

magnetic interaction effect and a corresponding disappearance of the difference frequency at very high fields. This corresponds to the results shown in Fig. 3.

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Non-Central-Force Model of LiH: Phonon Dispersion Curves and He Migration

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Two models for calculating defect properties of LiH (⁷LiD) are obtained using noncentral interionic potentials of the form $f(\theta, \phi)\phi(r)$, where $f(\theta, \phi)$ has cubic symmetry and $\phi(r)$ is a Born-Mayer repulsion taken from quantum-mechanical calculations. The parameters of the models were varied to give the best fit to the interionic spacing, the binding energy, and the elastic coefficients of LiH. Phonon dispersion curves, which can be obtained from only one of the models, are compared with experimental results. Calculations with the two models give 0.69 and 0.87 eV for the activation energy for migration of an interstitial He atom in LiH.

I. INTRODUCTION

IN order to calculate the theoretical values of such properties of point defects in solids as local strains and migration energies, it is necessary to have a "model" for the crystal lattice. Recently, several models of the LiH (⁷LiD) crystal have appeared in the literature. Verble, Warren, and Yarnell¹ have measured the phonon dispersion curves of LiH (⁷LiD) using neutron diffraction techniques and were able to obtain a satisfactory fit to their data with a seven-parameter shell model. Jaswal and Hardy² have applied the distortion-dipole model, including angle-bending forces, to the calculation of the phonon dispersion curves and frequency distribution of LiH (⁷LiD). They made use of the measured phonon dispersion curves of Verble, Warren, and Yarnell,¹ the interionic distance r_0 , the infrared dispersion frequency,^{3,4} and the Szegedi effective charge⁵ to determine the parameters in their model. Subhadra and Sirdeshmukh⁶ were unable to obtain a reasonable model of LiH using central forces alone and concluded that the measured values of the compressibility of LiH are in error. They assigned an upper limit of $2.15 \times 10^{-12} \text{ cm}^2/\text{dyn}$ to the compressibility. In none of these calculations was the interionic distance deter-

mined, i.e., it was always fitted by adjusting the parameters in the various models. Recent calculations of the repulsive interactions between the constituents of LiH by Fischer *et al.*⁷ give these interactions as a function of the H⁻ screening parameter δ . Thus the interionic distance, binding energy, and compressibility can now be determined for various values of δ . Using these central forces determined from first principles, it was found impossible to fit satisfactorily the crystal data. As in the Subhadra-Sirdeshmukh calculations, the compressibility was always too low when the interionic distance and binding energy were within reasonable limits.

The purpose of the present work is to obtain a model of LiH (⁷LiD) which gives a reasonable fit to the experimental values of interionic distance, binding energy, and elastic constants, and which can then be used to calculate the activation energy for diffusion of a He atom in LiH. Actually, two models were developed—the first gives a reasonable fit to all the experimental quantities mentioned above, but because of a few percent error in r_0 it cannot be used to predict phonon dispersion curves (the Kellerman⁸ formalism requires the crystal to be in equilibrium at r_0 and therefore even a few percent error in r_0 invalidates the method). A second model which includes first-nearest neighbors only was fit to r_0 (but fits other experimental quantities less accurately than model I) and used to predict the dispersion curves.

The potentials for the two models are developed in Sec. II, and the phonon dispersion curves predicted by

¹ J. L. Verble, J. L. Warren, and J. L. Yarnell, Phys. Rev. **168**, 980 (1968).

² S. S. Jaswal and J. R. Hardy, Phys. Rev. **171**, 1090 (1968).

³ D. J. Montgomery and J. R. Hardy, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Ltd., Oxford, 1965).

⁴ D. J. Montgomery and K. F. Yeung, J. Chem. Phys. **37**, 1056 (1962).

⁵ A. S. Filler and E. Burstein, Bull. Am. Phys. Soc. **5**, 198 (1960).

⁶ K. G. Subhadra and D. B. Sirdeshmukh, J. Appl. Phys. **40**, 2357 (1969).

⁷ C. R. Fischer, T. A. Dellin, S. W. Harrison, R. D. Hatcher, and W. D. Wilson, Phys. Rev. (to be published).

