Migration Energy of an Interstitial He Atom in LiH†

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The method of lattice statics is used to study the distortion of the LiH crystal with an interstitial He atom in the body-centered or face-centered position. In these calculations, one needs to know the defect–host-ion interaction potentials and the dynamical matrix of the undistorted host crystal. The Heitler-London method is used to estimate the defect–host-ion interaction potentials. The dynamical matrix of the perfect crystal is calculated on the basis of the deformation dipole model. The formation energies are computed for the two defect positions and their difference, 0.650 eV, gives the migration energy of an interstitial He atom in LiH. The calculated migration energy is discussed in light of the high-temperature experimental result for the activation energy of diffusion of He gas in LiH crystal (1.22 eV).

I. INTRODUCTION

THE method of lattice statics[1] used in studying the distortion of crystals containing defects is based on the discrete lattice theory. In this method the interactions of the defect with the host ions can be treated exactly, whereas the potential energy of the distorted crystal is normally treated in the harmonic approximation. The total potential energy of the crystal containing defects is minimized with respect to the displacements of the host ions. In the resulting equations, the displacements of the host ions are written in terms of the normal coordinates. The normal coordinates are determined by the Fourier transforms of the force constants of the perfect crystal and the forces between the defect and the host ions. The Fourier transforms of the force constants of the perfect crystal are the usual dynamical matrices without the ionic masses. Thus to solve the lattice statics equations one needs to know the dynamical matrices of the perfect crystal and the defect–host-ion interaction potentials.

The dynamical matrix for the LiH crystal in the deformation dipole approximation has been computed elsewhere.[2] Since these calculations are based on the experimental phonon dispersion curves, they should be quite good.

The evaluation of the defect–host-ion interaction potential is the difficult part of the problem. Of the He-Li^+ and He-H^- interactions, the latter are stronger and more difficult to estimate. We reported earlier a calculation[3] of the migration energy where we assumed the He-Li^+ and He-H^- interaction potentials to be of the Huggins-Mayer form.[4] Since Li^+ and H^- are isoelectronic with He, we computed the parameters in the potential from a known analytical form of He-He potential.[5] The ionic radius of He atom was taken to be the mean of the ionic radii of Li^+ and H^-. The values used for ionic radius of Li^+ are due to Huggins[6] and Fumi and Tosi[7] and the corresponding values of H^- ionic radius were calculated in Ref. 4. Both sets of radii gave about the same value for the migration energy[8] (0.7 eV).

As to how good this empirical potential is, especially for He-H^- interactions, it is hard to say. However, the direct quantum-mechanical calculation of these interactions should be more reliable. Thus, in this paper we present defect studies based on the quantum-mechanical estimates of these interactions.

The Heitler-London method is used to calculate the He-Li^+ and He-H^- interaction potential energies as functions of interatomic separations. The formation energy is calculated when an interstitial He atom is at the body-centered or face-centered position. The migration energy of an interstitial He atom in LiH, which is the difference of the two formation energies, is discussed in light of the high-temperature experimental value for the activation energy for diffusion of the He gas in LiH.

II. DEFECT–HOST-ION INTERACTION POTENTIALS

The main contributions to the atom-ion interaction potential come from the charge-induced dipole interaction, the van der Waals interaction, and the overlap repulsive interaction. Due to the crystal symmetry, the electric field at the defect in either of the two configurations considered here is zero, and hence the charge-induced dipole contribution is zero. Since we have no accurate estimate of the Van der Waals interaction, it is neglected in the present calculations. This approximation is not expected to be serious since the

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van der Waals interaction, in general, is very weak as compared with the repulsive overlap interaction for the atom-ion separations of importance here. (The major part of the formation energy is determined by the defect–first-neighbor interactions.) Thus the interaction potential is due to the repulsive overlap contribution only.

The He-Li^+ and He-H^- repulsive overlap interaction potentials are calculated quantum mechanically. Each atom or ion is assumed to be in its ground state with a closed-shell configuration (both electrons in the same atomic orbital). Each atomic orbital is approximated by a Slater-type $1s$ function

$$\psi_{1s}=(\alpha^3/\pi)^{1/2}e^{-\alpha r},$$

where α is the effective nuclear charge and r is the radial distance from the nucleus expressed in atomic units. (α is determined by minimizing the energy of an atom or an ion.) The total wave function is a single Slater determinant formed by the atomic spin orbitals of the interacting atom and ion. The expectation value of the Hamiltonian for this wave function is given by Slater.[9] To get the interaction potential for a given separation, the expectation value at the infinite atom-ion distance is subtracted from the expectation value at that separation. It has been shown[10] that this procedure gives good results for the He-He interaction potential for the interatomic separations of interest here when α is 27/16. (This value of α minimizes the He atom energy in the closed-shell configuration.)

