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Thermal expansion and zero-point displacement in isotopic lithium hydride

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The effect of substitution of one isotope for another in the lithium hydride crystal has been investigated by means of the localized-continuum model introduced in earlier publications in connection with calculations of elastic properties, thermal expansion, and melting phenomena. Theoretical analysis demonstrates that the observed lattice parameters can be accounted for within the experimental error and the accuracy of the Debye approximation by a combination of the effects of the zero-point displacement and thermal expansion. The contributions of both quantities vary for the different isotopic forms according to different values of the Debye temperature, which in turn varies approximately as the inverse square root of the cation-ion reduced mass. In addition, the analysis elucidates the nature of the quantized thermal oscillators in crystals.

I. INTRODUCTION

The lattice parameter at any given temperature is determined by three different contributions. First and most obvious is the size of the atomic radii and the nature of the chemical bonding between them, which are most important in determining interatomic spacings and crystal structure. Second is the effect of temperature on the distance between atoms which normally produces a volume expansion with increasing temperature. Finally, there is the effect of the zero-point displacement, which is a purely quantum effect having no classical analog. This last contribution results from the fact that the lowest-energy state of the system, the zero-point energy, generally corresponds in an anharmonic potential to an atomic displacement somewhat larger than that associated with the potential minimum.

Since the zero-point displacement is usually a small contribution to the lattice parameter at 0 K, its contribution is often ignored, particularly since its magnitude is difficult to determine experimentally. An important exception, however, are the crystals which are isotopic variants of lithium hydride. Since they are chemically identical, the contribution to the lattice parameters due to the atomic radii and chemical bonding may be taken as constant in all of them. Consequently, the differences in the lattice parameters at various temperatures may be attributed solely to differences in the thermal expansion and the zero-point displacement. As it happens, these differences are relatively large in these crystals mostly because of the large relative differences in the atomic masses in the three isotopic forms of hydrogen, and the relatively large changes which these produce in the anion-cation reduced masses. Because of this, the contributions of the zero-point displacements are accessible to evaluation and theoretical analysis in a way which would be quite difficult in other crystals.

Various investigators[1-4] have experimentally examined the effect of isotope substitution on the lattice parameter of the LiH crystal. These investigations demonstrate that the isotope effect on the lattice parameter and coefficient of thermal expansion shows a definite trend in which the lighter isotopes produce larger lattice parameters and smaller coefficients of thermal expansion than the heavier isotopes. The effects are more pronounced when the lighter element is substituted and at low temperatures. In addition, an interesting relationship between the lattice parameter a_0 and cation-anion reduced mass μ for the isotopic lithium hydrides was found[4] which is valid at any given temperature with a_0 expressed in units of 10^{-8} cm:

$$a_0 = A\mu^{-1/2} + B \, , \tag{1}$$

where the constants A and B are different for different temperatures.

An early explanation of the lattice-parameter differences[5] used the Debye theory to relate energy differences to the observed differences in thermal expansion. A more elaborate theory[6] related the change in molar volume induced by isotopic substitution to various thermodynamic variables evaluated empirically and from earlier quantitative work on NaCl. In the simpler treatment,[5] the use of the Debye temperature $\Theta_{\mathrm{LiH}} = 815$ K determined from experimental specific-heat data and $\Theta_{\mathrm{LiD}} = 611$ K from an assumed dependence on $\mu^{-1/2}$ yielded a plausible explanation mirrored in the more elaborate treatment[6] for the observed differences in thermal expansion. These differences produce the different lattice parameters since a lower Debye temperature produces a larger specific heat at low temperatures, and through the Grüneisen relation, a larger coefficient of thermal expansion. This effect diminishes at high temperatures. While partly successful, however, these analyses require empirical evaluation of thermodynamic variables and lack a detailed treatment of the zero-point displacement.