⁸ E. W. Kellerman, Phil. Trans. Roy. Soc. (London) **A238**, 513 (1940).

TABLE I. Born-Mayer coefficients for the central interaction as given by the quantum-mechanical results of Fischer *et al.* (Ref. 7). The A coefficients are in eV/(ion pair) and the B coefficients are in Å. δ is the screening parameter for the H⁻ ion.

	$\delta=0.66$	$\delta=0.6875$	$\delta=0.7208$	$\delta=0.75$	$\delta=0.82$	$\delta=0.90$	$\delta=0.95$
A_{+-}	131.96	145.78	155.48	168.41	203.48	257.38	293.26
B_{+-}	2.4392	2.5412	2.6371	2.7345	2.9635	3.2360	3.3968
A_{--}	...	-13.50	-7.7254	...	9.0797	29.28	49.73
B_{--}	...	1.8101	2.3940	...	1.5297	1.8819	2.0859

model II for ⁷LiD are given. The calculation of the He migration energy in LiH is presented in Sec. III.

II. NONCENTRAL POTENTIAL

We assume that the interaction between the constituents of LiH is given by

$$V_{lm}(\mathbf{r}_{ij}) = \phi_{lm}(r_{ij}) f_{lm}(x_{ij}, y_{ij}, z_{ij}),$$

$$f_{lm}(x_{ij}, y_{ij}, z_{ij}) = 1 + k_{lm} \left(\frac{x_{ij}^4 + y_{ij}^4 + z_{ij}^4}{r_{ij}^4} - \frac{3}{5} \right), \quad (1)$$

where \mathbf{r}_{ij} is the vector distance between ions i and j , $r_{ij} = |\mathbf{r}_{ij}|$, and x_{ij} , y_{ij} , and z_{ij} are the Cartesian components of \mathbf{r}_{ij} , $\phi_{lm}(\mathbf{r}_{ij})$ is the pairwise interaction between the ions of types l and m (l and m correspond to Li⁺ or H⁻). The term $f(x_{ij}, y_{ij}, z_{ij})$ contains the noncentral force parameter k_{lm} , and is invariant under all cubic symmetry operations.⁹ The central repulsive interaction was taken from the quantum-mechanical results of Fischer *et al.*,⁷ and has the Born-Mayer form

$$\phi_{lm}(r_{ij}) = A_{lm} \exp(-B_{lm}r_{ij}), \quad (2)$$

where the Born-Mayer parameters depend on the screening parameter δ for the H⁻ ion. The values of A_{lm} and B_{lm} for different values of δ are given in Table I. Note that A_{--} for $\delta=0.6875$ is negative indicating an *attractive* overlap interaction for a wave function near that of the free H⁻ ion, but a repulsive H⁻-H⁻ interaction is obtained for a more contracted wave function ($\delta \geq 0.82$).

Our first model contains four variable parameters: the H⁻ screening parameters δ_{+-} and δ_{--} for first- and second-nearest neighbors and the noncentral force parameters k_{+-} and k_{--} ($=k_{++}$). The Born-Mayer coefficients for the Li⁺-Li⁺ interaction were fixed at their free-ion values, $A_{++}=1610.0$ eV/(ion pair) and $B_{++}=7.2910$ Å⁻¹, the assumption being that such tightly bound charge distributions will not be much affected by the crystalline field. The effective ionic charge Z was fixed at 0.875e according to the experimental results of Pretzel¹⁰ and Calder¹¹ and the seven-parameter

shell-model calculations of Verble *et al.*¹ As was pointed out by Verble *et al.*,¹ this value is also consistent with the value of the Szigeti effective charge reported by Filler and Burstein.⁵

Our second model, chosen to fit the interionic distance accurately so that phonon dispersion curves could be calculated, is a first-nearest-neighbor model only, and hence contains only two adjustable parameters, δ_{+-} and k_{+-} . The reason why such a model fits r_0 better than model I is that the second-nearest neighbor (H⁻-H⁻) interaction is *attractive* and thus the interionic distance turns out to be lower than the experimental value. Of course, other values of the four parameters used in model I could also fit r_0 , but a wide variation of these parameters indicated that, if an exact agreement with r_0 is required, then one does not substantially improve the agreement with the elastic constants with such a model over the fit obtained using a simple first-neighbor model.

