Predicting Enthalpies of Molecular Substances: Application to $\mathrm{LiBH_4}$

N. A. Zarkevich[*,†] and D. D. Johnson[‡]

Department of Materials Science and Engineering, University of Illinois, Urbana-Champaign, Illinois 61801, USA

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For molecular substances exhibiting harmonic and nonharmonic vibrations, we present a first-principles approach to predict enthalpy differences between phases at finite temperatures, including solid-solid and melting. We apply it to the complex hydride $\mathrm{LiBH_4}$. Using *ab initio* molecular dynamics, we predict a structure for the high-T solid phase of lithium borohydride, and we propose an approximation to account for nonharmonic vibrations. We then predict the enthalpy changes for solid-solid transition, melting, and an H-storage reaction, all in agreement with experiment.

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Molecular substances are a broad class of materials composed of molecular units (neutral or ionic with counter ions), such as ice, carbon dioxide (dry ice), and complex hydrides. Atoms within molecular units have strong covalent bonds, while intermolecular forces are relatively weak. Strongly bonded molecules usually survive during phase changes, e.g., $\mathrm{H_2O}$ in ice-water-vapor. As a result, a vibrational spectrum [phonon density of states $g(\nu)$ vs frequency ν] of molecular substances consists of two parts: high-ν modes due to intramolecular harmonic vibrations and low-ν modes due to relative motion of molecular units and ions. A large number of interacting units results in a broadening of the low-ν modes, which typically overlap and form a continuous spectrum, in contrast to the high-ν sharp and narrow bands due to a finite number of atoms per molecule. Importantly, some of the low-ν vibrations are *not harmonic* even at moderate T [1,2]. Hence, free energy and enthalpy changes cannot be found within the harmonic approximation [3].

We present a first-principles approach for calculating finite-T enthalpy differences between phases of a molecular substance at fixed stoichiometry. Other approaches can be found in [4–7]. We illustrate ours in $\mathrm{LiBH_4}$, a complex hydride composed of $\mathrm{BH_4}^-$ and Li^+ ions, with 18.4 wt. % H [8–11]. $\mathrm{LiBH_4}$ exhibits a solid-solid phase transition at 381 K, and melts at 553 K. Because of its industrial importance, it has been extensively studied by experiment [12–29] and theory [1,2,30–34]. Although no consensus yet exists as to the space group of the high-T solid phase, we confirm (Fig. 1) that the assessed $P6_3mc$ structure is unstable [1,2]. Using *ab initio* molecular dynamics (MD), we predict a structure of the high-T solid phase (Fig. 2). We examine phonon modes and suggest an approximation to account for nonharmonic vibrations. We then calculate enthalpies of the solid-solid and melting transitions, as well as a chemical reaction enthalpy, and find agreement with experiment.

Background.—If molecules remain intact in various conformations (or phases), their internal vibrations (high-ν harmonic modes) hardly change. In different phases, however, relative molecular positions and, hence, low-ν vibrations are substantially different. Two easily distinguished parts of $g(\nu)$ are separated by a gap at ν_{gap}. For example, in the spectrum of solid $\mathrm{LiBH_4}$, e.g., Fig. 1 in [2], there are narrow high-ν modes at 70 THz (B–H breathing) and at 30–40 THz (H–B–H shear), and low-ν modes below 15 THz from relative ion motions. Thus, the internal energy of harmonic vibrations is

$$E_{\text{vib}} = \frac{r}{2}\left(\int_0^{\nu_{\text{gap}}} + \int_{\nu_{\text{gap}}}^{\infty}\right) d\nu\, g(\nu) h\nu \coth\left(\frac{h\nu}{k_B T}\right), \quad (1)$$

such that low- and high-ν contributions can be considered separately. Here r is the number of degrees of freedom (d.o.f.) in the unit cell; h and k_B are Planck and Boltzmann constants, respectively. For $\mathrm{LiBH_4}$, ν_{gap} lies between 16–30 THz. The high-ν modes remain harmonic to high T and can be calculated via a harmonic approximation. Importantly, the change in high-ν spectrum is small between various phases and these contributions cancel in enthalpy differences.

Hence, we propose a simple mode-counting means to obtain an accurate enthalpy difference $\Delta H(T)$ between two phases of a molecular substance. While nonharmonic modes are difficult to address analytically, there are two solvable limits in which each effective d.o.f. contributes $\frac{1}{2}k_B T$ to the enthalpy: (i) harmonic vibration in a parabolic potential giving $k_B T$ (2 d.o.f., kinetic plus potential), and (ii) nonharmonic free motion in a flat potential giving $\frac{1}{2}k_B T$ (kinetic only). Given $\Delta H(T_0)$ between two phases at a reference T_0 and a difference $\Delta r(T)$ in the effective number of d.o.f., we have

$$\Delta H(T) = \Delta H(T_0) + \Delta r \tfrac{1}{2} k_B (T - T_0). \quad (2)$$

Typically, with their higher enthalpy and entropy, higher-T phases have more nonharmonic modes and, consequently, fewer (potential) d.o.f.; hence ΔH and Δr have opposite signs. Often, in the relevant range of temperatures, Δr can be approximated by a constant.

