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Quasiharmonic approximation applied to $LiBH_4$ and its decomposition products

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The quasiharmonic approximation has been applied to the potential hydrogen storage material $LiBH_4$ and its decomposition products. Whereas the lattice constants that minimize the DFT potential energy give good agreement with the experimentally observed values, minimizing the quasiharmonic free energy with respect to the lattice constants results in a significant overestimation. The enthalpy of dehydrogenation of $LiBH_4$, including vibrational effects, is calculated to be 59 ± 1 kJ/mol H_2 at 0 K, or 62.5 ± 1.1 kJ/mol H_2 at 298 K.

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I. INTRODUCTION

An area of active research is the search for practical hydrogen storage materials.[1–8] An important aspect of assessing potential hydrogen storage materials is the accurate determination of the change in enthalpy of the system upon hydrogen release. Through the van't Hoff equation, the magnitude of the enthalpy change largely determines the pressure and temperature conditions at which hydrogen storage systems based on the material can operate.[1]

For many materials density functional theory[9–11] (DFT) or other electronic structure methods can give a good prediction of the reaction energy of decomposition reactions. However, these methods are restricted to calculating the total potential energy change for the relevant reactions. Electronic structure theories cannot directly calculate the contribution of the zero point energy (ZPE) to the total enthalpy of the system without further analysis. The change in potential energy is a good approximation to the observable low temperature enthalpy change when the total ZPE of the reactants and products are approximately equal, and thus cancel. However, for many systems, and hydride storage systems in particular, the ZPE of the reactants and products are significantly different.[12] Hence including vibrational ZPE is important in these systems, with the ZPE-corrected reaction enthalpy change differing from the reaction potential energy change by a sizable amount.

The vibrational degrees of freedom that potentially affect the calculated enthalpy changes of reactions also control thermal effects, such as thermal expansion and phase transitions. Thermal expansion is driven by the system seeking the minimum Gibbs free energy as the temperature changes.[13] Phase transitions can be predicted by examining the Gibbs energy as a function of temperature. Of two competing phases, the most stable and hence usually the observed structure at any particular temperature is the phase with the lowest free energy. The temperature at which the free energy of the two phases are equal is the transition temperature.

The Gibbs free energy of a crystal under constant pressure conditions (explicitly including only vibrational entropy) can be written as

$$G = E_0 + pV + F_{\mathrm{vib}}, \qquad (1)$$

where E_0 is the potential energy, p is the external pressure, V is the volume, and F_{vib} is the vibrational free energy. Only F_{vib} depends explicitly on the temperature. The F_{vib} term also includes the vibrational ZPE, remaining finite as the temperature approaches zero. In this 0 K limit the free energy is identical to the enthalpy, H. For consistency with finite temperature calculations and in the spirit of Eq. (1) we continue to denote the zero temperature, ZPE-corrected enthalpy as G and refer to it as the free energy. For a periodic treatment of the crystal, all extensive properties of the system (that is, all quantities in the above equation except the external pressure p) are expressed in quantities per unit cell or per formula unit (hereafter expressed F.U.) and the relevant vibrations are phonons. Both E_0 and F_{vib} depend on the volume of the unit cell of the crystal, giving explicit volume dependence to the free energy, $G(V)$, at any particular temperature. The variation with volume of E_0 and F_{vib} is in general anisotropic so that the total free energy depends on the unit cell shape as well as on its volume. Thus writing the conventional lattice parameters as a vector $\mathbf{a}=(a,b,c,\alpha,\beta,\gamma)$, one can write $G(\mathbf{a})$ for the free energy, showing the explicit dependence on the lattice parameters rather than just the volume. While $\mathbf{a}$ may be constrained by the symmetry of the point group of the crystal, we maintain this general notation $G(\mathbf{a})$ for the free energy calculated with the lattice parameters treated as independent variables, not determined solely by the volume (as discussed below).

Exact calculation of the free energy for an anharmonic crystal is difficult. Instead, the quasiharmonic approximation is often used.[14] In the quasiharmonic approximation, for any particular set of lattice parameters the correct potential energy for the system with relaxed atomic positions is used in conjunction with the harmonic vibrational free energy at that configuration. Thus some anharmonic effects are included through the potential energy, the changes induced in the atomic positions by the changes in the lattice parameters, and the lattice parameter dependence of the harmonic frequencies of the calculated vibrational modes. Usually the harmonic vibrational modes are softened as the size of the unit cell is increased.