Following the Fuchs method of evaluating the elastic constants,¹² we derived the following expressions for the shear elastic constants $C_{11}-C_{12}$ and C_{44} and the bulk modulus B for first- and second-neighbor interactions:

$$C_{11}-C_{12} = \frac{1}{2v_a} [2(1 + \frac{2}{5}k_{+-})(r_0^2\phi_{+-}'' + r_0\phi_{+-}') + \frac{1}{2}(1 - \frac{1}{10}k_{--})(r_1^2\phi_{--}'' + 7r_1\phi_{--}') + 6k_{--}\phi_{--} + \frac{1}{2}(1 - \frac{1}{10}k_{++})(r_1^2\phi_{++}'' + 7r_1\phi_{++}')] + 6k_{++}\phi_{++}] - \frac{5.31Z^2}{4r_0^4}, \quad (3a)$$

$$C_{44} = \frac{1}{2v_a} [2(1 + \frac{2}{5}k_{+-})r_0\phi_{+-}' - 8k_{+-}\phi_{+-} + \frac{1}{2}(1 - \frac{1}{10}k_{--})(r_1^2\phi_{--}'' + 3r_1\phi_{--}') + \frac{1}{2}(1 - \frac{1}{10}k_{++})(r_1^2\phi_{++}'' + 3r_1\phi_{++}')] + \frac{2.55Z^2}{4r_0^4}, \quad (3b)$$

⁹ F. C. Von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).

¹⁰ R. E. Pretzel, G. N. Reysert, C. L. Mader, E. K. Storms, G. V. Gritton, and C. C. Rushing, J. Phys. Chem. Solids **16**, 10 (1960).

¹¹ R. S. Calder, W. Cochran, D. Griffiths, and R. D. Londe, J. Phys. Chem. Solids **23**, 621 (1962).

¹² K. Fuchs, Proc. Roy. Soc. (London) **A153**, 662 (1936); **A157**, 444 (1936).

TABLE II. Parameters of the models.

	Model I	Model II
δ_{+-}	0.95	0.95
δ_{--}	0.6875	...
k_{+-}	-0.50	-0.55
$k_{--}(=k_{++})$	1.0	...
A_{+-} , eV/(pair)	293.26	293.26
B_{+-} , \AA^{-1}	3.3968	3.3968
A_{--} , eV/pair	-13.50	0
B_{--} , \AA^{-1}	1.8101	...

$$B = \frac{1}{3v_a} [(1 + \frac{2}{5}k_{+-})(r_0^2\phi_{+-}'' - 2r_0\phi_{+-}') + (1 - \frac{1}{10}k_{--})(r_1^2\phi_{--}'' - 2r_1\phi_{--}') + (1 - \frac{1}{10}k_{++})(r_1^2\phi_{++}'' - 2r_1\phi_{++}')] - \frac{2\alpha_M Z^2}{9r_0^4}, \quad (3c)$$

where r_0 is the interionic distance, $v_a = r_0^3$ (atomic volume), $\alpha_M = 1.7476$ (Madelung constant), and $r_1 = \sqrt{2}r_0$ (second-nearest-neighbor distance). The last terms of Eq. (3) are the electrostatic contributions and were taken from the work of Price.¹³ The primes in Eq. (3) indicate derivatives evaluated at the experimental value of $r_0(r_1)$ for the first- (second-) nearest-neighbor interactions. Since the interionic distance was determined independently of the elastic constants, care was taken to include the nonequilibrium contributions to the elastic constants. The expressions, therefore, reduce to those obtained by Huntington¹⁴ for fcc metals when the first-nearest neighbors and the noncentral force parameters are absent, with the exception of the non-equilibrium contribution. The binding energy U_0 and the theoretical interionic distance r_0 were determined from the usual relations.⁷

The four previously described parameters in model I were varied over a wide range to obtain C_{11} – C_{12} , C_{44} , B , r_0 , and U_0 with the least-sum-of-squares error. Since no experimental results are available for C_{12} , the well-known relation

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

was used to obtain C_{11} – C_{12} . The same procedure was followed in determining the two parameters in model II. The values of the parameters for each model are given in Table II, and the elastic constants, binding energies, and interionic distances appropriate to each model are given in Table III.