Now the problem is reduced to finding constants $H(T_0)$ and r in various phases. If the ground state structure is

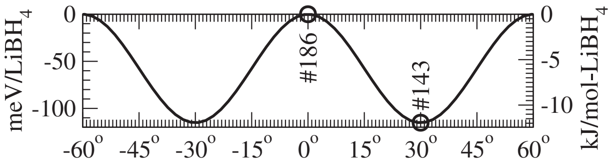

FIG. 1. DFT energy of $LiBH_4$ with hexagonal 12-atom cell relative to $P6_3mc$ [group #186] vs angle of two BH_4^- rotating around [0001] in opposite directions. While $P6_3mc$ is a maximum, structure #143 is also unstable, as BH_4^- can deviate from [0001] to lower energy (Figs. 2 and 3).

known, its enthalpy at 0 K is straightforward to calculate using density-functional theory (DFT) methods. At low enough T all vibrations are harmonic near global minimum (with approximately quadratic potential). Less trivial is finding $H(T)$ in a high-T solid phase with substantial structural disorder, where vibrations can be nonharmonic. $LiBH_4$ is especially interesting because the atomic structure of the high-T solid phase is not yet determined unambiguously.

We address finite-T structural disorder by *ab initio* MD. By fitting $H(T)$ data from MD for two solid phases, we can calculate ΔH and Δr and then find enthalpy of a solid-solid phase transition at a given T_c—this approach is beyond the *ab initio* methods listed in review [4]. When intermolecular solid bonds are destroyed, the restricted motion of molecular units changes to unrestricted, and the molecular solid melts. Melting enthalpy can be estimated from calculated potential barriers, which restrict relative molecular motion in the solid phase. Finally, enthalpy of a gas phase is given from the calculated enthalpy of a single molecule (with internal harmonic vibrations) and the gas equation. Below we use this approach to calculate the constants ΔH and Δr for solid-solid and solid-melt transitions in $LiBH_4$. We find that indeed Δr is roughly a constant in the relevant T range.

We calculate energies of atomic configurations via VASP [35] with projected augmented wave basis and generalized gradient approximation pseudopotentials [36,37] using 700 eV energy cutoffs and converged k meshes, e.g., 12^3 for the 24-atom orthorhombic cell. MD simulations were performed with 2^3 k points for 96-atom cells. For low-T and high-T solid phases, we initially fixed the center of mass (B atom) of the heavy BH_4^- units: this (i) reduces the cost of the MD simulation, (ii) eliminates long-period oscillations of enthalpy due to soft modes and introduces in each phase the same systematic error that is then canceled in enthalpy differences, and (iii) identifies common contributions to Δr in each phase. We then released the heavy atoms in the MD and identified those previously excluded low-ν modes in each phase.

Transitions and enthalpy differences in $LiBH_4$.—At low T $LiBH_4$ is orthorhombic (*Pnma*) [15,27], as we confirm in Fig. 2. At 381 K, it transforms to a (likely) hexagonal phase [23,24] and melts at 553 K [13,24]. Experiments [15,16,24,27] have provided Li and B positions in the solid phases, but H positions are difficult to assess due to the small scattering factor and substantial disorder above 381 K. Several symmetries for the high-T phase have been suggested from experiment: tetragonal C46-I41 or C4h6-I41/a [24,27] and hexagonal $P6_3mc$ [15,16].

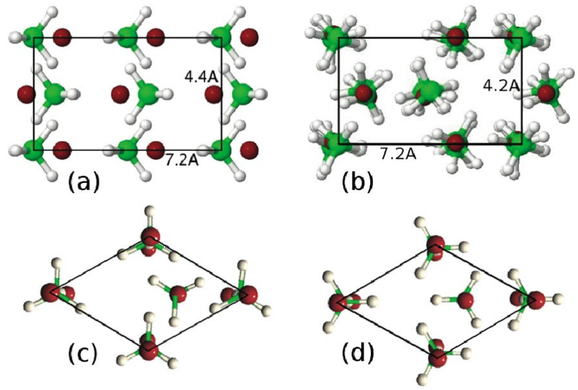

FIG. 2 (color online). $LiBH_4$ structures in [0001] projection. Upper: (a) low-T ortho (24-atom) *Pnma* [#62] and (b) predicted high-T phase. Lower: hex (12-atom) structure for (c) #143 with concerted BH_4 rotations, and (d) $P6_3mc$ [#186]. Structures (b)–(d) differ only by BH_4 orientation. In (c) and (d), BH bonds have angles of 0° and three 110° relative to [0001]. In (b) BH angles are 49°, 111°, 63°, and 137° to [0001]. Comparing (b) and (d) reveals the hex nature of the predicted high-T solid phase if H positional disorder is averaged.

