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The importance of vibrations in modelling complex metal hydrides

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Abstract

Crystalline materials have zero point energy (ZPE) associated with phonon vibrations. This ZPE not only significantly alters the energetics of reactions involving complex metal hydrides, but also alters the equilibrium structure of these materials as determined by first principles calculations. This paper focuses on the structural effect of ZPE in the potential hydrogen storage material $LiBH_4$.

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1. Introduction

Using hydrogen as an energy carrier is an attractive alternative to the current global dependence on hydrocarbon-based fuels, particularly for vehicular transport. Storing pure hydrogen on board passenger cars is unattractive from an engineering point of view, primarily due to the low density of hydrogen gas and the effort required to compress it to a reasonable volume. Currently one of the most promising ways to store hydrogen with high density is in complex metal hydride systems [1–3].

An important criterion for a chemical hydrogen storage material to be useful is its stability. Ideally the material should be stable with respect to the decomposition products, allowing for relatively simple storage conditions and to enable at least the possibility of recharging by applying hydrogen pressure. Yet it must not be too stable, lest too high temperatures be required to release the hydrogen. An enthalpy change on hydrogen release around 40 kJ/mol H_2 yields a material that would, kinetics aside, release hydrogen around the convenient conditions of 300 K and 1 bar [1].

Much of the exploration of potential hydrogen storage materials is being performed using computational investigations of known and hypothetical structures, typically using some flavour of density functional theory (DFT). Though not all DFT implementations were created equal [4,5], DFT in general is capable of accurately describing the structure and energetics of complex metal hydrides and their decomposition products.

However, DFT can only directly calculate the change in total potential energy upon hydrogen release. The zero point energy (ZPE), E_{ZPE}, of the system cannot be evaluated 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 [6–11]. 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, as the system seeks the minimum Gibbs free energy [12]. The Gibbs free energy of a crystal under constant pressure conditions can be written as

$$G = U + pV - TS = E + pV + F_{\mathrm{vib}} \tag{1}$$

where U is the internal energy, p and T are the pressure and temperature, V is the volume and S is the entropy. The U and TS terms can be recast as the potential energy E and the vibrational free energy F_{vib}, as per Eq. (1). Only F_{vib} depends explicitly on the temperature and $\lim_{T\to 0} F_{\mathrm{vib}}$ gives the vibrational ZPE. In this 0 K limit the free energy is identical to the enthalpy, H. 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

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Table 1
Low temperature and pressure enthalpy changes for dehydrogenation reactions (kJ/mol H_2)

Reaction	Without ZPE	With ZPE	$-\Delta(\Delta H)$	Reference
$LiBH_4 \rightarrow LiH + B + (3/2)H_2$	81	59	22	[6]
	75	56	19	[7]
$LiAlH_4 \rightarrow (1/3)Li_3AlH_6 + (2/3)Al + H_2$	3.8	−5.2	8.9	[8]
$Li_3AlH_6 \rightarrow 3LiH + Al + (3/2)H_2$	40	19	21	[8]
$NaAlH_4 \rightarrow (1/3)Na_3AlH_6 + (2/3)Al + H_2$	31	22	9	[9]
$Na_3AlH_6 \rightarrow 3NaH + Al + (3/2)H_2$	50	37	14	[9]
$NaH \rightarrow Na + (1/2)H_2$	87	89	−2	[9]
$LiNH_2 + LiH \rightarrow Li_2NH + H_2$	86	68	19	[10]
$Li_4BN_3H_{10} \rightarrow Li_3BN_2 + LiNH_2 + 4H_2$	29	6	23	[11]

unit cell or per formula unit and the relevant vibrations are phonons.

2. Methods

Vasp [13] was used for all DFT calculations performed by the author described in this work. Projector augmented wave (PAW) potentials [14] were used to represent the ionic potentials. Generally the PAW potentials that treated semi-core *s* states as valence were used if available. The generalised gradient approximation (GGA) exchange-correlation functional used was the PW91 functional [15]. Both Monkhorst-Pack [16] and Γ-centred *k*-point grids were used. *k*-point sampling and plane wave basis set cutoff energies were selected to provide convergence of the total energy to better than 1 meV per crystallographic unit cell. For the crystals discussed in this paper these were generally *k*-point grids around 4 × 4 × 4 or larger and cutoff energies of 800–1000 eV.

Harmonic phonon densities of states were calculated by the direct method [17] as implemented in Phonon [18]. In this implementation the second derivatives required to construct the dynamical matrices used in the direct method are determined by finite differencing from force calculations. Two-sided differences were used in the calculations described here. While the $3N$ second derivatives required for N atoms in three-dimensional space can thus naïvely be determined with $6N$ force calculations, the set of required displacements can be reduced (often greatly) by symmetry. The magnitude of the individual atomic displacements is a parameter that needs to be tested for convergence.

