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

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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 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-PW-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 Tₑ = 384 K, because BH₄ rotational barriers are smaller than \( k_BT \approx k_BTₑ = 33 \text{ meV} \). 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 2Θ = 16° [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 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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