Specifying the lattice parameters allows the straightforward optimization of the atomic positions by potential minimization. The phonon density of states, $g(\omega)$, under the influence of the interatomic interactions at that particular configuration, can then be calculated by a number of techniques. *Ab initio* phonon densities of states can be calculated using the so-called direct method[15] or from linear response theory.[16] Once the phonon density of states is known the free energy of the harmonic phonons at temperature T can be calculated as[13]

$$F_{\mathrm{vib}} \approx F_{\mathrm{vib}}^{\mathrm{har}} = rk_BT\int_0^\infty g(\omega)\ln\left[2\sinh\left(\frac{\hbar\omega}{2k_BT}\right)\right]d\omega, \quad (2)$$

where r is the number of degrees of freedom, k_B is the Boltzmann constant, and $\hbar$ is the Planck constant divided by 2π. For periodic boundary conditions $F_{\mathrm{vib}}^{\mathrm{har}}$ is calculated for the r degrees of freedom per unit cell.

The method described above can be applied within a number of frameworks. The vibrational analysis can be performed at the lattice parameters that minimize the potential energy. This approach can give a ZPE correction to calculated energies,[12,17–20] but has been more commonly applied to study phonon dispersion.[21–26] To model thermal expansion[27–31] and phase transitions[20,30–32] the unit cell must be allowed to change, possibly as a function of temperature, though often it seems the volume dependence is neglected for temperature-dependent transitions.

To obtain the true constant pressure prediction for the quasiharmonic approximation, one should find the lattice parameters $\mathbf{a}$ that minimize the free energy $G(\mathbf{a})$, by varying the lattice parameters as independent variables. Any anisotropy in $F_{\mathrm{vib}}^{\mathrm{har}}$ is thus included explicitly rather than letting only the potential energy determine the cell shape. However, analyzing the gradient of G with respect to $\mathbf{a}$ is relatively difficult, as most implementations cannot evaluate the derivatives of $g(\omega)$, depending as they do on the derivatives of the atomic positions and force constants with respect to the lattice parameters. (Gradients of the free energy are available when using certain model potentials.[33]) For this reason the quasiharmonic approximation is often applied as a "volume-only method,"[27,34–36] in which $G(V)$ is minimized [as opposed to $G(\mathbf{a})$]. In this approach the vibrational contribution to the free energy is evaluated for a particular temperature at the lattice parameters that minimize the potential energy at a particular volume. That is, $G(V)$ is shorthand notation for $G[\mathbf{a}^\dagger(V)]$, where $\mathbf{a}^\dagger(V)$ is the vector of lattice parameters that minimizes the potential energy under the condition that the volume V remains constant. Repeating this calculation (minimization of the potential energy and calculating the free energy for that configuration) for a number of volumes yields a volume-dependent free energy curve for the target temperature. The volume that gives the minimum free energy on this curve for each temperature is then taken as the equilibrium volume and the corresponding, potential energy minimizing lattice parameters are taken to describe thermal expansion. No attempt is made to find a lower free energy by varying elements of $\mathbf{a}$ beyond those that minimize the potential energy for a given volume. This approach assumes that the contribution of the vibrational free energy to the total energy is isotropic. Note that the volume-only method is equivalent to the full minimization of $G(\mathbf{a})$ in the case of cubic crystals, where there is a one-to-one correspondence between the volume and the only independent lattice parameter (being the lattice constant of the cubic lattice).

In this work we investigate the potential hydrogen storage material $\mathrm{LiBH_4}$.[37,38] This material contains 18.4% hydrogen by mass (13.8% available without the high-temperature decomposition of LiH) and decomposes via the reaction

$$\mathrm{LiBH_4} \rightarrow \mathrm{LiH} + \mathrm{B} + \tfrac{3}{2}\mathrm{H_2}. \quad (3)$$

The room temperature structure is well established as an orthorhombic *Pnma* structure. A number of previous studies have investigated $\mathrm{LiBH_4}$ and the reaction described in Eq. (3) using DFT.[12,17,39–41] In these studies the geometry that minimized the potential energy broadly reproduced the experimentally derived structure. Some differences were evident, with the calculations predicting regular $[\mathrm{BH_4}]^-$ tetrahedra while the experimental fits suggest distorted tetrahedra. The enthalpy of dehydrogenation [Eq. (3)] has been calculated both with and without ZPE effects included.[12,39] In both sets of published results the reaction energy calculated from differences in total potential energy [75 kJ/mol $\mathrm{H_2}$ (Ref. 12), 71 kJ/mol $\mathrm{H_2}$ (Ref. 39)] was larger than that derived from experimental data[42] (69 kJ/mol $\mathrm{H_2}$) while applying ZPE corrections calculated from the harmonic phonon density of states at the potential minimum geometry yielded a predicted enthalpy change [56 kJ/mol $\mathrm{H_2}$ (Ref. 12), 52 kJ/mol $\mathrm{H_2}$ (Ref. 39)] smaller than that derived from experimental data.