Using the Kellerman⁸ formalism modified to include the noncentral forces, the phonon dispersion curves of ^7LiD were calculated for model II. No attempt was made to fit any of the experimental phonon data and

¹³ W. J. Price, Phys. Rev. **72**, 514 (1947).

¹⁴ H. B. Huntington, Phys. Rev. **91**, 1092 (1953).

dipoles were not included in the calculation. The results are given in Fig. 1 for values of the reduced wave vector along the three principal directions indicated within the first Brillouin zone. The agreement with experiment for the acoustical modes is satisfactory, but the optical modes are entirely too high,^{1–3} which is not surprising for a model which excludes distortion dipoles. The acoustic branches are slightly high, but this is a consequence of the disagreement between the elastic constants given by model II and those predicted by the neutron scattering data. The same discrepancy exists between the compressibility predicted by the phonon dispersion measurements of Verble *et al.*¹ and the compressibility measured by Stephens and Lilley.¹⁵ That is, when the values of C_{11} and C_{12} obtained from the shell model are used in Eq. (4) to compute the compressibility (see Table III) the result is 40% above that given by the direct measurements of compressibility. It is not surprising, then, that model II, which gives too low a value for compressibility, does not predict the phonon dispersion curves exactly. It was not felt worthwhile to fit our model II parameters to the phonon dispersion results until further experiments better establish the value of the compressibility.

III. He MIGRATION

Recent experiments by Holt¹⁶ on the activation energy for diffusion of He in LiH indicate that 1.2 eV is required for the bulk diffusion process. Using the models determined in the previous section, we calculated the energies of formation of a He atom placed in the face-centered- and in the body-centered-cubic positions in the crystal. The method is that developed by Hatcher and Dienes¹⁷ and extended by Wilson *et al.*,¹⁸ in which the total energy relative to the perfect

TABLE III. Comparison of elastic constants, binding energies, and interionic distances for various models of ^7LiD .

	Experiment	Verble, Warren, and Yarnell ^a	This work Model I	This work Model II
$C_{11}, 10^{12} \text{ dyn/cm}^2$	0.626 ^b	0.693	0.646	0.759
$C_{12}, 10^{12} \text{ dyn/cm}^2$	0.214 ^c	0.030	0.210	0.355
$C_{44}, 10^{12} \text{ dyn/cm}^2$	0.419 ^b	0.471	0.424	0.479
$C_{11} - C_{12}, 10^{12} \text{ dyn/cm}^2$	0.412 ^c	0.663	0.436	0.404
$B, 10^{12} \text{ dyn/cm}^2$	0.351 ^d	0.251 ^e	0.355	0.490
$K(=1/B), 10^{-12} \text{ cm}^2/\text{dyn}$	2.85	3.98	2.82	2.04
$r_0, \text{\AA}$	2.03465 ^e	...	1.951	2.034
$U_0, \text{eV}/(\text{ion pair})$	-9.449 ^e	...	-8.50	-8.10

^a Reference 2.

^b S. P. Marsh as reported by Verble *et al.* (Ref. 2).

^c Obtained using Eq. (4).

^d Reference 14.

^e F. E. Pretzel, D. T. Vier, E. G. Sklarz, and W. B. Lewis, Los Alamos Scientific Laboratory Report No. LA-2463, 1961 (unpublished).

¹⁵ D. R. Stephens and E. M. Lilley, J. Appl. Phys. **39**, 177 (1967).

¹⁶ J. B. Holt (private communication).

¹⁷ R. D. Hatcher and G. J. Dienes, Phys. Rev. **124**, 726 (1961).

¹⁸ W. D. Wilson, R. D. Hatcher, R. Smoluchowski, and G. J. Dienes, Phys. Rev. **184**, 844 (1969).

