then, using the expression

$$\frac{1}{K} = \frac{1}{3} (C_{11} + 2C_{12}) \quad (4)$$

we calculated c_{11} and c_{12} using the experimental value of K.

In Figure I, the $\text{Li}^+ - \text{H}^-$ repulsive interactions for values of the H^- screening parameter, ρ , from $\rho = .66$ to $.95$ are plotted. One notes the uniform decrease in repulsive energy as the screening parameter increases, that is, as the H^- wave function contracts. The magnitude of the repulsion varies directly with the degree of overlap between Li^+ and H^- wave functions. Also to be noted is the exponential behavior of the interactions supporting the results of Dass and Saxena¹⁶ that the Born-Mayer form is valid for LiH. Of course, we have obtained the interactions over a large range of internuclear separations whereas Dass and Saxena have fit the Born-Mayer parameters to equilibrium crystal data.

Also in Figure I are plotted the $\text{Li}^+ - \text{H}^-$ interactions using Hartree-Fock free-ion and Hurst open shell wave functions. The former give the most repulsive energy values, although still exponential in behavior, and the Hurst functions yield an interaction similar to the screened hydrogenic functions with a screening parameter for H^- between $\rho = .72$ and $.75$.

In Table I the results of least squares fit of each of the interactions in Figure I to the Born-Mayer form, Ae^{-Br} , are given. The interionic distance and cohesive energy of LiH considering only first nearest neighbor interactions are also given. From the data it is clear that adjusting ρ to obtain a better interionic distance (experimental value = $2.042\text{\AA}$) causes a simultaneous lowering of the binding energy. That is, as the H^- wave function is allowed to contract and the repulsive energy decreases (see Fig. I), the Madelung energy begins to dominate. When r_0 is obtained to within 1% ($\rho = .95$), the binding energy is too low by 12.3% (experimental value = $-215.98\text{ K cal/mole}$).

In Figure II are plotted the $\text{H}^- - \text{H}^-$ "repulsive" interactions for several values of the screening parameter, ρ , and for the Hurst crystal and Hartree-Fock (HF) free ion functions. Evidently, the most diffuse wave function, HF, yields the most attractive interaction and the most contracted function, $\rho = .95$, the most repulsive. This is opposite to the $\text{Li}^+ - \text{H}^-$ results: the greater the overlap, the greater the attraction between the ions. Seitz¹⁷ has objected to the attractive nature of the $\text{H}^- - \text{H}^-$ interaction although there does not seem to be any reason why a pair of bonding and anti-bonding σ orbitals, each filled

Fig I
5(a)

Fig II
5(6)

TABLE I

Born Mayer parameters, interionic distance and cohesive energy
for first nearest neighbor interactions only.

	Screened Hydrogenic Functions, ρ = screening parameter							Hartree ^b -Fock	Hurst Crystal ^a open shell
	$\rho = .66$	$\rho = .6875$	$\rho = .7208$	$\rho = .75$	$\rho = .82$	$\rho = .90$	$\rho = .95$		
A in K cal/mole	131.96	145.78	155.48	168.41	203.48	257.38	293.26	90.676	105.60
B in $\text{\AA}^{-1}$	2.4392	2.5412	2.6371	2.7345	2.9635	3.2360	3.3968	2.1012	2.4787
r_0 in $\text{\AA}$	2.546	2.478	2.403	2.340	2.213	2.091	2.026	2.643	2.361
U in K cal/mole	-189.46	-195.20	-201.53	-207.29	-220.23	-234.29	-242.52	-190.88	-201.92

a - Ref. 5

b - The authors are indebted to Drs. A.W. Weiss and H.D. Cohen who supplied them with Hartree-Fock functions for the H^- ion.

with two electrons, must yield a net repulsion for a system, particularly one with the unusual properties of H^- . Several of the models discussed in this paper do include attractive $H^- - H^-$ interactions but do lead to a stable crystal since enough repulsion is provided by the $Li^+ H^-$ interaction.

In any event, we appropriately fitted (by least squares) each of the curves in Figure II to a polynomial, exponential or straight line. In no case was the interionic separation affected by the second nearest neighbor interaction by more than $\sim .08 \text{ \AA}$ nor the cohesive energy changed by more than $\sim .4.6 \text{ K cal/mole}$. That is, according to our analysis, r_0 and U are determined to within a few per cent by the first nearest neighbor interactions. From Table I, a value of ρ for H^- between .90 and .95 would fix the interionic distance to agree perfectly with experiment and the cohesive energy to within $\sim 10\%$ of experiment while ignoring second nearest neighbors entirely. On the other hand, if the H^- screening parameter has the same value of .95 for both the $Li^+ - H^-$ and $H^- - H^-$ interactions, the second nearest neighbor interaction puts the interionic distance at $2.16 \text{ \AA}$.

In order to use the same value of ρ for H^- for interactions between a Li^+ or another H^- , ρ would have to be $\sim .98$, that is each electron would act almost completely as it would in a hydrogen atom. Although this is an unreasonable result for a free ion, in the crystal environment it may be the case.

We made the admittedly arbitrary choice of fitting the $H^- - H^-$ ($\rho = .95$) interaction to the form Ce^{-br} and then adjusted C to fit r_0 while keeping D constant. This gives us a repulsive interaction labelled "final" in Figure II which should be appropriate to an H^- screening parameter between .72 and .75. In our model, then, the charge distribution of the H^- ion in the crystal is distorted: it is more extended toward another H^- than toward a nearest neighbor Li^+ .

Table II contains the values of the crystal parameters obtained using a screened hydrogenic H^- function with $\rho = .95$ for first nearest neighbors and $H^- - H^-$ interactions chosen in the following ways:

- A: no $H^- - H^-$ interaction
- B: H^- screened hydrogenic function, $\rho = .95$
- C: $H^- - H^-$ Born-Mayer (Ce^{-Dr}) parameters D for $\rho = .95$, C fit to r_0 .

For the He defect calculation, interaction C was chosen for $H^- - H^-$ and two values of the screening parameter, $\rho = .72$ and .95 were chosen for $H^- - He$ interactions.