In the following section we give some details of our computational method. Sections III and IV describe our determination of the equilibrium lattice parameters for $\mathrm{LiBH_4}$, LiH, and α-boron in the quasiharmonic approximation, including full free energy minimization. The reaction enthalpy for the decomposition of $\mathrm{LiBH_4}$ is presented in Sec. V, while the final two sections present some further discussion of the results and our conclusions.

II. COMPUTATIONAL DETAILS

The potential energy of the crystals was calculated using Kohn-Sham DFT.[9–11] The VASP program[43,44] was used to evaluate the total potential energy (the electronic and ion-ion energies) and its derivatives. Projector augmented wave (PAW) potentials[45–47] were used to represent the ionic potentials. The PW91 generalized gradient approximation (GGA) exchange-correlation functional[48] was used in general, with the local density approximation[49] (LDA) also being used in specified cases.

For the $\mathrm{LiBH_4}$ structure at the experimental geometry[50] and using the PW91 functional, a plane-wave cutoff of 1000 eV and a $6\times6\times6$ Monkhorst-Pack k-point grid[51] gave total energies converged to within about 1 meV per crystallographic unit cell. The same k-point sampling and a reduced plane-wave cutoff of 800 eV gave a similar level of convergence for the LDA calculations. For the other phases considered (LiH, α-boron, and $\mathrm{H_2}$) parameters were also selected to give convergence of the total energy at the experimental geometry to within about 1 meV. Lithium 1s electrons were included in the active space.

The free energies of the crystals were evaluated from the phonon densities of states calculated using the direct method[15] implemented in PHONON.[52] The direct method calculates the phonon density of states $g(\omega)$ of a crystal from the dynamical matrix constructed from the second derivatives of the total potential energy with respect to the atomic positions. The second derivatives are generally calculated by differencing, using the forces calculated for the crystal with atoms displaced from their minimum potential positions. While the direct method can be used to elucidate LO/TO splitting using elongated supercells,[53] no attempt was made to incorporate LO/TO splitting at the Γ point in this work. We do not expect this to lead to a significant error, as only a small region of reciprocal space would be affected by any such splitting which would have a very small effect on the Brillouin zone integration that leads to the phonon density of states, and thus the free energy.

The required supercell sizes for the phonon calculations were determined by examining the magnitude of the force constants at the edges of the supercells and by comparison with results from supercells extended in one direction. A 48-atom $1\times2\times1$ supercell was used for the phonon calculations on orthorhombic $LiBH_4$ and a cubic 64-atom $2\times2\times2$ supercell was used for LiH. For the covalent lattice of α-boron the crystallographic unit cell containing 12 atoms was found to be sufficiently large for the phonon calculations.

The implementation of the direct method that we used did not allow the evaluation of the gradient of the vibrational free energy. Thus the lattice parameters had to be optimized manually. Generally an alternating direction method was used, where steps were taken along one direction in lattice parameter space until the free energy along that direction was approximately minimized, before shifting to a new direction. Only a small number of iterations (cycling through the three degrees of freedom of the orthorhombic lattice) were required. Far from the minimum an explicit evaluation of the gradient of the free energy by differencing was found to be effective for determining search directions, making the procedure more steepest descent like.

Note that at external pressures similar to atmospheric pressure or less, changes in the pV term of Eq. (1) are negligible. A 10% change in the volume of $LiBH_4$ results in a change in the pV contribution to G of 0.003 meV/F.U. at 101 kPa. This is orders of magnitude smaller than changes in G due to other considered effects.

III. $LiBH_4$ LATTICE CONSTANTS

The free energy of the *Pnma* phase of $LiBH_4$ at 0 K was minimized using the potential energy and forces calculated with the LDA and PW91 functionals. The three lattice constants of the orthorhombic unit cell were varied as described above until the lattice constants that gave the minimum free energy were found. The tolerance to which the lattice constants were optimized was based on the estimated uncertainty in the free energy calculations. The free energy uncertainty was estimated by inspection of the variation in the calculated free energy with respect to a number of parameters, most notably the size of the atomic displacements used to evaluate the second derivatives of the potential, and from the Monte Carlo convergence involved in the evaluation of $g(\omega)$ with the direct method.

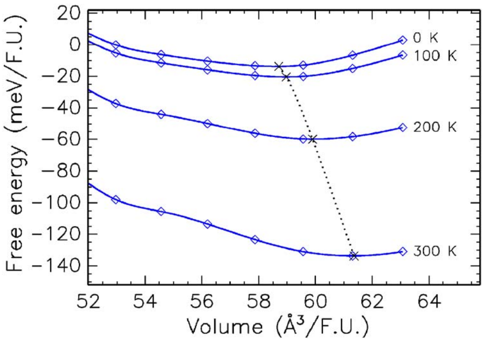

FIG. 1. (Color online) Free energy curves of $LiBH_4$ calculated using the volume-only method.