In this work, we will examine the lattice parameters of the various isotopic forms of LiH by means of the localized-continuum model which has been applied successfully to calculations of elastic properties, thermal expansion, and melting phenomena.[7–11] The motivation behind this model was to retain as much as possible of the usual picture of harmonic vibrations in the crystal, while at the same time introducing an anharmonic potential whose descriptive parameters would characterize both thermal expansion and elastic properties. This thermal potential was chosen to have the form of the Morse potential

$$V(r)=D\{1-\exp[-a(r-r_0)]\}^2$$

to take advantage of its known quantum-mechanical solutions. The lattice parameters will be calculated from the thermal-expansion formulas already derived from this model and the expression for the zero-point displacement which will be introduced in the next section. Results of the calculations will be shown to be within the experimental error and the accuracy of the Debye approximation. Moreover, the form of the lattice parameters will be seen to be approximately of the form of Eq. (1), with the Debye temperature approximately proportional to $\mu^{-1/2}$. This latter result is consistent with an earlier empirical observation that the Debye frequency of a wide range of monatomic and binary crystals is approximately proportional to the anharmonic force constant between adjacent atoms in the crystal. An additional result of the analysis is the conclusion that the observed lattice parameters confirm the three-dimensional nature of the quantized thermal oscillators.

II. CALCULATION OF THE LATTICE PARAMETER IN ISOTROPIC LiH

Since LiH has the NaCl structure, the lattice parameter as a function of temperature is simply $a_0(T)=2r_n(T)$ where r_n is the nearest-neighbor distance and is given by

$$r_n(T)=r_0+r_0'+\frac{\Delta l}{l}r_n(0)\ . \tag{2}$$

The leading contribution r_0 arises from the sizes of the atomic radii and the nature of the chemical bonding between them, and represents the position of the minimum of the thermal potential. The second term is the contribution of the zero-point displacement which is independent of temperature, while the last term gives the contribution from thermal expansion.

Formulas for the thermal expansion have been derived[7,8] based on the localized-continuum model in which the expressions are represented as expansions in inverse powers of D. The first two terms for the linear expansion, which are sufficient for our purposes, are

$$\left[\frac{\Delta l}{l}\right]_0=\frac{3kT}{2ar_nD}\left[\frac{T}{\Theta_D}\right]^3 f(x_D)\ , \tag{3}$$

$$\left[\frac{\Delta l}{l}\right]_1=\frac{3kT}{2ar_nD}\frac{kT}{4D}\left[\frac{T}{\Theta_D}\right]^3 f_1(x_D)\ , \tag{4}$$

where

$$f(x_D)=\int_0^{x_D}\frac{x^3dx}{e^x-1}$$

and

$$f_1(x_D)=\int_0^{x_D}\frac{x^4(1+e^x)dx}{(e^x-1)^2}\ .$$

The thermal expansion is then a function of the parameters of the Morse potential D and a (or ar_n) and the Debye temperature $\Theta_D=Tx_D$.

The contribution of the zero-point displacement may also be calculated with this model as a function of the same parameters. The leading contribution to the zero-point displacement of a Morse oscillator is given by[7] $3\hbar\omega/8aD$. Averaged over the Debye-frequency distribution, one gets for the average zero-point displacement of the crystal the result

$$\begin{aligned} r_0' &= \frac{3kT}{2aD}\left[\frac{T}{\Theta_D}\right]^3\int_0^{x_D}\frac{3}{4}x^3dx \\ &= \frac{9k}{32aD}\Theta_D \end{aligned} \tag{5}$$

Given the parameters of the thermal potential and the Debye temperature, the lattice parameters can be calculated if r_0 is deduced from the low-temperature data by using Eqs. (3)–(5). Since the Debye temperature has been obtained from specific-heat data only for naturally occurring LiH,[12] an experimental test of its relationship with the reduced mass is unavailable. The experimental data above 20 K have been interpreted as being consistent with a Debye temperature of 850 K,[12] although direct calculation using the data below 10 K gives an average value of 776 K. It should be remembered that because of the nature of the Debye approximation, the value of the

Debye temperature fluctuates significantly with temperature. The low-temperature thermal-expansion data for ^{6}LiD which is compared with previously obtained data[13] for LiH is consistent with a Debye temperature varying as $\mu^{-1/2}$ from the above values. Consequently, this relationship was used to make the small corrections due to thermal expansion at 83 K. The corrections themselves are generally smaller than the scatter in the values of B as determined from Eq. (1), so that the value of r_0 is completely uncertain in the last decimal place. The average of the values obtained is $2r_0=3.9941$.