Lundquist³ found upper and lower limits of -196.4 and $-203.9 \text{ K cal/mole}$ respectively for the binding energy using the molecular orbital method applied to the entire crystal and employing screened hydrogenic H^- wave functions with an adjustable screening constant. Using the same wave functions in our pairwise interaction model, the binding

TABLE II

Crystal parameters using screened hydrogenic wave functions

H ⁻ -H ⁻ inter- action	r_0 in 10 ⁻⁸ cm	⁻¹² in 10 cm/dyne	Born-Mayer Parameters				C	D
			C ₁₁ -C ₁₂	C ₄₄	C ₁₁	C ₁₂		
			in 10 ¹² dynes/cm				ev/molecules	in Å ⁻¹
A	2.026	1.54	.5298	.4735	.7004	.1706	0.	0.
B	2.160	1.92	-.0088	.5252	.3413	.3502	49.735	2.0859
C	2.042	1.59	.4490	.4841	.6466	.1976	5.0510	2.0859

energy is -195.20 K cal/mole. Lowdin¹ has pointed out the importance of three body forces in ionic crystal calculations. He estimates that including them adds 10-20 K cal/mole to the binding energy.

The small discrepancy in binding energy can also be accounted for in other ways. The inclusions of more intra shell correlation increases the binding of the crystal as is shown by Tables I and III. Also the binding energy would be increased if it is assumed

Table III LiH crystal Parameters from other Investigations*

Investigator	Cohesive Energy	Interionic distance
I Hylleraas ²	-219 K cal/mole	2.21A
II Lundquist ^a	-199.1 K cal/mole	2.05A
III Morita and Takahashi ⁴	-225 K cal/mole	Not Calculated
IV Hurst Closed Shell ^b	-200.0 K cal/mole	Not Calculated
V Hurst Open Shell (Crystal parameters)	-236.3 K cal/mole	Not Calculated

*Cases III-V have cohesive energies calculated at the experimentally determined lattice distance which is not necessarily where the minimum in the binding energy vs. interionic distance curve occurs.

a) See Ref. 3. The free ion values are used since the lattice parameter was obtained only for this case.

b) See Ref 5. Closed shell screened hydrogenic functions with $\rho_{H^-} = .77242$. Open shell parameters are given elsewhere.

that the LiH crystal has partially covalent character with one of the H^- electrons going into a σ orbital on each of the six first nearest neighbor Li^+ ions. Morita and Takahashi⁴ showed that the addition of a few per cent of the above covalent configuration increased Lundquist's binding energy value by ~ 25 K cal/mole. Our value would also increase if a small amount of covalency were added to any of the ionic configuration wave functions since a valence bond configuration for LiH leads to more binding than the ionic.¹⁸ This change would also improve the too large values for interionic distance by decreasing the slope of the repulsive interaction.

A comparison of the various calculated values of the interionic distance with the experimental value is a more stringent test of any model: A plot of B.E. vs. r (eq. 2) has a shallow minimum and a change in the binding of just a few K cal/mole can change the position of the minimum by $\sim 0.3A$ as is shown in Tables I and III. Employing the free ion H^- wave function (screening parameter $\rho = 0.6875$) and including interactions up to sixth order, Lundquist obtained $r_0 = 2.05A$ while our result was $r_0 = 2.48A$. As

stated earlier, the many body effects in LiH are important here. Lundquist also included the effect of distant ions but this is not as important a factor since Hurst's closed shell calculation ⁵ gave a screening parameter $\rho = 0.77242$ which is not large enough to yield a good value for the interionic distance. This parameter had to be increased to ~ 0.95 for the H^- ion in our model, apparently to simulate the antisymmetrization effect of the many body calculation.

Using the free ion Hartree-Fock function for H^- resulted in very poor agreement with experiment. This is consistent with the results employing the various screened hydrogenic functions as the Hartree-Fock function results in the most extended charge distribution of any of the functions studied.

The open shell function yields a charge distribution which is markedly different than the screened hydrogenic ¹ and includes enough correlation energy to bind the H^- system, yet the repulsive interaction it predicts for the crystal is very similar to the one given by the screened hydrogenic function with screening parameter $\rho \sim 0.73$. However a comparison of Table III with Table I shows that our pairwise type of calculation yields less binding than Hurst found ⁵ using the same wave function in his calculation.

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(b) Calculations of Three and Seven Ion Interactions for a Model of the perfect LiH crystal.

The pairwise interaction model discussed in part (a) does not completely take into account the exchange correlation effects which are particularly important in Lithium Hydride due to the extension of the H^- ion. These effects have been shown to be important by work of Lundquist¹ and Westin et al². The calculation discussed in part (a) also shows that it is difficult to find a fit to perfect crystal LiH data with a diatomic model.

To overcome this difficulty, we have started SCF calculations, using the POLY-ATOM³ system of programs, to obtain total interaction energies between:

(1) Two Li^+ ions and one H^- or two H^- ions and one Li^+ ion arranged as linear triatomic molecules.

(2) Six Li^+ ions surrounding one H^- ion and six H^- ions surrounding one Li^+ ion arranged as in the LiH crystal.

In both the three and seven ion cases the interaction energy is plotted as a function of interionic distance to determine the repulsive interaction in LiH. These calculations are in a preliminary stage. They should result in an improved model as the redistribution of electronic charge due to exchange effects is taken into account to a greater extent than in the diatomic case.

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(c) He- Li^+ Interaction Energy at Small Internuclear Distances

A neutral helium atom has been considered as one of the interstitial defects in LiH. Before this problem could be done the interaction energy between He and Li^+ as well as between He and H^- was required. The attached preprint with the above title details the work done on this problem. The paper has been accepted for publication in the Journal of Chemical Physics.

(d) Interactions of Li^+ with other ions in crystal problems.

In the previous year of the contract work was undertaken to consider Li^+ as a defect in other alkali halides. One paper has now appeared in the Physical Review on off-center Li^+ in KCl and another paper has been submitted on nuclear quadrupole resonance shifts of off-center ions in KCl. A reprint and a preprint of these two papers are attached. It is expected that we will investigate the possibility of off-center ions in LiH.