In order to get reliable estimates of these interaction potentials, one needs to know the crystal wave functions for the corresponding atoms or ions. Since the electrons in Li^+ ion are relatively tightly bound, we do not expect their wave functions to change much as we go from free ion to the crystal. Thus we take α for Li^+ to be 43/16. Even though electrons in He atoms are somewhat less tightly bound than in Li^+, we assume α for He to be the same as for a free atom, i.e., $\alpha(\mathrm{He})=27/16$. As far as an H^- ion is concerned, we know that the closed-shell configuration does not make a stable free ion. It has been shown by Chandrasekhar[11] that the H^- ion has a very loosely bound outer electron which is further supported by a very large polarizability[12] (230 a.u.) of this ion. However, the polarizability of the H^- ion in LiH is quite small[2] as compared to the free-ion value. Thus the H^- electrons are more confined in the crystal than in the free ion. Therefore the closed-shell configuration approximation should be reasonable in the crystal and the cohesive-energy calculations[13] bear this out. On the basis of very extensive calculations of the cohesive energy, compressibility, and electron density in LiH, Tseng[14] concludes that $\alpha(H^-)=11/16$. In these calculations he finds it necessary to include overlaps up to seventh neighbor. Thus the H^- ion is still quite extended, and hence the many-body effects are very important. This is supported by the violation of the Cauchy relation in this crystal.[15] Since it is extremely difficult to take many-body effects into account explicitly in the defect–host-ion interactions, we are interested in a wave function of H^- which makes the many-body effects negligible and at the same time gives a reasonable value for the cohesive energy of the perfect crystal. The three- and four-body contribution to the cohesive energy is appreciable and negative while the two-body overlap contribution is positive when $\alpha(H^-)=11/16$. However, when $\alpha(H^-)$ is increased to one, the cohesive energy remains about the same while the many-body contribution becomes negligible. Thus, $\alpha(H^-)$ equal to 1 gives the H^- wave function required in the present calculations because it gives an effective two-body potential which leads to about the same cohesive energy as that due to the real many-body potential in the crystal. For comparison we also include here the results based on $\alpha(H^-)$ equal to 11/16 (two-body potential only).

The numerical calculations for the potential energy curves are carried out by expanding Slater orbitals into ten Gaussians.[16] The results for the He-Li^+ and He-H^- interaction potentials as functions of interatomic separations are plotted in Fig. 1.

III. DEFECT CALCULATIONS AND RESULTS

With the defect as origin of our coordinate system, the total potential energy of a crystal with a defect can be written

$$\Phi=\sum_{l\kappa}\psi(r(l\kappa))+\Phi_0+\tfrac{1}{2}\sum_{\substack{\alpha l\kappa\\ \alpha' l'\kappa'}}\phi_{\alpha\alpha'}(ll',\kappa\kappa')\times U_\alpha(l\kappa)U_{\alpha'}(l'\kappa')+\cdots, \quad (1)$$

where $\psi(r(l\kappa))$ is the interaction potential of the defect with the κth host ion in the lth unit cell of the crystal, with $r(l\kappa)$ being the distance between the defect and the host ion in its displaced position; the second and third terms are the first two nonzero terms in the expansion of the potential energy of the distorted crystal, with $\phi_{\alpha\alpha'}(ll',\kappa\kappa')$ being the usual force constants of the perfect crystal and $U_\alpha(l\kappa)$ being the αth component of the displacement of ion $(l\kappa)$ from its equilibrium position in the perfect crystal. We treat the distorted crystal potential energy in the harmonic approximation. Using the

