Łodziana and Vegge Reply: In the Comment to our Letter [1], Zarkevich and Johnson argue [2] that our methodology cannot be used to study $LiBH_4$ at high temperatures. We show that the claims in [2] are not physically justified.

In agreement with our findings and those of others [3], Zarkevich and Johnson present data showing (Fig. 1 in [2]) that $LiBH_4$ is not stable in the experimentally proposed $P6_3mc$ symmetry [4]. Unfortunately, no information about a stable symmetry of $LiBH_4$ at high temperatures is presented in [2]. The statement "hexagonal structure with rotational modes" is unclear to us, since all molecular structures like $LiBH_4$ intrinsically posses translational, rotational ("librational" in [1]), and stretching modes.

Every ordered nonmagnetic crystal system belongs to exactly one of 230 space groups, which are unequivocally defined via their point and lattice symmetry operations [5]. The (quasi) harmonic approximation assumes harmonicity of the potential energy at equilibrium (the free energy minimum). A system which is unstable within the harmonic approach can be stabilized by entropy, in which case it must posses more than dynamical disorder. With additional configurational disorder, the equilibrium symmetry is different (perhaps lower, as we show [1]) and the definition of the space group would require designation of site occupancy.

Figure 1 in [2] presents the calculated energies for 0°, 30°, and 60° rotations of BH_4 around [0001] (C_3 here) connected by a periodic potential displaying a puzzling sixfold symmetry, which is absent for any site in $P6_3mc$—in particular for the $3m$ symmetry of the "b" site of B and H. Accurate calculation of the rotation of individual BH_4 units requires large systems (≥ 96 atoms), whereas a 12 atom supercell (used in [2]) corresponds to a speculative unison rotation. In fact, no barrier for rotation is found in [2], but a lower energy configuration where half of the BH_4 units are rotated 30°.

In [1], we specifically addressed the instability of the $P6_3mc$ structure, however for clarity, the calculated BH_4 rotational barriers for the $P6_3mc$ structure are presented here in Fig. 1. The large barriers along C_3 possess proper symmetry and they exclude free rotation of BH_4 around this axis, which was originally proposed in [4] and restated in [2]. Rotations of the BH_4 tetrahedron around various axes possesses minima other than the equilibrium orientation of BH_4 in the $P6_3mc$ symmetry, see Fig. 1(b). There are actually more modes with this property [1], not only one as investigated in [2], many of which have translation-rotation coupling. In that sense, the harmonic approximation is not justified to study thermodynamics of $LiBH_4$ in the $P6_3mc$ symmetry, which is why no conclusions are drawn in [1] about the $P6_3mc$ structure from the harmonic approximation, except the fully justified conclusion that it is unstable. A simple analysis gives different alignments of BH_4 which are slanted from their orientation along [0001] and the resulting symmetry is $P2_1$; mode coupling results in the $Cmc2_1$ and Cc symmetry.

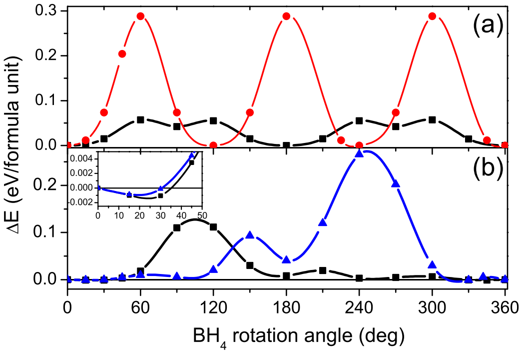

FIG. 1 (color online). (a) Adiabatic rotational barriers for BH_4 rotation around the C_3 (red circles) and C_2 (black squares) axes in the $P6_3mc$ structure of $LiBH_4$. (b) Barriers for BH_4 rotation around the [0100] (black squares), and [1100] (blue triangles) directions; the inset shows local minima for the BH_4 orientation. Lines are guides to the eye.

At least two structures of $LiBH_4$ at high temperatures have been proposed experimentally, i.e., a tetragonal [6] and a hexagonal [4]. The x-ray diffraction pattern of the Cc structure in [1] is slightly different from the experimentally ascribed $P6_3mc$ hexagonal structure. However, when considering anisotropic temperature effects (cannot be handled within the quasiharmonic approximation) the fit of the preserved Cc structure to the experimental pattern is reasonable. An anisotropic thermal expansion can shift the four asymmetric peaks at $T = 0$ K (Fig. 3 in [1]) to three symmetric peaks of the Cc phase (as found for $P6_3mc$) with only a minor features at higher angles.

We fully acknowledge the limitations of both density functional theory and diffraction experiments with respect to the determination of hydrogen positions at finite temperatures, however, no physically justifiable new insight is presented in the preceding Comment [2].

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Received 19 May 2006; published 14 September 2006
DOI: 10.1103/PhysRevLett.97.119602
PACS numbers: 61.50.−f, 63.20.Dj, 64.70.Kb, 71.15.Mb

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