(e) Summary of Working Computer Programs and an Indication of Capability to Carry Out Quantum Mechanical Mo-SCF Calculations.

An improved version of the Corbato-Switendick program DIATOM¹ has been in use by our group for the past eighteen months. In conjunction with a recently written program to calculate the total energy of a diatomic system using the Lowdin formula for non orthogonal orbitals², DIATOM may be used to calculate the interaction energy between any pair of atoms or ions. Wave functions must be supplied in the form of linear combinations of Slater orbitals.

This system may be used to obtain interactions between ions and atoms for a variety of defect calculations -- vacancy, substitutional ion, interstitial atom or ion, H center, etc.

If the diatomic system contains more than about forty to fifty electrons, computer time becomes an important factor, even on the CDC 6600 used by our group. Also, relativistic effects must be considered for high atomic number. Therefore interactions obtained by this method are not too reliable if the atomic number of one of the atoms or ions is much larger than about thirty.

The other system of programs presently in use is called POLYATOM³. This system calculates all one and two electron quantum mechanical integrals over four or fewer centers using Gaussian orbitals and then performs either an open or closed shell SCF calculation. In principle any number of electrons and centers may be handled in a single calculation, but the number of two electron integrals becomes prohibitively large if the basis set approaches a hundred functions.

We have applied POLYATOM to calculate properties of crystals and to determine interaction energies for atom-molecule and ion-molecule scattering.

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(f) Frequency Distribution for LiH

A point ion model for LiH where the repulsive interactions are obtained from part (a) was used to obtain the frequency distribution function and the resonant frequency.

The resonant frequency corresponds to the frequency obtained for a zero wave vector. This yielded the value

$$\omega_t = 11.22 \times 10^{13} \text{ rad/sec.}$$

which is in excellent agreement with the experimental value. The longitudinal frequency comes out larger than determined by experiment, a feature which occurs for all point ion models. It is to be noted that despite the introduction of next nearest neighbours in the repulsive interaction, the resonant frequency depends only on the $\text{Li}^+ - \text{H}^-$ nearest neighbour interaction. A check on the next nearest neighbour interactions can be provided by a study of the frequency distribution over a uniform set of points in wave vector space. We chose a subdivision of $1/16$ in wave vector space and calculated the frequencies associated with each inequivalent point in this space. The results are shown in the table below in which the relative frequency distribution is given as a function of ω in a range of $\Delta \omega$ of $.5 \times 10^{13}$ rad/sec. From these values the specific heat as a function of temperature will next be calculated and as well the infrared absorption and reflection and the equation of state of LiH.

Table I. $f(w)$ vs. " w "

w	$f(w)$	$f(w)$ w	$f(w)$	w	$f(w)$
0-.5	0	16	540	32	216
.5-1	0		486		198
1.0-1	16	17	360	33	224
1.5-2	24		276		128
2. -2.5	114	18	258	34	158
2.5-3	88		228		60
3	204	19	144	35	110
	292		216		34
4	458	20	240		
	1120		108		
5	1452	21	192		
	1254		48		
6	1382	22	220		
	944		60		
7	712	23	60		
	600		0		
8	386	24	48		
	1050		72		
9	1089	25	72		
	464		60		
10	336	26	204		
	192		156		
11	196	27	144		
	328		204		
12	480	28	240		
	528		216		
13	564	29	291		
	516		222		
14	550	30	330		
	480		240		
15	732	31	144		
	408		242		

II. Methods for calculation of defect problems.

(a) A new method for handling the polarization energy

Since the classical Mott and Littleton¹ calculation of the long-range polarization effects resulting from the introduction of a charged defect in ionic crystals (v.g. vacancies and interstitials) many suggestions and improvements have been made. Brauer² included elastic effects in his treatment of the problem; Boswarva and Lidiard³ included deformation dipoles resulting from the nearest neighbor overlap of the charge distributions⁴. Boswarva and Lidiard also performed a rather detailed comparison of the energies of Schottky defect formation which obtain with reasonable variations of the basic model. That is, calculations were performed using different forms for repulsive interactions and the importance of the vander Waals terms was determined. Their results indicate that the Born-Mayer-Verwey⁵ potential ($\sim r^{-12}$ for $r < r_0$ and $\sim e^{-br}$ for $r > r_0$) is an unnecessary and unjustifiable form which fortuitously gives reasonable Schottky pair energies (W_s) when the old Born-Mayer repulsive parameters are used. They also found that vander Waals forces accounted for $\sim .2$ ev of the W_s but that inclusion of deformation dipoles only affects the W_s value $\sim .1$ ev.

In all the above calculations, a polarizable continuum is added after only a few nearest neighbor relaxations and dipoles are exactly calculated. Scholz⁶ was the first to perform an extended computer calculation of the vacancy formation energy and he permitted 256 ions surrounding the defect to relax. The long-range polarization effects in his calculation were determined by an iterative procedure which we shall later demonstrate was not carried far enough. Also, the Jones and Ingham⁷ - type continuum which he adds to his large region I (256 ions) uses the static dielectric constant K_0 of the salt. We have determined the number by which this summation should be weighted, E , by direct calculation and attribute the difference, $K-E$, to the surface polarization of the substance.

The energy of formation of a positive or negative ion vacancy is written as the sum of the electrostatic, polarization, repulsive and vander Waals energy contributions:

$$E_{\text{vac}} = E_{\text{stat}} + E_{\text{pol}} + E_{\text{rep}} + E_{\text{van}}$$

each relative to the perfect crystal. Following Scholz⁶, a region of 256 ions surrounding the vacancy (region I) was allowed to relax with displacement parameters $P_1, \dots, P_{23}$. The electrostatic, repulsive, and vander Waals energies were then calculated without approximation by the method of Hatcher and Dienes⁸. Despite the small difference in the electrostatic potentials of an ion in its normal and relaxed positions due to all other ions in their fixed positions we have included this term also in order to avoid the possibility of this being a cumulative effect. (Indeed, we calculated this result of neglecting this quantity with the final values of relaxations for a negative ion vacancy in KCl to be $\sim .01$ ev). For the repulsive and vander Waals energies, all ions within cubes of side N surrounding each relaxing ion

were included. With N equal to 2 and 3 the differences in E_{rep} and E_{van} were found to be .00001 ev and .001 ev respectively. We subsequently used the $N = 2$ value thus estimating our error in each of these terms to be $< .001$ ev.

