

Comment on “Structural Stability of Complex Hydrides: LiBH₄ Revisited”

In [1] a high-temperature LiBH₄ phase was studied in the harmonic approximation [2] and a new monoclinic *Cc* structure was proposed, while the experimentally observed [3,4] hexagonal *P6₃mc* structure was rejected based on observation of imaginary (i.e., absolutely unstable) modes in its harmonic phonon spectrum [1,5]. However, experimentalists [3,4,6] proposed a hexagonal structure in which BH₄ units can rotate (see Fig. 5 in [3]), with the measured rotational barriers of 5 ± 5 kJ/mol [6]: this is no longer *P6₃mc* after rotation of BH₄ units.

To check which structure is correct, we used the *Vienna ab initio simulation package* [7] with the projected augmented plane-waves [8] with 400 eV kinetic energy cutoff within the generalized gradient approximation [9] (VASP-PAW-GGA, same as in [1]) to calculate the rotational barriers in hexagonal LiBH₄ with a 12-atom unit cell. The result is in Fig. 1. It shows that indeed the *P6₃mc* structure is unstable, and indeed BH₄ units rotate above the solid-solid phase transition at $T_c = 384$ K, because BH₄ rotational barriers are smaller than $k_B T \geq k_B T_c = 33$ meV. Our calculations confirm results of the experiment [6], but show that harmonic approximation is invalid for both *P6₃mc* and high-*T* hexagonal LiBH₄ structure with rotational modes. Hence, the high-temperature LiBH₄ phase cannot be studied within harmonic approximation and the “systematic approach” used in [1] fails.

So far we have shown that harmonic approximation results do not exclude the hexagonal LiBH₄ structure with rotational modes. But could the monoclinic *Cc* structure proposed in [1] be real? Comparing calculated (Fig. 3 in [1]) and experimental (Fig. 2 in [3]) x-ray diffraction (XRD) patterns, it is not difficult to see the difference. In particular, the monoclinic structure (Fig. 3 in [1]) produces 4 asymmetric peaks around $2\Theta = 16^\circ$ [Fig. 1 in [3] shows similar 4 peaks for LiBH₄ at room *T* (orthorhombic phase); the shift in 2Θ is due to difference in λ], where the more symmetric hexagonal structure has 3 equidistant peaks (Fig. 2 in [3])—observed in experiment at 408 K. Thus, contrary to the claim in [1], the calculated XRD pattern of the *Cc* phase does not agree with experiment at $T > 384$ K even using lattice expansion as an excuse, while that of the hexagonal phase obviously does [3].

In conclusion, we explained why the harmonic approach used in [1] failed to address the high-temperature LiBH₄ phase. We showed that indeed the *P6₃mc* structure is

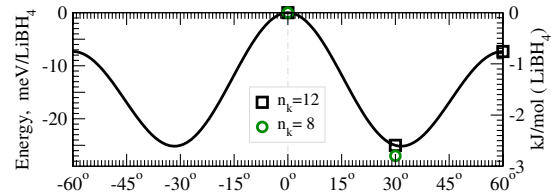


FIG. 1 (color online). Calculated energy of hexagonal LiBH₄ with one BH₄ unit rotated around [0001] versus angle relative to *P6₃mc*, using n_k^3 points in Monkhorst-Pack mesh [12].

unstable, while the hexagonal LiBH₄ phase has very low rotational barriers (in agreement with experiment), thus it cannot be addressed within harmonic approximation. Our results will help to better understand the high-temperature phase of LiBH₄—an important material for reversible hydrogen storage [10,11].

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