The first step in the calculation is the evaluation of the parameters of the thermal potential. Procedures for doing this have been set forth[8,9] for insulating crystals. To achieve accuracy, however, it is easier to make a comparison of LiH with previous calculations on LiF. Previous work suggests that two crystals having the same crystal structure and lattice parameter should have essentially the same values for the thermal-potential parameters. With the use of thermal-expansion data for LiF, the low-temperature value of r_n for this crystal is 2.00, which is virtually the same as the values for the various forms of LiH after the large and widely varying values of the zero-point displacement are subtracted out. Consequently, the values of D and a will be assumed to be the same for the two crystals. The calculated values[8] for LiF are $D=0.52$ eV and $ar_n=1.98$. However, the calculated values of the thermal expansion for LiF are about 3% smaller than the observed values. Since the calculated values are proportional to $(Dar_n)^{-1}$ except at high temperatures, we conclude that the calculated $Dar_n=1.03$ is too large by 3%. The correct value then should be $2Da=1.00$ for LiF, with D again taken as 0.52 eV. These values will also be used for LiH. With these values for the parameters one can compute the melting temperature of LiH as a check on their accuracy. Using a theoretical formula[10] which has been found to be valid for a wide range of cubic binary insulating crystals having group-a metal ions, we obtain a predicted value $T_m=1020Dar_n=1037$ K in rather good agreement with the observed value 956 K.

The problem of the choice of Debye temperatures was handled in two steps. First, a Θ_D for ^{6}LiH was determined by a self-consistent calculation of the lattice parameter at 83 K which assumed that the Debye temperature is the same for both the zero-point displacement and the low-temperature thermal expansion. The value obtained is that for which the calculated lattice parameter agrees with the observed value. It was found to be 744 K in fairly good agreement with the value obtained from low-temperature specific-heat measurements. Next, the lattice parameters for the higher temperatures were calculated using this same Θ_D. The lattice parameters for the other crystals were then calculated by assuming that the Θ_D for each crystal varies as $\mu^{-1/2}$. The results of this calculation are listed in Table I with the experimental values[4] included for comparison. Next, a separate calculation was made in which the Debye temperature was determined for each observed value of the lattice parameter to bring the calculations into agreement with observation. These results are displayed in Table II, and represent a check on the first set of calculations and on the degree of variability of Θ_D.

Examination of the results in Table I reveals that the assumption of the $\mu^{-1/2}$ variation of Θ_D fits the observed data quite well. From Table II we can infer that the Debye temperatures follow the basic trend encountered in the specific-heat data, in that they increase by about 10% from 0 K to room temperature. The relationship between Θ_D and the reduced mass agrees with an empirical observation[8] that the Debye frequency is approximately proportional to the frequency associated with the anharmonic force constant which for the Morse potential

TABLE I. Calculated and observed lattice parameters for isotopic LiH. The observed values are in parentheses and are taken from Ref. 4.

Isotopic			Lattice parameters			
composition	$\mu^{-1/2}$	Θ_D (K)	83 K	298 K	413 K	513 K
^{6}LiH	1.0763	744	4.0666	4.0851	4.1019	4.1181
			(4.0666)	(4.0851)	(4.1013)	(4.1218)
^{6}LiH	1.0652	736	4.0659	4.0845	4.1013	4.1175
			(4.0657)	(4.0829)	(4.1005)	(4.1224)
^{6}LiD	0.8139	563	4.0495	4.0732	4.0915	4.1086
			(4.0499)	(4.0708)	(4.0888)	(4.1110)
^{7}LiD	0.7993	553	4.0486	4.0725	4.0909	4.1080
			(4.0477)	(4.0693)	(4.0893)	(4.1119)
^{7}LiT	0.6886	476	4.0416	4.0680		
			(4.0403)	(4.0633)		

TABLE II. Calculated values of the Debye temperature in K for isotopic LiH at various temperatures based on the observed lattice parameters. The values at 83 K and for the zero-point displacement are assumed to be the same.

Isotopic composition	Zero point	298 K	413 K	513 K
^{6}LiH	744	744	762	657
^{7}LiH	734	789	764	625
^{6}LiD	567	622	618	506
^{7}LiD	544	622	579	467
^{7}LiT	464	566		

is $a(2D/\mu)^{1/2}$. Since the Einstein and Debye approximations give virtually the same specific-heat curves except at low temperatures if one chooses $\Theta_E = 0.75\Theta_D$, a choice which gives identical values of the zero-point energy, it is not too surprising that the Debye frequency can be approximated by the use of a single-force constant and the reduced mass.