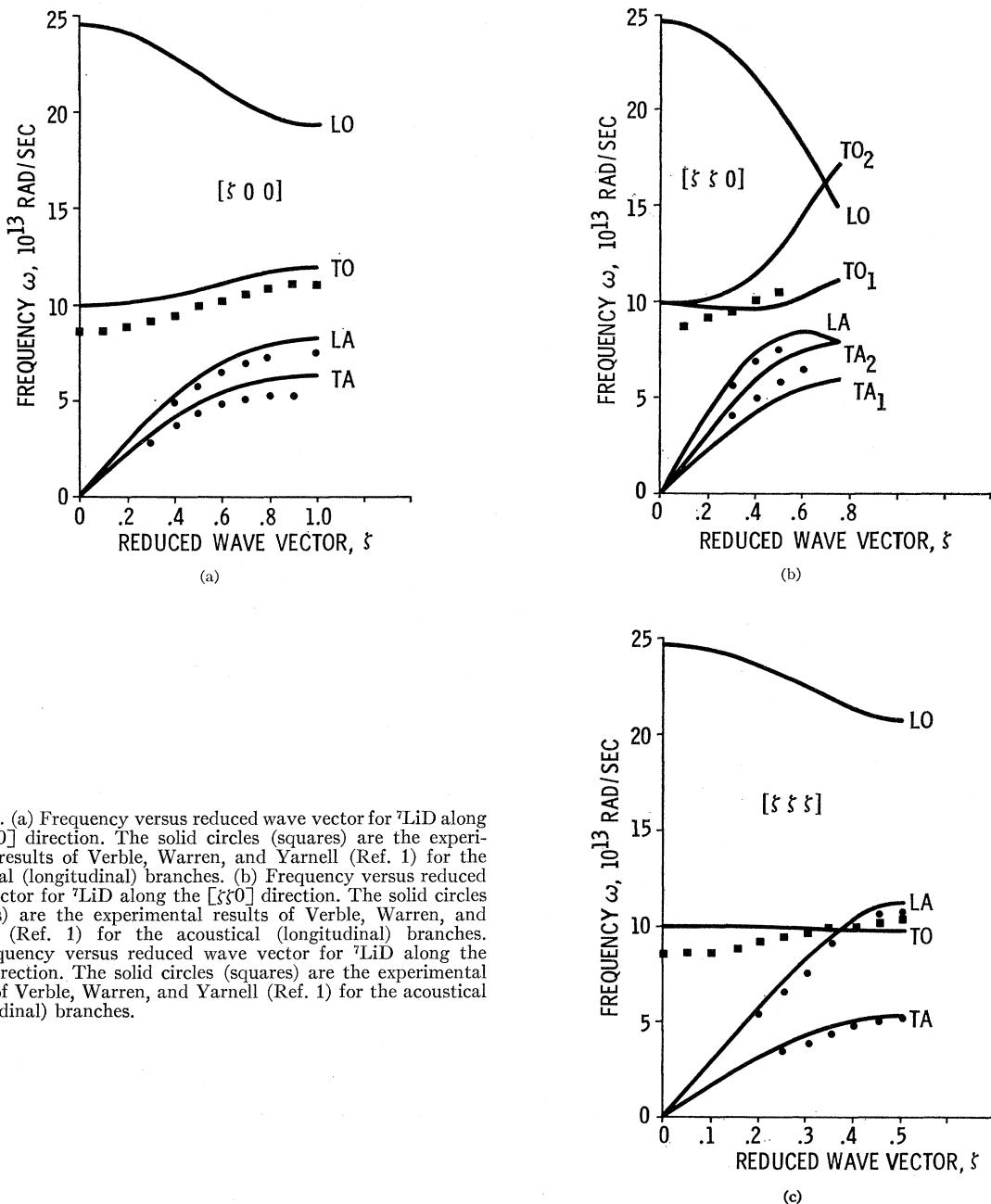


FIG. 1. (a) Frequency versus reduced wave vector for ^7LiD along the $[\xi 00]$ direction. The solid circles (squares) are the experimental results of Verble, Warren, and Yarnell (Ref. 1) for the acoustical (longitudinal) branches. (b) Frequency versus reduced wave vector for ^7LiD along the $[\xi\xi 0]$ direction. The solid circles (squares) are the experimental results of Verble, Warren, and Yarnell (Ref. 1) for the acoustical (longitudinal) branches. (c) Frequency versus reduced wave vector for ^7LiD along the $[\xi\xi\xi]$ direction. The solid circles (squares) are the experimental results of Verble, Warren, and Yarnell (Ref. 1) for the acoustical (longitudinal) branches.