From the frequency-dependent phonon density of states $g(\omega)$ thus obtained the vibrational contribution to the free energy at temperature T can be calculated, per unit cell, as

$$F_{\mathrm{vib}}^{\mathrm{har}} = rk_{\mathrm{B}}T\int_0^{\infty} g(\omega)\ln\left[2\sinh\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right)\right]\mathrm{d}\omega \qquad (2)$$

where $\hbar$ is Planck's constant divided by 2π, r is the number of degrees of freedom in the unit cell and k_{B} is Boltzmann's constant. In the zero temperature limit this reduces to the ZPE,

$$E_{\mathrm{ZPE}}^{\mathrm{har}} = \frac{\hbar r}{2}\int_0^{\infty}\omega g(\omega)\,\mathrm{d}\omega \qquad (3)$$

a simple weighted integral over the phonon density of states.

The potential energy E clearly depends on the lattice parameters of the crystal. Thus the vibrational quantities defined above also depend on the lattice parameters, through the second derivatives of E and thus $g(\omega)$. Minimising the harmonic free energy with respect to the lattice parameters leads to the quasiharmonic approximation, where certain anharmonicities in the potential are reflected in the dependence of the harmonic free energy on the lattice parameters. While in the general case one must minimise the free energy $G(\mathbf{a})$ with respect to all lattice parameters $\mathbf{a}$, often for computational simplicity the ratios of the lattice parameters are taken to be those that minimise the potential energy for a particular volume, making the free energy a function of volume only [$G(V)$]. Strictly speaking this is only valid when the symmetry of the crystal reduces the set of lattice parameters to a single lattice constant.

3. Hydride stability

There is a growing appreciation that ZPE changes in dehydrogenation reactions of complex metal hydrides are significant. The change in ZPE is primarily due to the tight covalent bonding of hydrogen to the p-block elements in these compounds giving a high contribution to the total reactant ZPE. Table 1 lists some example complex metal hydride dehydrogenation reactions with calculated reaction enthalpies. The reaction energies determined using just the change in electronic (potential) energies are shown along with the effect of including the ZPE of all the phases present.

In all complex metal hydride cases the inclusion of ZPE significantly reduces the enthalpy from the potential energy only value, with the reduction typically being of the order of 10–20 kJ/mol H_2. The decomposition of $Li_4BN_3H_{10}$ is a consummate example, with the reaction enthalpy at 0 K being reduced by almost 80% by the addition of ZPE. An arguably more extreme case is $LiAlH_4$. While crystalline $LiAlH_4$ is a stable stationary point on the potential energy surface, the addition of ZPE raises the energy of $LiAlH_4$ to above that of the decomposition products, making $LiAlH_4$ metastable at best. It should be noted that similar analysis by Løvvik et al. [19] (not included in Table 1 as they did not publish 0 K values) concluded that pure $LiAlH_4$ was thermodynamically stable and attributed the observed spontaneous room temperature decomposition [20–22] to the potentially destabilising effect of impurities.

Also included in Table 1 is the decomposition of NaH. This example demonstrates that what is true for complex metal hydrides with regard to ZPE is not true for hydrides in general. For NaH, inclusion of ZPE increases the stability of the hydride [9]. This is easily rationalised by considering the bonding within the material. NaH exhibits ionic bonding between Na^+ and H^- ions, a relatively weak and low frequency bonding that contributes little ZPE. Complex metal hydrides, on the other hand, typically contain ionic bonding between cations and $(AH_n)^{m-}$ anions. The latter units typically exhibit covalent-character bonding between the hydrogen and p-block element, a much stiffer bond that correspondingly contributes a much higher ZPE to the crystal phonon energy.

The van't Hoff equation not withstanding, the enthalpy change upon dehydrogenation does not tell the whole story. Temperature, pressure and entropy effects are only included when considering the Gibbs free energy. However, few computational studies of the decomposition of complex metal hydrides [8,9] yet consider the Gibbs free energy to determine stability.

4. ZPE-driven expansion

The lattice parameters that minimise the potential energy (or, in principle equivalently, the stress calculated from DFT calculations) are only approximations to the true theoretical lattice parameters. The true lattice parameter predictions are those that minimise the free energy. Adding the ZPE in general leads to more expanded crystals. Thus it has become common to calculate the free energy curve of a crystal as a function of unit cell volume and take the volume giving the minimum free energy as the equilibrium volume [9,10,23–25].

Treating the free energy as a function of volume only assumes that the ZPE of the crystal is isotropic. However, unless constrained by symmetry (such as in the case of a simple cubic lattice), there is no reason to assume that the ZPE can be expressed purely as a function of volume. Rather, the free energy should be minimised with respect to all lattice parameters independently. Any anisotropy in the ZPE is thus included explicitly rather than letting only the potential energy determine the cell shape. However, analysing the gradient of G with respect to all lattice parameters $\mathbf{a}$ is relatively difficult. Thus the free energy must usually be calculated on some grid-like set of lattice parameters.

Complex metal hydrides generally exhibit anisotropy in vibrational properties. Despite this, the volume-only approach to quasiharmonic free energy minimisation has been applied to the isotropic complex metal hydride crystals of the sodium alanates [9] with surprisingly accurate results. Additionally a minimisation with respect to both independent lattice constants has recently been published [26]. Inclusion of anisotropy in the ZPE contribution to the free energy resulted in a 7% smaller ZPE-driven volume increase.