III. THE THREE-DIMENSIONAL NATURE OF THE QUANTIZED THERMAL OSCILLATORS IN CRYSTALS

Because the zero-point displacement is a purely quantum phenomenon, the information obtained from the above analysis can be used to elucidate the nature of the quantized thermal oscillators in crystals. In using the wave functions for the interatomic potential, different results are obtained for the matrix elements depending on whether there is one- or three-dimensional motion between atoms. If the atoms can rotate freely in three dimensions, the solutions are those of the three-dimensional wave equation with interatomic potential of the form $V(r-r_0)$. As is well known, the wave equation is separable, with the wave function having the form

$$\psi(r,\vartheta,\phi) = r^{-1}R(r)\Theta(\vartheta)\Phi(\phi) \ .$$

For s states, the three-dimensional wave equation for $R(r)$ resembles the one-dimensional wave equation, but there is a fundamental difference in the solutions because $0 \le r < \infty$, whereas $-\infty < x < \infty$. Superficially, it might appear that the one-dimensional solutions are more appropriate for the diatoms in the crystal since their motion is primarily confined to the vicinity of a single axis. However, we will see that this is not the case, and that the actual situation is confirmed by the experimental information concerning the zero-point displacement in isotopic LiH.

As a practical matter, the great differences between the one- and three-dimensional cases occur because of symmetry conditions on the matrix elements,[14] since r does not take on negative values. The solutions for the three-dimensional free-rotator vibrator have been considered in detail for several different potential functions.[15] Because of the separability of the wave equation, the vibrator and rigid-rotator problems can be considered separately to a first approximation, with the radial wave functions for the Morse potential well characterized. In the case when free rotation is not allowed, but rather limited to the vicinity of the z axis, the model Hamiltonian is $H_0 + V(\vartheta)$, where H_0 is the free rotator-vibrator Hamiltonian and $V(\vartheta)$ restricts the rotation to the vicinity of the z axis. A particular form of $V(\vartheta)$ that has been considered for the rigid rotator is $V_0(1-\cos 2\vartheta)$.[15] The solution associated with this Hamiltonian is also separable.

The use of the three-dimensional hindered rotator-vibrator Hamiltonian as a prototype of the three-dimensional motion of the diatoms in the crystal can now be tested by using the information concerning the zero-point displacement in isotopic LiH. Based on the assumption that the hindered rotation of the diatoms in the crystal do not appreciably change the solutions to the three-dimensional radial equation, the leading term in the displacement for the Morse potential was found[7] to be proportional to $2(m+\frac{3}{4})$, where m is the principal quantum number. The corresponding contribution for the one-dimensional case is proportional to $3(m+\frac{1}{2})$.[16] From this, we can see that the zero-point displacement which comes from the second term is the same in the two cases. However, the first term, which yields the leading contribution to the thermal expansion in this model is larger in the one-dimensional case by a factor of 1.5.

Thermal-expansion data alone cannot distinguish between these two possibilities since the parameter a of the potential can be adjusted to account for this factor.[17] However, if one combines information concerning both the zero-point displacement and the thermal expansion, the two cases are readily distinguishable. If the potential parameters are adjusted for the one-dimensional solution so that agreement is reached with thermal expansion in isotopic LiH, then the Debye temperatures are the same as those listed in Table II, except for the case of the zero-point displacement. For that case, the value for ^{6}LiH is 1116 K, with the values for the other crystals proportionally higher. These values are so inconsistently higher than the other values and those of the experimental specific heat that they must be rejected along with the one-dimensional solution. This then is an example where the slightest movement in three dimensions produces a quantum jump in an observable phenomenon compared with that associated with one-dimensional motion.

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[14] It should be remembered that the original solution for the three-dimensional Morse potential is approximate since it used what amounts to a one-dimensional boundary condition $-\infty < r - r_0 < +\infty$, although it is generally recognized to be quite accurate for most applications. The large differences between the one- and three-dimensional cases occur when symmetry considerations produce greatly different values for the matrix elements.

[15] See, for example, L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill, New York, 1935).

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[17] Adjustment of the value of Θ_D cannot reconcile the two cases since it does not affect the high-temperature thermal expansion and the connection between thermal expansion and melting discussed in Ref. 10.