lattice is expressed as a function of the displacement parameters describing the relaxations about the defect. This total energy is the sum of the electrostatic E_s , polarization E_p , and repulsive E_r energies. Attempts were made to include the same number of ions in each calculation so that the relative energies of the face- and cube-centered defects would have meaning although the symmetry prevents exact agreement. Therefore, 28 ions surrounding each position were allowed to relax with 6(13) displacement parameters required to describe the relaxations in the cube- (face-) centered posi-

tions. A larger region was allowed to polarize—104 ions in the face-center case and 108 ions in the cube-center case. The polarization energy contributed to each “shell” or set of ions having the same symmetry relative to the defect, was calculated in order to insure that this small difference in the number of polarizable ions does not effect the activation energy.

In order to avoid the possibility of a “polarization catastrophe,” that is, a situation where the repulsive energy is insufficient to prevent a small ion from relaxing beyond physically reasonable bounds, we let the anions

TABLE IV. Nearest-neighbor displacement parameters and energies relative to the perfect lattice for He^0 face- and cube-centered configurations.^a

	Model I		Model II	
	Face	Cube	Face	Cube
P_1	0.145	0.07	0.145	0.08
P_2	0.185	0.15	0.200	0.185
E_s	-2.42	-2.14	-3.68	-3.57
E_p	-4.46	-7.76	-5.93	-10.04
E_r	9.51	11.84	11.15	14.28
E_t	2.63	1.94	1.54	0.67
Activation energy	0.69		0.87	

^a Energies given in eV.

have a variable polarizability. In calculations for the properties of Li^+ in KCl , Quigley and Das¹⁹ argued that the polarizability of the Cl^- ion is proportional to the distance to a neighboring Li^+ . Thus, we let the polarizability of the H^- ions vary linearly with the shortest distance of approaching to a neighboring ion and obtain 1.90 \AA^3 (1.45 \AA^3) for the cube- (face-) centered case in the minimum-energy configuration. Further justification of the linear form is provided by the quantum-mechanical calculations of Goldberg.²⁰

The overlap interactions between $\text{He}-\text{H}^-$ and $\text{He}-\text{Li}^+$ were taken from Fischer²¹ who calculated them using an H^- screening parameter of 0.95. This value of δ is consistent with our first-nearest-neighbor Li^+-H^- values in each model.

¹⁹ R. J. Quigley and T. P. Das, Phys. Rev. **164**, 1185 (1967).

²⁰ C. Goldberg (private communication).

²¹ C. R. Fischer (private communication).

The energies and displacement parameters for the first-nearest neighbors of the He in the face- and cube-centered positions for models I and II are given in Table IV. Parameters P_1 and P_2 in the table are the cartesian coordinates of the outward displacements of the H^- and Li^+ ions nearest to the He, respectively, in units of the interionic distance, r_0 . In the cube-centered case [He at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$], the x , y , z displacements are the same; in the face-centered case [He at $(\frac{1}{2}, \frac{1}{2}, 0)$], the z component is zero. Note that P_1 and P_2 are larger in the face-centered case for each model, which is consistent with the closer packing in that configuration. The Li^+ ions move more than the H^- ions in all cases because of their smaller size. If one assumes that the cube-centered configuration is the most stable configuration for a He atom in LiH , and that the face-centered configuration represents the saddle-point configuration for He migration, the activation energy for migration is 0.69 eV and 0.87 eV for models I and II, respectively—values quite close considering the difference in the models. Both of these values are lower than the experimental value of Holt¹⁶ indicating that some other mechanism besides normal interstitial diffusion is operative in LiH . That is, the movement of He atoms may be impeded by trapping in vacancies or in vacancy clusters through the crystal.

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