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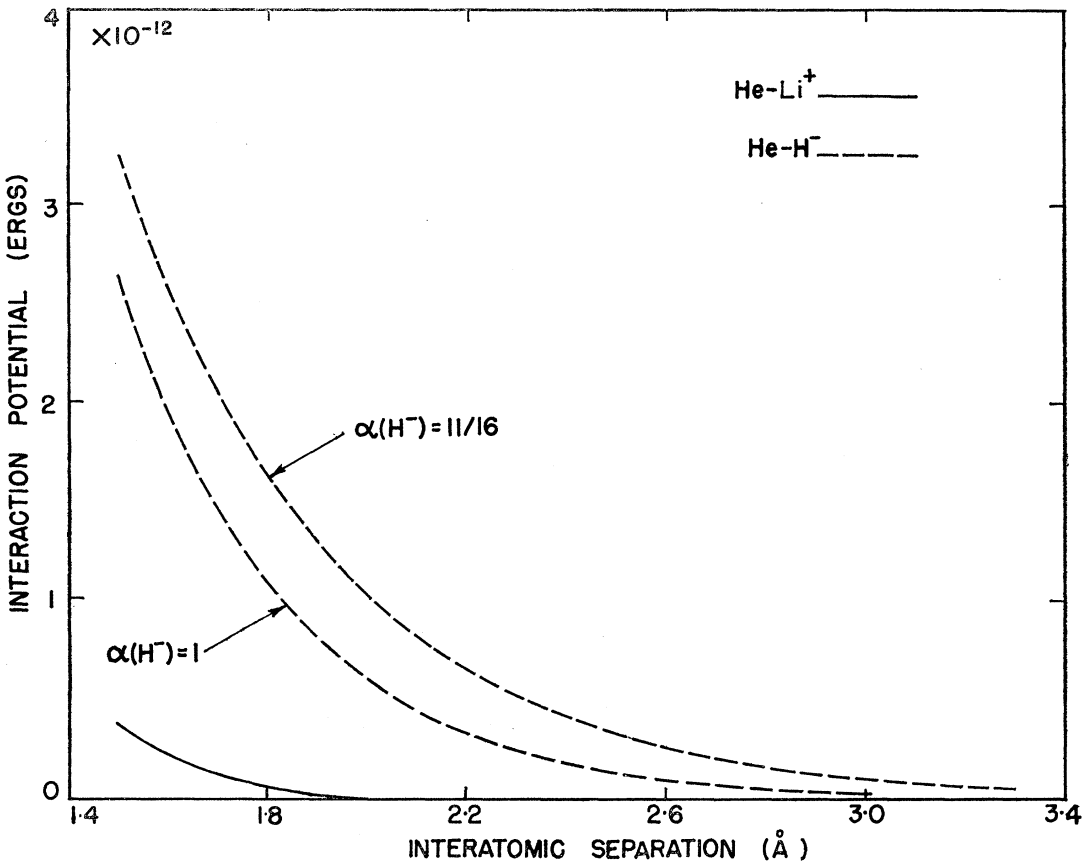

FIG. 1. He-Li$^+$ and He-H$^-$ repulsive overlap interaction potentials as functions of interatomic separations.

equilibrium condition

$$\partial\Phi/\partial U_\alpha(l\kappa)=0,$$

we get

$$F_\alpha(l\kappa)=-\partial\psi(r(l\kappa))/\partial U_\alpha(l\kappa)$$
$$=\sum_{\alpha' l'\kappa'}\phi_{\alpha\alpha'}(ll',\kappa\kappa')U_{\alpha'}(l'\kappa'), \quad (2)$$

where $F_\alpha(l\kappa)$ is the force on ion $(l\kappa)$ due to the defect when the host ion is in its displaced position. We write the displacements in terms of normal coordinates as follows:

$$U_\alpha(l\kappa)=\frac{1}{N}\sum_{\mathbf{q}}Q_\alpha(\mathbf{q}\kappa)e^{i\mathbf{q}\cdot\mathbf{r}_0(l\kappa)}, \quad (3)$$

where N is the number of unit cells in the crystal, $\mathbf{r}_0(l\kappa)$ is the equilibrium position vector of ion $(l\kappa)$ in the undistorted crystal, and $Q(\mathbf{q}\kappa)$ is the normal coordinate of ions of type κ corresponding to the wave vector $\mathbf{q}$.

Substituting (3) in (2) and with some additional manipulations, we get

$$\sum_l F_\alpha(l\kappa)e^{-i\mathbf{q}\cdot\mathbf{r}_0(l\kappa)}=\sum_{\alpha' l'\kappa'}\phi_{\alpha\alpha'}(ll',\kappa\kappa')$$
$$\times\exp\{-i\mathbf{q}\cdot[\mathbf{r}_0(l\kappa)-\mathbf{r}_0(l'\kappa')]\}Q_{\alpha'}(\mathbf{q}\kappa'). \quad (4)$$