The polarization energy is given by:

$$E_{\text{pol}} = -\frac{1}{2} \sum_i \vec{p}_i \cdot \vec{E}_i^{\text{chg}} \quad (1)$$

where $\vec{p}_i$ is the induced electronic dipole on ion i due to charges and dipoles external to it, and $\vec{E}_i^{\text{chg}}$ is the electric field at ion i due only to the asymmetrical distribution of charges surrounding the vacancy and the field of the vacancy itself. There is no great difficulty in obtaining $\vec{E}_i^{\text{chg}}$. The field at ion i in its relaxed position due to all other ions in their fixed positions (out to ∞) is given simply by the gradient of the Ewald potential. Only the contributions due to the relaxations remain and these were readily calculated by the computer.

The calculation of the $\vec{p}_i$ is the difficulty. If $\vec{E}^{\text{tot}}$ is the total electric field on ion i due to charges and dipoles external to ion i ,

$$\vec{p}_i = \alpha_i \vec{E}_i^{\text{tot}} = \alpha_i \sum_{j \neq i} \frac{e_j \vec{r}_{ij}'}{|\vec{r}_{ij}'|^3} + \alpha_i \sum_j \alpha_j \left\{ \frac{3 \vec{r}_{ij}' (\vec{E}_j^{\text{tot}} \cdot \vec{r}_{ij}') - \vec{E}_j^{\text{tot}} |\vec{r}_{ij}'|^2}{|\vec{r}_{ij}'|^5} \right\} \quad (2)$$

where α_i is the polarizability of ion i (taken from Tessman, Kahn and Schockley⁹) $\vec{r}_{ij}'$ is the vector distance from ion i to ion j in their relaxed positions. The most common approach to solving (2) is to write

$$\vec{E}_i^{\text{tot}} = \vec{E}_i^{\text{dip}} + \vec{E}_i^{\text{chg}} \quad (3)$$

with $\vec{E}_i^{\text{dip}}$ being the field at ion i due only to the dipoles external to it. Eqs. (2) and (3) can then be substituted in eq. (1) to obtain

$$E_{\text{pol}} = -\frac{1}{2} \sum_i \alpha_i |\vec{E}_i^{\text{chg}}|^2 - \frac{1}{2} \sum_{i,j} \alpha_i \alpha_j \left\{ \frac{3(\vec{r}_{ij}' \cdot \vec{E}_i^{\text{chg}})(\vec{E}_j^{\text{chg}} \cdot \vec{r}_{ij}')}{|\vec{r}_{ij}'|^5} \right. \\ \left. - \frac{(\vec{E}_j^{\text{chg}} \cdot \vec{E}_i^{\text{chg}})|\vec{r}_{ij}'|^2}{|\vec{r}_{ij}'|^5} - \frac{1}{2} \sum_{i,j} \alpha_i \alpha_j \left\{ \frac{3(\vec{r}_{ij}' \cdot \vec{E}_i^{\text{chg}})(\vec{E}_j^{\text{dip}} \cdot \vec{r}_{ij}')}{|\vec{r}_{ij}'|^5} \right. \right. \\ \left. \left. - \frac{(\vec{E}_j^{\text{dip}} \cdot \vec{E}_i^{\text{chg}})|\vec{r}_{ij}'|^2}{|\vec{r}_{ij}'|^5} \right\} \right\} \quad (4)$$

The first term of eq. (4) is the monopole polarization energy, the second term is usually considered to be the dipole-dipole correction, and the third term, considered of higher order, is neglected.

One way to improve the above approximation is to calculate $\vec{E}^{\text{dip}}$ by an iterative procedure. That is, the field due to the charges alone produces dipoles on all ions i . These dipoles are then modified by the dipoles on ions j which in turn modify the dipoles on ions i , etc. Thus, by successive iterations, one can obtain the final dipole on each ion. This is the method employed by Scholz as mentioned earlier but however Scholz only performed the first iteration.

An alternative method is to express eq. (2) as

$$\vec{P}_i = \alpha_i \vec{E}_i^{\text{chg}} + \alpha_i \sum_j \left\{ \frac{3 \vec{r}_{ij}' \vec{r}_{ij}' - I |\vec{r}_{ij}'|^2}{|\vec{r}_{ij}'|^5} \right\} \vec{P}_j \quad (5)$$

in which I is the unit dyadic. Eq. (5) is then a set of linear simultaneous equations in the $\vec{P}_j$'s. For the 256 ions allowed to relax, these equations were exactly solved by known techniques and the polarization energy of region I therefore calculated without approximation¹⁰. In order to obtain the polarization energy contribution due to the ions outside region I, the following procedure was adopted: eq (5) was solved for 738 ions surrounding the defect (only 256 of which were allowed to relax) and the difference in the E_{pol} so obtained was equated to a Jones and Ingham summation,

$$E_{\text{pol}}^{256} - E_{\text{pol}}^{738} = \frac{1}{\epsilon} \left\{ \alpha + \sum_{\substack{+ \text{ ions} \\ 257}}^{738} \frac{Q^2}{r^4} + \alpha - \sum_{\substack{- \text{ ions} \\ 257}}^{738} \frac{Q^2}{r^4} \right\} \quad (6)$$

where $-Q$ is the charge of the vacancy and ϵ is the weighting factor. Using the value of ϵ obtained from eq. (6) we then used the Jones and Ingham summation for all ions (to ∞) outside region I.

It might be argued that in using a simple Jones and Ingham continuum rather than a Mott and Littleton approximation for ions outside the relaxed region we are neglecting the relaxations of these ions. Our decision to do this was based on numerical values for the displacement parameters of the region I ions which were sufficiently small as the region I boundary was approached to estimate that any relaxation of ions outside this region will not significantly contribute to the formation energy. Also, we calculated E (from E_{pol}^{256} and E_{pol}^{740}) without relaxations and the error involved was 9% even in such a crude approximation. Therefore, since the added polarization energy of ions outside region I is $\sim .5$ ev we feel that neglecting relaxations of these ions could not introduce more than a .05 ev error in our calculation.