For the PW91 functional the optimal lattice constants were also calculated with the volume-only method, where $F_{\mathrm{vib}}^{\mathrm{har}}$ is assumed to be isotropic. This method has the advantages of being much less computationally demanding than the full search described above, and of providing predictions of thermal expansion without further calculations. The free energy curves from the volume-only approach are shown in Fig. 1. In this figure the solid lines show a spline interpolation of the discrete free energy calculations, from which the minimum energy volume for each temperature was determined. This thermal expansion trajectory is shown as the dotted curve.

The lattice constants determined using various methods are presented in Table I. In this table, the lattice constants labeled "Min. E_0" are those determined by stress minimization (with simultaneous atomic relaxation) on the DFT potential energy surface. This is the type of "optimal" lattice parameter usually reported from periodic electronic structure theory calculations for crystals. The lattice constants labeled "Min. $G(\mathbf{a})$" are those that minimize the quasiharmonic free energy after manually searching the lattice constant space. Those labeled "Min. $G(V)$" are from the volume-only method calculations, where the $a{:}b{:}c$ ratios as the unit cell increases in volume are not influenced by F_{vib}.

When compared to the experimentally-determined lattice constants, the traditional Min. E_0 lattice constants present a familiar scenario with respect to the exchange-correlation functional.[54] The LDA calculations produce lattice constants smaller than the experimentally-determined ones by a few percent, while the GGA PW91 results reproduce the experimental results well (with a slight tendency toward overestimation). However, adding the effect of zero point vibration in the quasiharmonic approximation changes that picture considerably. Both the LDA- and PW91-derived unit cells increase in volume on the addition of zero point effects, by 6% and 8%, respectively. While this increase is not sufficient to bring the LDA results into accord with the experimental lattice constants, the PW91 results can no longer be considered obviously superior to the LDA results. If one ignores any isotope effect and takes the consistently smaller $LiBD_4$ lattice constants determined at 10 K by Wenger *et al.*[55] to be a more accurate representation of the 0 K situation being modeled than the room temperature $LiBH_4$ results of Soulié *et al.*,[50] the cell volume predicted by the LDA calculations is

TABLE I. Lattice constants (Å) and cell volume (Å^3) for orthorhombic LiBH$_4$. Calculated free energy minimum values are for 0 K.

		a	*b*	*c*	Volume
PW91	Min. E_0	7.193	4.387	6.713	211.8
	Min. $G(\mathbf{a})$	7.55±0.07	4.52±0.04	6.71±0.04	229±6
	Min. $G(V)$	7.68	4.51	6.76	234
LDA	Min. E_0	6.983	4.203	6.350	186.4
	Min. $G(\mathbf{a})$	7.07±0.03	4.31±0.03	6.46±0.03	197±3
Expt.	LiBH$_4$[a]	7.179	4.437	6.803	216.7
	LiBD$_4$[b]	7.116	4.406	6.673	209.2

[a] X-ray powder diffraction, room temperature, Ref. 50.

[b] Neutron powder diffraction, 10 K, Ref. 55.

more accurate than that predicted by the PW91 calculations.

It is clear that the volume-only approach to minimizing G gives a free energy greater than or equal to that found by manual optimization; the two approaches only match if the zero point vibration effect is isotropic. This was borne out by the free energies actually calculated, with the free energy found at the manually-optimized $G(\mathbf{a})$ minimum representing a 5% greater relaxation from the free energy at the E_0 minimum than that found at the volume-only $G(V)$ minimum. In addition, the volume-only method predicts generally larger lattice constants than those at the true quasiharmonic free energy minimum, even further from the experimental values.

Wenger *et al.*[55] measured the rate and anisotropy of thermal expansion of *Pnma* LiBD$_4$. They found anisotropic expansion, with the *a* lattice constant increasing nearly linearly with temperature at a faster rate than the *b* and *c* constants. The *b* and *c* lattice constants exhibited complex behavior above 300 K. At 302 K the *a* constant had increased by 1.8% from its 10 K value, while the *b* and *c* constants both increased only 0.5%, yielding a total volume increase of 2.8%.

The quasiharmonic free energy minimum at 300 K was determined from PW91 DFT results by manually searching the lattice constant space. The resultant lattice constants are shown graphically in Fig. 2, along with the volume-only method results. Lattice constant increases at 300 K of (6±2)%, (2±2)%, and (0±2)% were observed for *a*, *b*, and *c*, respectively. Thus the quasiharmonic method does predict the experimentally observed preferential increase in the *a* lattice constant on heating, but significantly overestimates the degree of expansion. Though not reflecting the true quasiharmonic free energy minimum, the volume-only method gives percentage increases in the lattice constants at 300 K that are in closer accord with the experimental increases than the free energy minimum: 2.5%, 1.3%, and 0.9% increase for *a*, *b*, and *c*, respectively.