Both volume-only and full three-dimensional minimisation have been performed for $LiBH_4$ [6]. The results of these optimisations are shown in Table 2. Like in the case of $NaAlH_4$, the optimised lattice constants are slightly in error when using both LDA and GGA exchange-correlation functionals, with the LDA lattice constants undershooting and the GGA lattice constants overshooting the experimentally determined values. The changes induced by including the ZPE in the minimisation were much larger than for $NaAlH_4$, with the unit cell volume increasing by 8%. Volume-only optimisation lead to even greater expansion of 10%. The calculations reproduced the preferential expansion in the a direction observed in neutron diffraction experiments [27], as increasing the temperature from 0 to 300 K lead to increases in the a and b lattice constants of around 6% and 2%, respectively, though the magnitudes of these increases are larger than those observed experimentally. No clear increase in the c lattice constant was observed.

Table 2
Lattice constants (Å) and cell volume (Å^3) for orthorhombic $LiBH_4$[a]

	a	*b*	*c*	Volume
PW91				
Min. *E*	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*	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.				
$LiBH_4$[b]	7.179	4.437	6.803	216.7
$LiBD_4$[c]	7.116	4.406	6.673	209.2

[a] Calculated free energy minimum values are for 0 K.

[b] X-ray powder diffraction, room temperature, Ref. [29].

[c] Neutron powder diffraction, 10 K, Ref. [27].

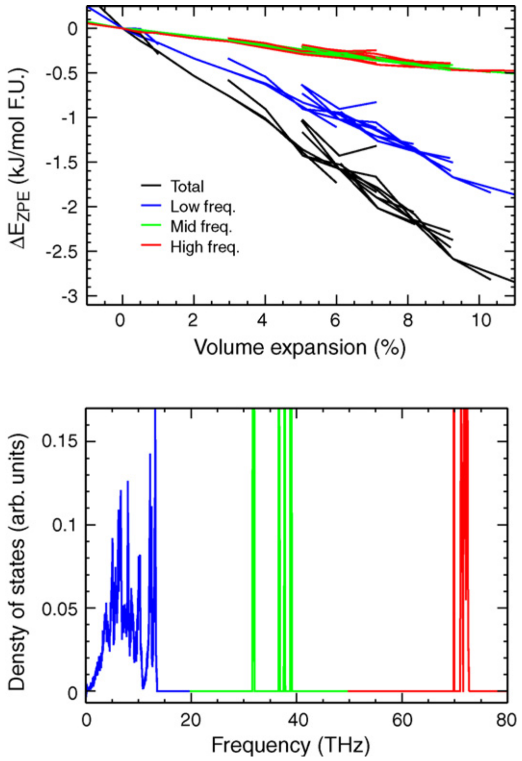

Fig. 1. Sample phonon density of states (lower) and change in ZPE decomposed into frequency groups (upper).

Some further insight can be gained by looking more closely at the ZPE calculated for $LiBH_4$. Fig. 1 shows the phonon density states, clearly separated into three distinct parts associated with $Li^+–(AlH_4)^-$ motion (low frequency) and $(AlH_4)^-$ bending and vibrational modes (mid and high frequencies) [7]. The upper plot shows the change in the calculated ZPE decomposed into contributions from each group of modes (or rather ranges of frequencies). The data has been flattened into a function of volume only, so that different lattice constant extensions that give the same volume are plotted at the same point on the x axis. The reason that the theoretically flawed volume-only method is reasonably successful can be seen from Fig. 1, in that the change in the ZPE can be reasonably approximated by a single-valued, volume dependent function. That the volume-only approach is in fact flawed is demonstrated by the fact that the change in the total ZPE is not single valued as a function of volume; different lattice constant ratios lead to different changes in the total ZPE.

It is also clear that while the high frequency phonons associated with $(AlH_4)^-$ internal vibrations contribute most to the total ZPE (and thus the correction to the reaction enthalpy), it is the low frequency phonons associated with Li^+– $(AlH_4)^-$ motion that contributes the greatest change to the ZPE as the unit cell changes (around 60%) and hence has the strongest effect on the equilibrium volume.

5. Conclusion

It is clear that including the ZPE of phonons has a very significant effect on the calculation of the enthalpy change upon dehydrogenation of complex metal hydrides. As such, it is vital to include consideration of ZPE to have any chance of calculating accurate enthalpy changes for these reactions. This is not necessarily the case for less complex hydrides where the bonding is primarily ionic.

It has been shown that the ZPE also has an effect on the equilibrium lattice parameters. One might expect that materials containing lightweight ions would be the most strongly effected, which has proven to be the case for $NaAlH_4$ [26] and even more strongly for the current $LiBH_4$. As the effect has been demonstrated for LiH [6,10], among other similar hydrides [28], ZPE-driven expansion is not restricted to complex metal hydrides.

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