(b) Test case - Vacancy in K Cl without relaxations.

We first consider the polarization energy of 256 ions surrounding a negative ion vacancy which are not allowed to relax. No ions outside this region are included. Each ion is allowed to polarize in the field of the vacancy and both the iterative and exact polarization energies are determined. In fig. 1 the polarization energy of this system of ions is plotted as a function of the number of iterations. Actually, fig. 1 is a fitted curve,

$$E_{\text{pol}}(N) = -.56322e^{-.66985N} \cos \pi N - 1.2370 \quad (7)$$

N being the number of iterations. Eq. (7) fits the data such that the maximum deviation from the calculated values is less than 1%.

From fig. 1 it is clear that ~ 11 iterations are required to fix the polarization energy to within .001 ev. If only one iteration were performed⁶, the polarization energy of the system would be in error by ~ 240 .

The exact solution of Eq. (5) gave -1.2370 ev as the polarization energy of this system.

The next step in our procedure was to solve eq. (5) for 738 ions surrounding the anion vacancy and determine ϵ in this unrelaxed case from eq. (6). The polarization energy of the 738 ions was -1.3233 ev and consequently $\epsilon = 1.60$. It is interesting to note that if one calculates the ratio of the field on an ion due only to the excess charge of the vacancy and divides by the total field on that ion (i.e. the field due to the vacancy and the surrounding induced dipoles) different values for ions in various "shells" are obtained. Fig. 2 is a plot of the number so obtained as a function of the shell; that is, the ions surrounding the vacancy can be considered to belong to various shells (100 type ions, etc.) with the shell number increasing with distance. Fig. 2 indicates that the values of this "dielectric constant" oscillate about 1.60 giving support to our independent calculation of ϵ . It is to be emphasized that ϵ is not the dielectric constant because 1) the ions have not been allowed to relax and hence we have a fictitious physical case 2) the ions are considered to be stationary, that is, all dynamical motion is neglected and 3) the electric field is not taken as the "average" value in a region.

(c) Vacancies in K Cl with relaxation.

Here we repeat the calculations of Section (b) but allow the 256 ions to relax using 23 displacement parameters. For a negative ion vacancy in K Cl we obtained $E_{\text{pol}}^{256} = -.4204$ ev and $E_{\text{pol}}^{738} = -.4987$ ev from which ϵ was determined to be 1.76. As mentioned earlier, this is only a 9% change from the value obtained by neglecting relaxation. We subsequently fitted on to our 256 ion region I a Jones and Ingham summation with a weighting factor of 1.76. Again we attribute the difference between this number and the static dielectric constant for K Cl of 4.68 to the effects mentioned in (b).

ITERATION
Polarization Energy for a
Fig 1. Negative Ion Vacancy in KCl as a function
of the Iteration

Fig 2. Dielectric Constant vs. number of shell

Using the methods outlined above and $\epsilon = 1.76$ we are now in a position to calculate the Schottky pair energy in K Cl and to extend our method to do charged interstitials in K Cl ~~or~~ also. In Table I we give the 23 displacement parameters and contributions to the formation energy of positive and negative ion vacancies. When the binding energy per ion pair, -7.18 ev^6 , is added to the sum of these formation energies,

$$W_s = E_{\text{tot}}^+ + E_{\text{tot}}^- + E_{\text{bind}}$$

the energy of formation of a Schottky defect pair, W_s , results. The final result, $W_s = 2.18 \text{ ev}$ is in excellent agreement with experiment (2.22 ev^{11}).

(d) Interstitial defects in K Cl

Using the same method, we have also calculated the formation energy of a Cl^- ion in the center of a cube and in the center of a face of host ions in K Cl. We used a reduced number of displacement parameters however, letting 56 (49) ions relax with 6 (10) displacement parameters and calculating the polarization energy of 280 (300) ions exactly using Eq. (5) in the body (face) centered case. The parameters were chosen as in the He defect calculation in LiH to be treated later in this report. The Jones and Ingham "continuum" was fitted using $\epsilon = 1.76$ after the 280 (300) ion region I.

The results are as follows - the formation energies of the cube and face centered interstitials are 4.38 ev and 5.94 ev respectively. If the migration of the Cl^- is along a $\langle 100 \rangle$ direction from the center of a cube to an adjacent cube our calculations indicate an activation energy for this process of 1.56 ev. Tharmalingam¹² obtained an activation energy of 2.16 ev for the same process in NaCl. Since the experimental migration energy is .025 ev in K Cl¹³ the above is not the mechanism of migration. Instead the Cl^- 's prefer to move along the body diagonal ($\langle 111 \rangle$) and the pair-state configuration must be calculated¹². We have already begun this calculation - the saddle-point configuration is much like that of an H center¹⁴ (with an additional charge).

Table I

Displacement parameters and energy contributions for positive and negative ion vacancies in KCl

Displacement Parameter, P_i (a)	Positive Ion Vacancy	Negative Ion Vacancy
1	.067	.090
2	-.017	-.023
3	.005	.001
4	-.021	.010
5	.005	.008
6	.013	.008
7	-.002	-.004
8	-.001	-.004
9	-.004	-.003
10	-.029	-.025
11	.005	.004
12	.005	.003
13	-.012	-.004
14	-.003	-.002
15	.006	.004
16	.002	.002
17	-.003	-.004
18	.007	.006
19	.005	.003
20	-.003	-.004
21	-.002	.003
22	-.002	0.0
23	-.016	-.008
Estat ^(b)	5.218	4.969
E_{p1}	-.972	-.694
E_{van}	.092	.230
E_{rep}	.232	.281
E_{tot}	4.570	4.786

$$W_s = 2.18$$

a - in units of the interionic distance (for KCl - 3.147)

b - in ev.

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(e). The effect of a small additional charge in a lattice.

The response of a crystal lattice to the introduction of a small test-charge was studied to ascertain whether the various shells surrounding the test-charge would respond in a way that could be characterized by a value of the dielectric constant that was reasonably constant from shell to shell. The special case treated was one where an additional charge of $.1/e$ was added to a K^+ ion in KCl. This case was treated first rather than one involving LiH as we had been using KCl to test out polarization method.