In this work the total ZPE of LiBH$_4$ was calculated to be 106.5±0.1 kJ/mol per unit cell at the potential minimum, in good agreement with the previous results of 108 kJ/mol calculated by Łodziana and Vegge[17] and 103 kJ/mol calculated by Miwa *et al.*[12] At the free energy minimum lattice constants this value dropped slightly to 104.9±0.1 kJ/mol.

The calculated internal coordinates of the atoms and selected interatomic distances are shown in Tables II and III for three sets of lattice constants: those that minimize the potential energy and those that minimize the free energy $G(\mathbf{a})$ at 0 K and 300 K. It can be seen from Table II that the atomic coordinates that minimize the potential energy do not depend strongly on the lattice constants in the region of the various minima, as one would expect. Two Li-B distances are shown in Table III, being distances between atoms connected by a line nearly parallel to the *a* axis (denoted [100]) and connected by a line lying in a plane nearly parallel to the {100} plane (denoted [011]). Consistent with previous DFT studies,[12,17,39] the calculated B-H distances do not show the strong distortion of the $[\mathrm{BH}_4]^-$ tetrahedra that is observed in published fits to powder diffraction patterns[38,50] (though recently a fit to neutron diffraction data was obtained without the strong distortion[55]). Note that bond length extension due to anharmonicity in the potential along B-H stretching modes is not captured in the quasiharmonic approximation,

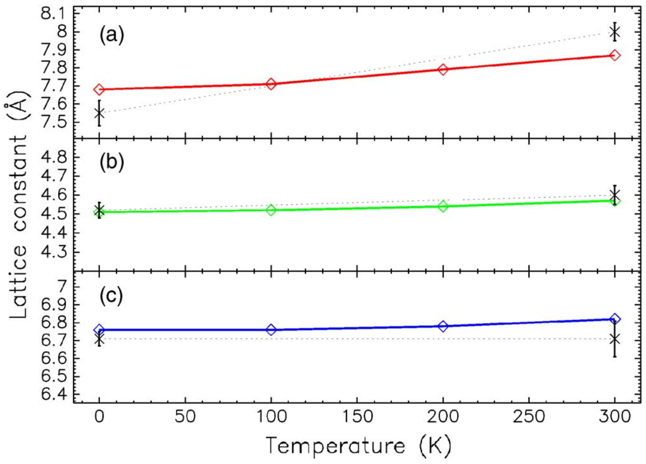

FIG. 2. (Color online) Calculated lattice constants of *Pnma* LiBH$_4$ upon heating. Solid lines show results from the volume-only method. Black crosses show the manually minimized lattice constants at 0 K and 300 K.

TABLE II. Internal atomic coordinates for $LiBH_4$ (space group *Pnma*, #62).

Site	Minimum	*x*	*y*	*z*
Li, 4c	E_0	0.1575	0.25	0.1114
	$G(\mathbf{a})$, 0 K	0.1557	0.25	0.1127
	$G(\mathbf{a})$, 300 K	0.1512	0.25	0.1158
	Expt.[a]	0.1568	0.25	0.1015
B, 4c	E_0	0.3071	0.25	0.4255
	$G(\mathbf{a})$, 0 K	0.3170	0.25	0.4196
	$G(\mathbf{a})$, 300 K	0.3291	0.25	0.4154
	Expt.[a]	0.3040	0.25	0.4305
H1, 4c	E_0	0.9080	0.25	0.9277
	$G(\mathbf{a})$, 0 K	0.9130	0.25	0.9327
	$G(\mathbf{a})$,300 K	0.9173	0.25	0.9354
	Expt.[a]	0.900	0.25	0.956
H2, 4c	E_0	0.4010	0.25	0.2728
	$G(\mathbf{a})$, 0 K	0.4073	0.25	0.2700
	$G(\mathbf{a})$, 300 K	0.4146	0.25	0.2631
	Expt.[a]	0.404	0.25	0.280
H3, 8d	E_0	0.2062	0.0258	0.4251
	$G(\mathbf{a})$, 0 K	0.2202	0.0293	0.4192
	$G(\mathbf{a})$, 300 K	0.2386	0.0342	0.4147
	Expt.[a]	0.172	0.054	0.428

[a] X-ray powder diffraction, room temperature, Ref. 50.

where atomic positions are determined solely by the position of the minimum potential energy. The interatomic distances of Table III show that the geometry of the $[BH_4]^-$ tetrahedra is not particularly sensitive to the free energy driven expansion of the lattice, which is consistent with the significantly-covalent bonding within the $[BH_4]^-$ tetrahedra being much stronger than the primarily ionic bonding between Li^+ ions and $[BH_4]^-$ tetrahedra. Thus one may expect that the $[BH_4]^-$ tetrahedra remain stable as $LiBH_4$ is heated through the observed polymorphic transition and toward, possibly even beyond, the melting temperature. Such hydride tetrahedra stability has recently been observed[56] for the related complex metal hydride $NaAlH_4$.