The nonzero terms in the summation on the left-hand side of Eq. (4) are due to only those ions which interact with the defect. This equation can be written

$$F_\alpha(\mathbf{q}\kappa)=\sum_{\alpha'\kappa'}V_{\alpha\alpha'}(\mathbf{q},\kappa\kappa')Q_{\alpha'}(\mathbf{q}\kappa'), \quad (5)$$

where $V_{\alpha\alpha'}(\mathbf{q},\kappa\kappa')$ is the usual dynamical matrix without the ionic masses. In matrix form

$$F^{\mathbf{q}}=V^{\mathbf{q}}Q^{\mathbf{q}} \quad \text{or} \quad Q^{\mathbf{q}}=(V^{\mathbf{q}})^{-1}F^{\mathbf{q}}. \quad (6)$$

Since $F^{\mathbf{q}}$ is a function of the displacements of the ions which interact with the defect, substitution of (6) in (3) gives us a set of coupled equations for these displacements. Knowing the interaction potentials and the dynamical matrices of the perfect crystal, one can solve the coupled equations simultaneously for the displacements of these ions.

Now the summation in Eq. (3) extends over the whole first Brillouin zone whereas one normally calculates the dynamical matrices only in 1/48th of the zone. However the vectors $Q(\mathbf{q}\kappa)$ in the rest of the zone are related to the ones in 1/48th of the zone by symmetry operations. These relations are easily obtained from Eq. (5).

The details of a method to compute the dynamical matrix on the basis of the deformation dipole model are

TABLE I. Displacements of the neighbors[a] due to a body-centered interstitial He atom in LiH for two values of $\alpha(H^-)$.

		Displacements (Å)					
		U_1		U_2		U_3	
$\alpha(H^-)=$		1	11/16	1	11/16	1	11/16
Positive ions	(1,1,1)	0.0519	0.0573	0.0519	0.0573	0.0519	0.0573
	(3, −1, 1)	0.0296	0.0416	−0.0219	−0.0271	0.0219	0.0271
	(3,1,3)	0.0169	0.0222	0.0029	0.00481	0.0169	0.0222
Negative ions	(1, 1, −1)	0.157	0.186	0.157	0.186	0.157	0.186
	(3,1,1)	0.00175	0.0137	0.00853	0.0109	0.00853	0.0109
	(3, −1, 3)	0.0361	0.0477	−0.00958	−0.0126	0.0361	0.0477

[a] The position coordinates of the neighbors are in units of half the nearest-neighbor distance in the crystal.

given elsewhere.[2] We carry out calculations for 8000 points in the first Brillouin zone.

In order to study the migration of an interstitial He atom in LiH crystal, we need to consider the defect at the body-centered and face-centered positions of the smallest cubic cell with four positive and four negative ions at its corners. We assume that the defect–host-ion interactions extend up to second neighbor in the body-centered position and third neighbor in the face-centered position. This gives us six independent displacement components for the body-centered position and ten for the face-centered position to be determined from Eqs. (3) and (6) in each case. Using the potential-energy curves computed in Sec. II and the dynamical matrices mentioned above we solve, numerically, the coupled equations simultaneously for the displacement components both for the body-centered and the face-centered positions. Now we can use Eq. (6) to determine $Q(\mathbf{q}\kappa)$ and then the displacement of any ion in the crystal from Eq. (3). Displacements of some of the neighbors of the defect in both the positions are given in Tables I and II.

The change in energy of the crystal due to the defect, the formation energy, is given by

$$E_f=\sum_{l\kappa}\psi[r(l\kappa)]+\tfrac{1}{2}\sum_{\substack{\alpha l\kappa\\ \alpha' l'\kappa'}}\phi_{\alpha\alpha'}(ll',\kappa\kappa')U_\alpha(l\kappa)U_{\alpha'}(l'\kappa'). \quad (7)$$

This can also be written

$$E_f=\sum_{l\kappa}\psi[r(l\kappa)]+\tfrac{1}{2}\sum_{\alpha l\kappa}F_\alpha(l\kappa)U_\alpha(l\kappa). \quad (8)$$

Equation (8) is used to calculate the formation energy of the defect when it is in the body-centered or face-centered position and the migration energy is just the difference of the two formation energies. The results are listed in Table III. Since $\alpha(H^-)=1$ gives an effective two-body potential which is reasonable, the proper migration energy from the present calculations is 0.65 eV. This value is slightly lower than the one we obtained using an empirical potential mentioned in the Introduction.