The results of the calculation are shown in the table following. 80 ions in the 6 nearest shells were allowed to relax with the use of 8 arbitrary parameter using the polarization method described in (a). For each shell and parameter involved a quantity called a dielectric constant, d , was evaluated as follows

$$d = \frac{\text{Electric field due to the additional charge}}{\text{Total electric field due to additional charge, relaxed ions and induced dipoles .}}$$

In each case the component of the field were taken in the direction of the motion of the parameter involved. It is clear from the results that the concept of a "dielectric constant-" is not borne out in this case. It is possible that insufficient ions were allowed to relax in which case if many more ions were employed, the value of d would settle down as in the case of a vacancy without relaxation. Certainly for the initial sets of ions it appears necessary to employ an exact calculation rather than employing the measured value of the dielectric constant in bulk. The negative values for parameters 2 and 3 can be explained on the basis that the total field at these ions almost vanished and was in the opposite direction to the field of the additional charge.

Table

<u>Parameter</u>	<u>Displacement</u>	<u>Ions</u>	<u>Parameter</u>	<u>Charge of ion</u>	<u>d</u>
1	-.0135	100	1	-	1.85
2	.0010	110	1	+	-9.97
3	-.0010	111	1	-	-69.6
4	.0020	200	1	+	.68
5	-.0010	210	1	-	3.26
6	-.0015	210	2	-	1.53
7	.0005	211	1	+	3.57
8	.0005	211	2	+	4.32

Displacements are given in distances in units of the interionic distance and are measurement along the axes of the crystal.

The energy of relaxation was made up as follows:

Electrostatic	- .040 ev.
Polarization	- .010
Vander Waals	- .002
Repulsive	+ .016
Total	<u>- .036 ev.</u>

The total energy of relaxation comes mostly from the first group of ions surrounding the defect (- .034 ev.). This occurs here because the second and third set of shells move only a very small amount.

III Applications to LiH.

(a) Positive and negative ion vacancies in LiH.

Having established that our methods give good agreement with experiment for KCl, we apply the same techniques to LiH taking the repulsive parameters from the quantum mechanical investigation described earlier. In the interest of being consistent with our treatment of He in LiH, we chose a value of $1.00 \times 10^{-24} \text{ cm}^3$ for the polarizability of H^- . Allowing 23 parameters to relax once again but not completely finishing the iterations, that is, here we only fixed the displacements to $\pm 0.02 r_0$, we obtained 5.98 and 6.38 eV, respectively for the formation energy of positive and negative ion vacancies in LiH.

We estimate that each of these values could be lowered by ~ 0.2 eV by obtaining the relaxations to $\pm 0.001 r_0$ where r_0 is the interionic distance. With the binding energy of -9.45 eV per ion pair we obtain 2.91 eV as the Schottky defect pair energy. The experimental value of 2.4 ~~± 0.2~~ eV is in good agreement with this when the additional relaxation energy is taken into account. Table I gives the results.

(b) Activation Energy for He Migration in LiH.

A. General Considerations

We assume that a He atom defect will migrate through the crystal by an interstitial mechanism. That is, the He in its lowest energy configuration sits in the center of a cube of ions and migrates via thermal activation to an adjacent cube-centered position through the center of a face. The activation energy is given by the difference between the face and body-centered positions each relative to the perfect lattice. From symmetry considerations, it is not expected that a higher activation energy will occur when the He is in some intermediate position between the face- and body-centered positions.

With the He atom fixed in each of the positions, the total energy relative to the perfect crystal is written as a function of several displacement parameters assigned to the surrounding Li^+ and H^- ions. This energy is then minimized with respect to these parameters by successive iterations on a digital computer (CDC6600 at Brookhaven National Laboratory) until the energy of each configuration is determined to ~ 0.05 eV.

Following the method of Hatcher and Dienes, the total energy is expressed as the sum of electrostatic, polarization and repulsive terms. A Taylor series expansion of the Ewald potential due to Scholz was utilized to somewhat reduce the computer time involved in calculating electrostatic energy changes. The repulsive energy excluding the defect was calculated using the Born-Mayer parameters determined in Section I (a). He- Li^+ interactions were determined by the methods of the preceding Sections to be $A=615.99 \text{ eV/pair}$ and $B=5.0680 \text{ \AA}^{-1}$ (in eV^{-1}). For He- H^- interactions, two values of the H^- screening parameter ($\rho = 0.7208$ and $\rho = 0.95$) were chosen in order to obtain a measure of the sensitivity

Table I

Displacement parameters and energy contributions for positive and negative ion vacancy in LiH.

Displacement parameter- p_i	Positive Ion Vacancy	Negative Ion Vacancy
1	.103	.12
2	.001	-.023
3	-.001	.011
4	-.080	-.010
5	.010	.010
6	.030	.020
7	0.0	-.010
8	0.0	0.0
9	-.02	-.01
10	.01	.05
11	0.0	0.0
12	.01	.01
13	0.0	0.0
14	0.0	0.0
15	.01	.01
16	0.0	.01
17	-.01	0.0
18	.01	.01
19	.01	0.0
20	0.0	0.0
21	0.0	0.0
22	0.0	0.0
23	-.01	0.0
$E_{\text{stat}}^{(b)}$	5.816	6.442
E_{pol}	-2.236	-.828
E_{van}	0.0	0.0
$E_{\text{rep.}}$	2.405	.763
$E_{\text{tot.}}$	5.985	6.378

$$W_S = 2.92$$

a) in units of interionic distance $r_0=2.0415$

b) in e.v.

defect and 280 ions surrounding it calculated without approximation. In actual practice, the 280X3 dimensional matrix which must be solved is reduced by symmetry to a 44 dimensional matrix. The resulting set of equations can be solved on the CDC6600 in ~ 2 sec.