IV. LiH AND α-BORON LATTICE PARAMETERS

Clearly, the solid LiH and boron phases can also show a quasiharmonic free energy dependence on the lattice parameters. The rock salt structure LiH case is computationally simple to deal with from the point of view of minimizing the free energy, with the structure of the crystal being completely specified by a single lattice constant. There is no distinction between the volume-only method and any other quasiharmonic free energy minimization. The potential energy and the quasiharmonic free energy can be calculated from a scan of the lattice constant. Performing such a scan indicates that while the potential energy is minimized for a lattice parameter of 4.018 Å, the minimum of the 0 K quasiharmonic free

TABLE III. Selected atom-atom distances (Å) for $LiBH_4$.

Minimum	B-H1	B-H2	B-H3	Li-B "[100]"	Li-B "[011]"	B-B
E_0	1.224	1.228	1.222	2.533	2.536	3.676
$G(\mathbf{a})$, 0 K	1.224	1.229	1.225	2.543	2.594	3.696
$G(\mathbf{a})$, 300 K	1.226	1.230	1.229	2.585	2.669	3.749
Expt.[a]	1.035	1.250	1.286	2.542	2.521	3.706

[a] X-ray powder diffraction, room temperature, Ref. 50.

TABLE IV. Lattice constant (Å), rhombohedral angle and internal coordinates for α-boron (space group $R\bar{3}m$, #166).

	a	α	B1 x	B1 z	B2 x	B2 z
Min. E_0	5.0492	58.08°	0.0101	0.6541	0.2209	0.6309
Min. $G(\mathbf{a})$	5.07±0.01	58.1°	0.0099	0.6545	0.2203	0.6317
Expt.[a]	5.057	58.06°	0.0104	0.6573	0.2206	0.6323

[a]Reference 65.

energy occurs for a lattice parameter of 4.14±0.02 Å. Again the uncertainty is based on estimates of the variation of the free energy with the calculation parameters. The potential energy minimum lattice constant is smaller than the experimental value[57] of 4.07 Å and the free energy minimum lattice constant is again larger. While the increase in lattice constant on the inclusion of ZPE is of a similar magnitude to that calculated previously for LiH,[58–60] the final lattice constant calculated in this work was larger than previous determinations using similar methods. The lattice constants of 4.112 Å published by Barrera *et al.*[59] (PBE exchange-correlation functional) and 4.09 Å published by Herbst and Hector[60] (PW91 exchange-correlation functional) are both closer to the experimental value than the present result.

α-boron exhibited a much weaker ZPE effect on the 0 K structure than that observed for $LiBH_4$ and LiH. The expansion of the cell volume in going from the potential energy minimum to the free energy minimum was just 1.3%, compared to more than 10% for $LiBH_4$ and 9.4% for LiH. The difference can be rationalized on the basis that one would expect a greater ZPE effect in less rigid materials, combined with the observation that the bulk modulus of boron[61] is an order of magnitude larger than that of[41] $LiBH_4$ or LiH.[57] Possibly due to this low ZPE-driven expansion, the volume-only approach gave a structure virtually indistinguishable from the true quasiharmonic free energy minimum structure. Thus only one free energy minimum structure is listed in Table IV, which gives all the calculated structural parameters. Both the potential energy minimum and free energy minimum structures agree approximately equally well with the experimentally-derived structure. Note that no uncertainty is listed in Table IV for α, the rhombohedral angle. As the profile of the quasiharmonic free energy was quite flat as α was varied, this degree of freedom was not explored beyond the degree required to unambiguously identify the angle giving the minimum free energy. The uncertainty in this parameter, based on the observed variation of the free energy with respect to the phonon calculation parameters, is believed to be of the order of 0.1°.

V. ENTHALPY OF DEHYDROGENATION

The enthalpy change of the reaction described in Eq. (3) has been published previously by Miwa *et al.*[12] (PBE functional, 75 kJ/mol H_2 without ZPE corrections, 56 kJ/mol H_2 with ZPE correction) and by Frankcombe *et al.*[39] (PW91 functional, 71 kJ/mol H_2 without ZPE corrections, 52 kJ/mol H_2 with approximate ZPE correction). Both of these calculations were performed at the potential energy minimum.