IV. DISCUSSION

The high-temperature experimental value[17] for the activation energy for diffusion of the He gas in LiH is 1.22 eV, whereas our computed value, based on $\alpha(H^-)$ equal to 1, for the migration energy of an interstitial He atom in LiH is 0.650 eV. Our method of calculations is based on the harmonic approximation and requires the knowledge of the dynamical matrix of the perfect crystal and defect–host-ion interaction potentials. Since the dynamical matrix is based on the phonon dispersion curves in the symmetry directions, it should be quite good. On the basis of the discussion in Sec. II we also believe that the defect–host-ion interaction potentials are reasonable when He-H^- interaction is based on $\alpha(H^-)$ equal to 1. From Tables I and II we note that the displacements of the negative ions near the defect are quite large, especially when the defect is in the face-centered position. Thus the harmonic approximation may not be very realistic for the negative ions near the

TABLE II. Displacements of the neighbors[a] due to a face-centered interstitial He atom in LiH for two values of $\alpha(H^-)$.

		Displacements (Å)					
		U_1		U_2		U_3	
$\alpha(H^-)=$		1	11/16	1	11/16	1	11/16
Positive ions	(−1, 1, 0)	−0.0913	−0.0974	0.0913	0.0974	0	0
	(1,1,2)	0.0787	0.0823	0.0787	0.0823	0.0963	0.106
	(3,1,0)	0.0270	0.0368	0.0519	0.0538	0	0
Negative ions	(1,1,0)	0.248	0.272	0.248	0.272	0	0
	(1, −1, 2)	0.119	0.132	−0.119	−0.132	0.237	0.263
	(3, −1, 0)	0.160	0.178	−0.0813	−0.0900	0	0

[a] The position coordinates of the neighbors are in units of half the nearest-neighbor distance in the crystal.

[17] B. Holt (private communication).

TABLE III. Formation and migration energies of an interstitial He atom in LiH for two values of $\alpha(H^-)$.

$\alpha(H^-)$	Formation energy (eV) Body-centered position	Face-centered position	Migration energy (eV)
1	2.077	2.727	0.650
11/16	3.351	3.835	0.484

defect. Because of the larger displacements, the error due to this approximation is greater when the defect is in the face-centered position than when it is in the body-centered position. Since the harmonic approximation usually underestimates the displacements, the lowering of the formation energy due to more realistic calculations should be more in the face-centered position than in the body-centered position. This would give a lower value for the migration energy as compared with the one obtained here. Thus the difference between the experimental result mentioned above and our calculated value seems to be real. This may be due to the trapping of a significant fraction of the He gas in intrinsic defects such as vacancies, divacancies, etc., which would lead to a higher value for the activation energy of diffusion. This appears to be the case for the migration of some of the rare gases in several alkali halides as shown by Norgett and Lidiard.[18] We are currently exploring this as well as the anharmonicity aspect of the present problem.

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Stark Effects in *F*-Center Emission*†

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The effect of an applied electric field on the emission spectrum of the *F* center has been measured in the range 5–50 kV/cm and 2–150°K for six alkali halides (KCl, KF, RbCl, NaCl, NaF, and CsF). The changes induced by the field are quadratic in the field strength and isotropic with respect to the crystalline axes, and at $T \lesssim 30$°K are as follows: an enhancement of the emission polarized parallel to the field direction with a compensating decrease of the emission polarized perpendicular to the field, a red-shift of the band in both polarizations, and a broadening in certain cases. At higher temperatures the polarization and broadening diminish. The effects in CsF are anomalously small. In several crystals, field-induced quenching of the emission due to Schottky or field ionization also appears. These results are analyzed in terms of Stark mixing in the relaxed excited state of the *F* center. The model assumes that the relaxed states consist of nearly degenerate $2p$- and $2s$-like states which are strongly mixed by crystal-field fluxtuations on the order of 200 kV/cm. For KCl, the resulting $2s'$ mixed state is lower in energy by 0.017 eV and has approximately 40% admixture of the $2p$ states. This mixed-state model is able to give a semiquantitative explanation for the Stark effects observed, as well as a consistent explanation for the magnitude and temperature dependence of *F*-center radiative lifetimes and other excited-state phenomena.

I. INTRODUCTION

UNTIL recently, the usefulness of the Stark effect in identifying optical transitions has been limited to narrow line spectra for which the electric field perturbation is larger than the linewidth. However, with the introduction of modulation and phase-sensitive detection techniques for measuring small changes in line shapes it has become possible to use the Stark effect to investigate broad-band optical transitions, such as those of the *F* center in alkali halides.

The *F* center, an electron trapped at a negative-ion vacancy, has been the object of many experimental and theoretical studies and most of its important features are by now well established.[1] It is known that optical absorption occurs from a $1s$-like (Γ_1^+) ground state to a $2p$-like (Γ_4^-) excited state. Recent Stark-effect experiments of Chiarotti *et al.*[2] in *F*-center absorption

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