Recently, monoclinic *Cc* was suggested [2], but the calculated x-ray diffraction pattern disagrees [1] with experiment. Also, the experimentally suggested ideal $P6_3mc$ structure [15,16] (Fig. 2) is unstable [1,2]; see Fig. 1. Calculated and measured structural parameters are given in Table I, and Fig. 2 gives the calculated BH_4 orientational angles, with the results of others summarized in [34].

Reliable but incomplete structural information from experiment can be used to accelerate calculations and predict the finite-T structures. For example, as the measured diffraction patterns [15,16,24,27] agree, we assume that the assessed Li and B positions are correct. Using the heaviest atom (i.e., B) positions and the unit cell size from experiment, we perform *ab initio* MD simulations (accounting for the usual reduction in DFT lattice constants). We equilibrate the system with 96 atoms at 450 K, slowly cool it to find $H(T)$, determine equilibrium atomic

TABLE I. $LiBH_4$ structural parameters (Å) for low-T *Pnma* and high-T hex phases from theory and experiment (exp) [15]. The hexagonal structure is viewed as orthorhombic with $a = b\sqrt{3}$ (Fig. 2).

	a	b	c	Ref.
Pnma	7.26	4.38	6.67	DFT at 0 K
	7.17858(4)	4.43686(2)	6.80321(4)	Exp. at 293 K
hex	7.406786	4.27631(5)	6.94844(8)	Exp. at 408 K
	7.20534	4.16 × 2	6.74 × 2	*ab initio* MD

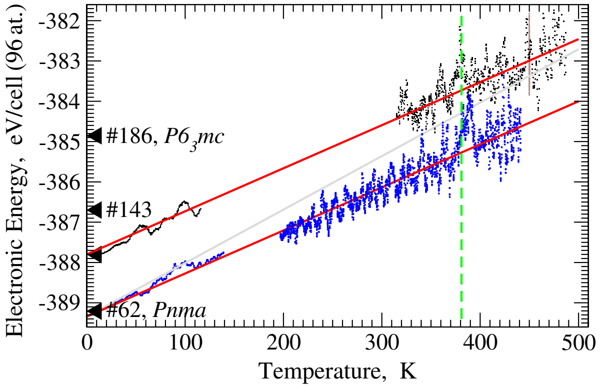

FIG. 3 (color online). MD electronic energy per 16 $LiBH_4$ (96 atoms) for solid phases with fixed B atoms, with observed T_c marked by the vertical dashed (green) line. Solid (red) lines fitted to MD data have slopes of $\frac{3}{2}k_BT$ per moving atom. The gray line is fitted to MD data with unrestricted B motion (not shown), where little change is found for the high-T phase. 0 K energies of structures in Fig. 2 are marked.

positions at 0 K using conjugate gradient, and verify cooling data by slow heating; see Fig. 3. Our cooling and heating MD data agree well (no hysteresis). Table I and Fig. 2 show structural data for predicted high-T phase. Averaging over BH_4 orientational disorder in the cell (Fig. 2), the high-T phase looks hexagonal, as assessed experimentally.

Solid-solid transition enthalpy.—The *ab initio* MD electronic energy is shown in Fig. 3. $\Delta H(0)$ is 96.4 meV/$LiBH_4$ (or 9.3 kJ/mol) and almost constant versus T; that is, with B atoms fixed, Δr is zero. Thus, the high-ν phonons in the two phases are very similar, and the only nontrivial contribution to Δr in Eq. (2) is from a difference in the motion of the centers of mass of heavy molecular units, or lowest-ν modes. By relaxing B atoms in the MD and determining the difference in the slopes of two lines fitted to average $H(T)$ data, we find that $-2.75 < \Delta r < -3.25$, so $\Delta r = -3$. From the slopes and MD data, we conclude that all vibrations in the low-T ortho phase are harmonic (although motion of heavy B atoms results in very long-period oscillations), while in the high-T solid phase B atoms perform nonperiodic (nonharmonic) motion. From the change in the number of d.o.f. due to nonharmonic $BH_4{}^-$ motion in the high-T phase, the calculated enthalpy difference at the 381 K phase transition is 4.6 kJ/mol (Fig. 4), in agreement with measured values of 4.2–4.3 kJ/mol [38,39].

Melting enthalpy.—Liquids are difficult to address by *ab initio* MD due to enormous computational cost. Instead, knowledge of potential energy barriers can be used to estimate enthalpy change related to melting. When the energy barriers can no longer restrict motion of molecular units, solid bonds are destroyed, and a molecular solid melts, becoming a molecular liquid.