The potential energy difference at the potential energy minimum structures calculated in this work was 81 kJ/mol H_2. Adding the effect of ZPE at this geometry yields a value for the enthalpy change at 0 K of 59±1 kJ/mol H_2. Calculating the internal energy of the solid phases at 298 K and incorporating ideal gas and rigid rotor contributions for hydrogen at 101.3 kPa, the standard enthalpy change was determined to be 62.5±1.1 kJ/mol H_2. These values compare to the experimentally derived, room temperature value of 68.9 kJ/mol H_2.[42] Note that the H_2 ZPE contribution (25.7 kJ/mol) was calculated by fitting a quadratic function to the potential energies calculated for H_2 molecules of various bond lengths in a box of edge length 12 Å. Note also that the difference between the potential energy change calculated previously using the same PW91 functional[39] and that calculated in this work may be due to differences between the ultrasoft pseudopotentials of the former and the PAW atomic potentials used in this work.[62]

To be consistent with the quasiharmonic approach the enthalpy change should be calculated at the lattice parameters that minimize the quasiharmonic free energy. However the energetic effect of the free energy minimization—as opposed to the structural effect—was quite small. While the potential energy difference at the free energy minimum structures was very slightly larger, a small increase in the calculated ZPE difference (primarily due to the LiH ZPE change outstripping that of $LiBH_4$) meant that the calculated low pressure enthalpy change was not effected, coming out again at 59±1 kJ/mol H_2.

VI. DISCUSSION

While the $LiBH_4$ lattice constants that minimize the potential energy using the PW91 GGA exchange-correlation functional agree well with the experimentally determined lattice constants, the free energy-minimizing lattice constants are considerably larger. The lattice constants obtained by minimizing the potential energy calculated with the LDA functional were shorter than the experimentally derived lattice constants, as expected. Including ZPE effects in the quasiharmonic approximation increased these lattice constants toward the experimental values. Indeed, the lattice constants given in Table I indicate that the PW91 and LDA functionals give values with similar levels of agreement to the experimental values. Only in the c lattice constant can the PW91 results be said to be superior to those calculated with the LDA, with the free energy minimizing lattice constant being of the order of 0.1 Å shorter than the experimental value determined by Soulié *et al.*,[50] compared to the LDA lattice constant being around 0.35 Å shorter. Indeed, the a lattice constant determined using the LDA lies significantly closer to the experimental value than that determined using the PW91 functional.

This work fits with a trend observable in the literature. It is well established that GGA functionals usually predict larger lattice constants that minimize the potential energy than the LDA, often giving better agreement with experimental values.[54] The addition of vibrational effects by minimizing the free energy usually leads to larger lattice constants.[27,29–31,58,59,63] Thus one should carefully assess calculations that show good agreement with experimental lattice constants if vibrational effects have not been included. Particularly for compounds containing light elements where ZPE effects are strong, inclusion of vibrational effects are likely to lead to larger lattice constants which may decrease the agreement with experimental data. This has recently been demonstrated for a range of alkali hydrides.[59]

There is considerable anisotropy in the harmonic free energy with respect to the material lattice constants. This is reflected in the different lattice constants determined by treating the free energy as a function of volume only (with the $a:b:c$ ratios being determined by the underlying potential energy surface) or by minimizing $G(\mathbf{a})$ with respect to a, b, and c. This should come as no surprise given the differences in the lattice constants—the a/b ratio is greater than 1.6—and the lack of equivalent directions in the orthorhombic *Pnma* space group.

There is also experimental evidence of anisotropic free energy. Thermal and isotope effects in the lattice constants are due to differences in the vibrational contribution to the free energy. Thus experimental indications of anisotropy in the free energy come directly from the measured anisotropic expansion of $LiBD_4$ reported by Wenger *et al.*[55] and indirectly from the changes in lattice constant between $LiBH_4$ and $LiBD_4$. While the a and b lattice constants for 10 K $LiBD_4$ determined by Wenger *et al.*[55] were contracted by less than 1% from the room temperature $LiBH_4$ lattice constants of Soulié *et al.*,[50] the c lattice constant is reduced by nearly 2% by the combined thermal and isotope effects, indicating considerable anisotropy in the vibrational free energy dependence on the lattice constants. Apparently experimental indications such as these are regularly ignored in applications of the quasiharmonic approximation to noncubic crystals, where the minimum of the "volume only" free energy $G(V)$ is often taken to be the minimum free energy (see, for example, Ref. 27). In fairness, it should be pointed out that applying volume-only minimization of the free energy is likely to yield lattice parameters closer to the true quasiharmonic free energy minimum than those from conventional potential energy or stress minimization, at considerably less computational cost than doing full free energy minimization.