It is important to note that the parameters, P_i , given in Table II are not the actual minimum energy positions of the ions surrounding the He defect but were somewhat arbitrarily chosen. This is because we used the dipole-dipole correction method (I) for the polarization energy initially and found that our model became unstable for certain values of the displacement parameters. That is, when the energy due only to the He itself (repulsive energy) was subtracted from the total energy relative to the perfect lattice, a negative number was obtained. Since this implied that it required a negative energy to put the He in an interstitial position, we rejected the result. Having obtained the model, (repulsive parameters) by quantum-mechanical means, and having approximated the polarization energy, we wanted to make quite sure that the reason for the instability of the lattice was the model and not the polarization energy. We subsequently developed the exact method of solution only to find that despite the improvement in the defect calculation the lattice was still unstable. Improvements in the model are presently being made, but for the purposes of this work we chose to reduce the polarizability of the H^- ion to $1.00\text{\AA}^3$. With this value, the lattice was stable but we cannot say whether some intermediate value, $1.00 \geq \alpha_{H^-} \geq 1.93$ would not have accomplished the same result. It did not seem worth the computer time to better establish which α_{H^-} was necessary for our model to be stable because we are presently improving the model anyway.

In any case, the results given in Table II show that neglecting terms after the dipole-dipole correction in equation (8) is quite serious. Indeed the neglected terms are of the same order of magnitude as the dipole-dipole energy!

In Table I the results of our calculation of the cube-centered formation energy are given (with $\alpha_{H^-} = 1.00\text{\AA}^3$). Note that two values of the formation energy are obtained depending upon the He H^- interaction. Method II was employed for the polarization energy. All parameters were determined to within $\pm .01$ in units of the interionic distance. Note that the He- H^- interaction with $\rho = .7208$ is harder and requires more energy to accomodate the He. The relaxations of the first nearest neighbors are therefore greater in this case.

Since the minimum energy position of the He atom is in the center of a cube, the volume expansion of the lattice per He defect can be estimated from Table I. If the change in volume ΔV is associated only with the average first nearest neighbor displacement then

$$\Delta V = r_0^3 \left(\frac{1 + P_1 + P_2}{\sqrt{3}} \right)^3 - r_0^3$$

For $\rho = .95$, $\Delta V = 5.0\text{\AA}^3$; for $\rho = .7208$, $\Delta V = 5.6\text{\AA}^3$. Both values for ΔV are about one

of the activation energy to the H^- wave function. The Born-Mayer parameters for these interactions are given in Table I. Two methods were used in this calculation, Method I employing the Hatcher-Deines procedure and Method II using the matrix method described in section II (a).

B. Cube - Centered Position

The He is fixed at the center of a cube of ions in LiH. A total of 56 ions surrounding the defect are allowed to relax (out to third nearest neighbors) with six displacement parameters assigned to them. Two parameters are required for each equidistant shell of ions about the defect: one for the positive ions and another for the negative ions. Hence, parameters P_1, P_3, P_5 (assigned to the H^- ions) and P_2, P_4, P_6 (assigned to the Li^+ ions) describe the displacement of the first, second and third nearest neighbors to the He respectively. All displacements are constrained to be radial from the defect with a positive sign indicating an outward relaxation.

The electrostatic terms are calculated without approximation. The repulsive terms are calculated for all ions allowed to relax (and the defect) with interactions out to third nearest neighbors to each of these ions being taken into account. For the calculation of the polarization energy using Method I, the dipoles on a total of 280 ions surrounding the defect were included, 56 of which were allowed to relax. This number was felt to be more than sufficient by analogy with a previous Li^+ in KCl problem where 93 ions were found to determine the polarization energy to $\sim .001$ ev.

The polarization of the Li^+ ($.029\text{\AA}^3$) was taken from Tessman, Kahn and Schockley², and that of the He atom ($.203\text{\AA}^3$) from Pauling³. There is a large uncertainty in the value of the H^- polarizability - many widely varying values are reported in the literature⁴. We determined the α_{H^-} from the relation

$$\frac{\eta^2 - 1}{\eta^2 + 2} = \frac{2\pi}{3r_o^3} (\alpha_{Li^+} + \alpha_{H^-})$$

where r_o is the interionic distance and η the refractive index ($=1.984$) taken from Pretzel, Vier, Szklarz and Lewis.⁵ The resulting value, $1.93\text{\AA}^3$, is much smaller than the free ion polarizabilities reported in the literature but is consistent with the more contracted wave function for H^- which we have chosen. As we shall see, we found it necessary to reduce this value in order that the introduction of the He does not cause the LiH crystal, according to our model, to become unstable.

Table II contains the results of our calculation of the polarization energy, with $\alpha_{H^-} = 1.93\text{\AA}^3$, using the two methods described above. E_{pol} in the table refers to the first term, $-1/2 \sum_i \alpha_i |\vec{E}^{chg}|^2$, in equation (8); $E_{dip-dip}$ refers to the second term. E_{pol} is the result of our calculation by Method II; that is, E_{pol} is the polarization energy of the

half the experimental value $^5(\sim 12.4\text{\AA}^3)$. A higher polarizability for H^- would cause larger relaxations and considerably improve this result.

C. Face - Centered Position

With the He fixed at the center of a face we allowed 48 ions surrounding it to relax using 10 displacement parameters. Parameters P_1, P_3, P_5, P_7, P_9 and $P_2, P_4, P_6, P_8, P_{10}$, are assigned to the first, second, third, etc. nearest neighbor H^- and Li^+ ions respectively. In this case, out to fifth nearest neighbors are included because we wanted to keep the number of ions allowed to relax approximately the same in the face and body centered cases. For the calculation of the polarization energy, 300 ions surrounding the defect were included.

Table II contains the results of our calculation of the polarization energy, again for a representative set of displacement parameters, using both methods. The exact calculation again indicates that the terms commonly neglected are of the same order of magnitude as the dipole-dipole energy.

In Table III, the displacement parameters and contributions to the total formation energy of the He in its face - centered position are given. The two values for HeH^- interaction are again used.

From Tables I and III one obtains an activation energy for He migration of .27ev (for $\rho = .7208$) or .25ev (for $\rho = .95$). The activation energy is therefore not sensitive to the H^- wave function. If the vibrational frequency of the He is taken to be $\sim 5 \times 10^{13} \text{sec}^{-1}$, this activation energy corresponds to $\sim 88^\circ\text{K}$. Roughly speaking, the He should begin to move at liquid nitrogen temperatures.