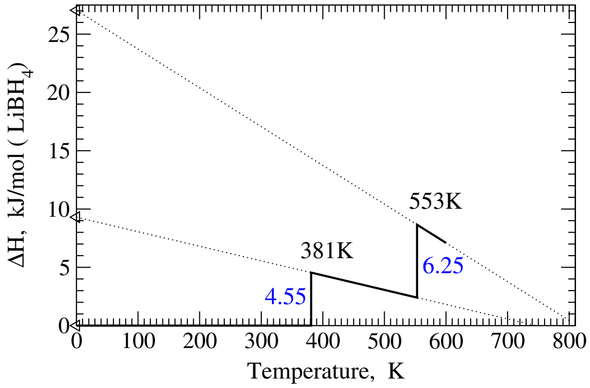

FIG. 4 (color online). Predicted enthalpy of $LiBH_4$ high-T solid and melt phases relative to *Pnma*. Calculated (measured [39]) enthalpies of the solid-solid and melting transitions are 4.6 (4.3) and 6.3 (6.9) kJ/mol at 381 K and 553 K, respectively.

Calculated energy barriers for rotations of BH_4 in $LiBH_4$ are in [1] and in Fig. 1. When BH_4 units overcome the barrier and rotate, bonds between units are destroyed and $LiBH_4$ melts. At 0 K, see Figs. 3 and 4, the potential energy maximum for rotations around [0001] is at $P6_3mc$, and 26.2 kJ/mol-$LiBH_4$ above the ground state (or 4.35 eV/cell with 16 $LiBH_4$). While atomic vibrations within the strongly bonded units are still harmonic, unrestricted motion of $BH_4{}^-$ and Li^+ ions in the liquid phase is definitely not; thus, they contribute only $\frac{1}{2}k_BT$ per each of 9 nonharmonic d.o.f. (3 translations per Li^+; 3 translations and 3 rotations per $BH_4{}^-$), in contrast to $1k_BT$ per harmonic mode in the ground state; hence $\Delta r = -9$ between the liquid and the low-T solid phases. Again, taking into account differences in the number of d.o.f., the calculated enthalpy difference between the liquid and the high-T solid phases is 6.3 kJ/mol at 553 K (melting), compared to the measured value of 6.9 kJ/mol [39]; see Fig. 4. Calculating enthalpy of a single gas molecule, counting its external d.o.f., and using the gas equation determine the gas enthalpy, allowing an estimate of the specific heats of evaporation and sublimation.

Chemical reaction enthalpies.— If enthalpies of all reaction components are known, enthalpies of chemical reactions can be estimated. However, we must consider the relevant phases at a given T. In particular, as described elsewhere [40], we find an enthalpy change of 41 kJ/mol-H_2 at 600 K for the H-storage reaction (11.4 wt% H_2)

$$2LiBH_4 + MgH_2 \leftrightarrow 2LiH + MgB_2 + 4H_2, \qquad (3)$$

agreeing with 41 kJ/mol-H_2 assessed at 588–636 K [39]. (Systematic DFT errors are directly canceled in the calculated enthalpy difference, and we estimate a relative error of ±1 kJ/mol-H_2.) We accounted for the melted phase (the correct phase at 600 K) and considered both harmonic and nonharmonic vibrational contributions. In contrast, $\Delta H(T)$

estimates of 66.8 kJ/mol-H_2 at 0 K and 52.2 kJ/mol-H_2 at 298 K [30,41], from rapid searches for H-storage media, assumed only harmonic vibrations and considered the low-T $Pnma$ phase (correct only below 381 K). As they cited, Alapati *et al.* [41] tried to include very roughly our results for rotational effects in the van't Hoff plot and also approximated the energy of the hex phase with $P6_3mc$, which is wrong; this gives a significant error (enthalpy change is ~30% too high). Our present method permits proper consideration of relevant phases at relevant temperatures, e.g., liquid $LiBH_4$ above 553 K for dehydrogenation reactions observed in the van't Hoff measurements, and dramatically improves accuracy of predicted reaction enthalpies with simple and correct mode counting.

In conclusion, we have proposed a first-principles approach for predicting enthalpy differences between phases of a molecular substance at the same stoichiometry that includes the contributions of both nonharmonic and harmonic vibrational modes, and also can be used to improve the accuracy of predicted reaction enthalpies. We demonstrated its reliability using lithium borohydride (interesting for its high-capacity hydrogen storage) and found agreement between theory and experiment for the solid-solid and melting transition enthalpies, as well as for the reversible destabilized H-storage reaction.

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*Current address: University of California, Davis, CA 95616, USA.

†zarkevic@ucdavis.edu

‡duanej@uiuc.edu

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