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Comment on "Structural Stability of Complex Hydrides: LiBH4 Revisited"

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In [1] a high-temperature $LiBH_4$ phase was studied in the harmonic approximation [2] and a new monoclinic Cc structure was proposed, while the experimentally observed [3,4] hexagonal $P6_3mc$ 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 BH_4 units can rotate (see Fig. 5 in [3]), with the measured rotational barriers of 5 ± 5 kJ/mol [6]: this is no longer $P6_3mc$ after rotation of BH_4 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 $LiBH_4$ with a 12-atom unit cell. The result is in Fig. 1. It shows that indeed the $P6_3mc$ structure is unstable, and indeed BH_4 units rotate above the solid-solid phase transition at $T_c = 384$ K, because BH_4 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 $P6_3mc$ and high-T hexagonal $LiBH_4$ structure with rotational modes. Hence, the high-temperature $LiBH_4$ 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 $LiBH_4$ 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 $2\Theta = 16°$ [Fig. 1 in [3] shows similar 4 peaks for $LiBH_4$ 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 $LiBH_4$ phase. We showed that indeed the $P6_3mc$ structure is
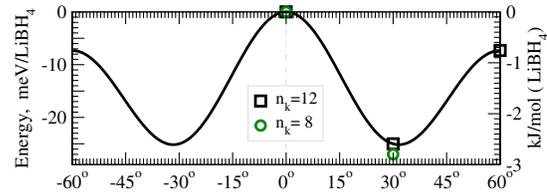

FIG. 1 (color online). Calculated energy of hexagonal $LiBH_4$ with one BH_4 unit rotated around [0001] versus angle relative to $P6_3mc$, using n_k^3 points in Monkhorst-Pack mesh [12].

unstable, while the hexagonal $LiBH_4$ 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 $LiBH_4$—an important material for reversible hydrogen storage [10,11].

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[1] Z. Lodziana and T. Vegge, Phys. Rev. Lett. **93**, 145501 (2004).
[2] K. Parlinski, computer code PHONON, Kraków, Poland, 2004.
[3] J-Ph. Soulié *et al.*, J. Alloys Compd. **346**, 200 (2002).
[4] S. Gomes *et al.*, J. Alloys Compd. **346**, 206 (2002).
[5] K. Miwa *et al.*, Phys. Rev. B **69**, 245120 (2004).
[6] H. Hagemann *et al.*, J. Alloys Compd. **363**, 129 (2004).
[7] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996); Comput. Mater. Sci. **6**, 15 (1996).
[8] P. E. Blöchl, Phys. Rev. B **50**, 17 953 (1994).
[9] J. P. Perdew *et al.*, Phys. Rev. B **46**, 6671 (1992).
[10] A. Züttel *et al.*, J. Power Sources **118**, 1 (2003).
[11] J. J. Vajo *et al.*, J. Phys. Chem. B **109**, 3719 (2005).
[12] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).