The uncertainties in the calculated free energies expressed in this work are based on the observed variation in the calculated free energy with the calculation input parameters. The lattice constant uncertainty is based on this free energy uncertainty. A drawback of this approach is that no consideration is taken of the relative weaknesses of the two calculated components of the total free energy: the DFT potential energy and the direct method vibrational free energy. As can be seen from Fig. 3, the dependence of the total free energy on the lattice constants is the sum of the dependence of the potential energy and the vibrational free energy on the lattice constants. Two lattice constant dependences of opposite sign combine to give a much shallower curve, magnifying the sensitivity of the position of the minimum to the accuracy of the energy calculations. These two components are calculated using very different techniques, so one cannot expect cancellation of errors between them. Any inaccuracy in the lattice constant dependence of one of the two components will have a significant effect on the lattice constant dependence of the total free energy, and thus on the determined equilibrium lattice constants. No analysis of the sensitivity of the calculated equilibrium lattice constants on such inaccuracies has been attempted in this work.

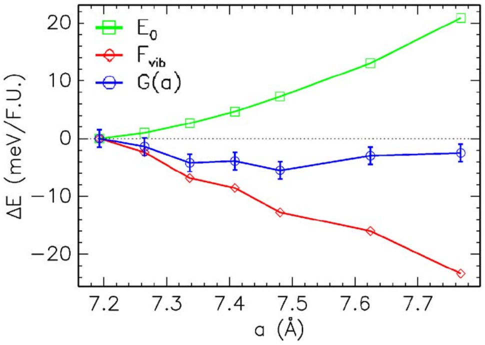

FIG. 3. (Color online) The change in potential energy (E_0), vibrational free energy at 0 K (ZPE, F_{vib}) and total free energy of $LiBH_4$ $[G(\mathbf{a})]$ as a function of the lattice constant a. $b=4.475$ Å and $c=6.713$ Å held fixed.

$LiBH_4$ is known to undergo a phase transition on heating,[37,38,50,64] with the transition temperature being around 380 K. There is considerable speculation as to the structure of the high-temperature phase, with the experimentally-fit $P6_3mc$ structure being shown to be unstable in DFT calculations.[12,17,39] Nonetheless, for any high temperature structure candidate theoretical determination of the phase transition temperature can be performed by calculating the equilibrium free energy as a function of temperature for the ground state *Pnma* and high temperature structures. The predicted transition temperature is given by the point at which the two free energies are equal. Thermal expansion should be included in such a calculation. Given the magnitude of the expected 0 K free energy differences between the ground state and candidate high temperature structures (of the order of 20 meV/F.U.),[17] the uncertainties in the lattice constants obtained in this work and the corresponding uncertainties in the calculated free energies (of the order of 5 meV/F.U.), we feel that a critical assessment of the errors involved in performing a phase transition temperature prediction for $LiBH_4$ using the quasiharmonic approximation would yield an uncertainty in the calculated transition temperature so large as to make such a prediction of questionable value. Uncertainties of up to ±100 K should be expected, which would tend to make any predictions qualitative only.

VII. CONCLUSION

The quasiharmonic approximation is one of the few viable approaches to calculating the free energy of a crystal from first principles. In all the phases considered in this work (orthorhombic $LiBH_4$, α-boron, and LiH), minimizing the free energy with respect to the lattice parameters resulted in a ZPE-corrected unit cell larger than that given by the traditional, potential-energy minimizing lattice parameters. These free-energy minimizing lattice parameters are in principle more relevant for comparison to experimental data. With this in mind it may be appropriate to reassess some of the claimed successes of DFT with GGA exchange-correlation functionals in predicting material lattice constants.

Treating the lattice parameters, rather than the cell volume, as independent variables in the free energy minimization, thus including the effect of anisotropy in the vibrational free energy, is important for complex crystals such as $LiBH_4$. Treating the locus of the lattice parameters with increasing unit cell volume as being defined only by the potential energy leads to a significantly different prediction for the equilibrium lattice parameters as a function of temperature. Correctly minimizing the free energy is, however, significantly more computationally demanding. The free energy minimization process would be considerably easier were computational implementations developed that could evaluate the derivatives of the phonon density of states with respect to the lattice parameters, and thus the vibrational contribution to the stress tensor.

The 0 K enthalpy of dehydrogenation of $LiBH_4$ was calculated to be 59 ± 1 kJ/mol H_2, including ZPE effects. Though slightly larger than that obtained in previous calculations, this value was not influenced by whether it was evaluated at the potential energy minimum structures of the relevant compounds or at the correct low temperature free energy minimum structures. At standard conditions of room temperature and atmospheric pressure the enthalpy change was calculated to be 62.5 ± 1.1 kJ/mol H_2, in good agreement with the corresponding experimental value of 68.9 kJ/mol H_2.

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