Table I

Displacement Parameters and Energies of Formation of a He Atom in the Center of a Cube.

Displacement parameters, P_i , and Energies in eV.	Born-Mayer Parameters for He-H ⁻ interaction ^a	
	$\rho = .7208$ $A = 75.682 \text{ eV/pair}$ $B = 2.426 \text{ \AA}^{-1}$	$\rho = .95$ $A = 119.72 \text{ eV/pair}$ $B = 2.832 \text{ \AA}^{-1}$
P_1	.170	.150
P_2	.150	.140
P_3	0.	0.
P_4	0.	0.
P_5	.04	.040
P_6	.03	.030
E_{stat}	-1.8863	-1.6438
E_{pol}	-.5363	-.4771
E_{rep}	5.3745	4.3135
E_{tot}	2.9519	2.1926

^a ρ is the screening parameter for the H⁻ wave function. A and B are the Born-Mayer parameters in Ae^{-Br} .

Table II

Comparison of Methods of Calculation of Polarization Energy

Displacement Parameters, P_i , and Energies in eV.	Cube-centered position $\alpha_{H^-} = 1.93 \text{ \AA}^3$	Face-centered position $\alpha_{H^-} = 1.93 \text{ \AA}^3$
P_1	.170	.215
P_2	.260	.310
P_3	-.005	.040
P_4	-.035	.085
P_5	.050	-.010
P_6	.065	-.025
P_7		.020
P_8		.020
P_9		.020
P_{10}		.020
E'_{pol}	-2.9520	-2.6318
$E_{dip-dip}$	.1965	.4353
$E_{pol} + E_{dip-dip}$	-2.7555	-2.1965
E_{pol}	-3.8357	-2.3121

Table III

Displacement Parameters and Energies of Formation of a He Atom in the Center of a Face

Displacement parameters, ρ_i , and Energies in eV.	Born Mayer Parameters for $\rho = .7208$ A= 75.682ev/pair B= 2.426A ⁻¹	He - H ⁻ interaction ^a $\rho = .95$ A=119.72ev/pair B=2.832 A ⁻¹
P ₁	.250	.240
P ₂	.200	.180
P ₃	.03	.010
P ₄	.03	.010
P ₅	0.	0.
P ₆	.03	.030
P ₇	.03	.030
P ₈	.02	.020
P ₉	.03	.030
P ₁₀	.03	.030
E _{stat}	-1.1748	-1.0308
E _{pol}	-.4710	-.3974
E _{rep}	4.8646	3.8688
E _{tot}	3.2188	2.4406

^a ρ is the screening parameter for the H⁻ wave function. A and B are the Born-Mayer parameters in Ae^{-Br}.

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(c) Quantum Mechanical Calculation of He Migration in LiH.

The calculation of Helium migration in LiH reported on in (b) is being redone by a method which takes the many body forces mentioned in part 1 (b) partially into account. The method employs the POLYATOM system and is an LCAO-MO-SCF calculation of the formation energy of He in LiH in the body centered and face centered positions.

Electron orbitals representing the helium atom and its first and second nearest neighbor Li^+ and H^- ions are filled and then the system is surrounded by over 700 point ions arranged to represent the rest of the crystal.

A self consistent field (SCF) calculation is then carried out for four configurations as follows:

- a) Body centered, no He present
- b) Body centered with He defect
- c) Face centered, no He present
- d) Face centered with He defect

The minimum energy configuration in the presence of the defect is obtained by starting from the relaxed positions of the ions near the defect and varying ion positions to minimize the energy. When this has been done, the activation energy for a helium defect to move through the crystal is simply the difference in formation energies in the body and face centered positions and may be calculated from the total energies of the SCF calculations a, b, c, d.

The polarization energy is taken from the calculation of (b).

This calculation should yield an improved value of the energy due to repulsive forces which is required for the activation energy of He.

(d). Fluorescence Due to Interstitial Lithium in a Lithium Fluoride Crystal

Farge, Lambert and Guinier ¹ of ORSAY, France have observed fluorescence at $9,100 \text{ \AA}$ in Lithium Fluoride which they feel is due to Li^+ formation in the crystal. We are carrying out an LCAC-MO-SCF calculation on this open shell system using the open shell part of the POLYATOM system to obtain ground state and excited state energy vs. inter-nuclear distance curves in an attempt to explain the fluorescence. The crystalline environment should be taken into account as calculation of the $^2 \sum_u^+$ excited state of Li_2^+ by Pfeiffer and Ellison ² yielded a repulsive interaction and therefore could not explain the fluorescence. Apparently the crystal plays an important part in stabilizing the excited state. This work has a bearing on the LiH system because of the possibility of Li_2^+ being formed there also.

References

1. Y. Farge, M. Lambert and A. Guinier, Private communication.
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(e). Summary of other work on Li H.

Work has been started on the migration of both neutral and charged interstitial hydrogen ions (H^0 and H^-) in LiH.

In the case of interstitial H^- initial results indicate that the energy of the crystal with an H^- present is less than the energy of the perfect lattice, thus indicating the instability of the lattice to its presence.

In the case of neutral H^0 ions it appears that the $H^- - H^0$ interaction is slightly attractive for distances relevant to their likely separation in the crystal. It is therefore then very possible that the interstitial H^0 combines with an H^- ion to form the molecular ion H_2^- , similar to the case of the H-center in KCl where a Cl_2^- ion is formed. Considerable work on this latter problem had been performed by us¹ prior to this contract and a calculation on H_2^- in LiH is now being set up similar to that work. A copy of the H^- center paper is appended.

As is clear from the above discussion, our model gives reasonable values for the energy of formation of defects in LiH. We are now in a good position to do several other defects also. Of major interest to us are the impurity complexes because it is clear that the introduction of substitutional impurities such as Na^+ for Li^+ in sufficient number will affect the migration of other ions and atoms in the crystal. By properly doping the crystal, then, it may be possible to prevent the build-up of clusters which grow to disastrous dimensions

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