Theoretical study of disorder-order transition of sodium borohydride

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ABSTRACT

The disorder-order phase transition of $NaBH_4$ from the cubic to tetragonal structures has been studied based on density functional theory. The disordered high temperature phase is expressed as a statistical average of three substructures with a hypothesis that each BH_4^- tetrahedron has a fixed orientation. Our calculations show that the phase transition is mainly induced by synergic rotation of BH_4^- ion and the energy barrier is sensitive to volume change. We also investigated the role of van der Waals corrections in describing phase transition with DFT-D2 and vdW-DF methods.

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1. Introduction

The strong demand for new clean power sources has intensified the interest in materials for energy storage. Sodium borohydride ($NaBH_4$) is one of the most promising candidates for fulfilling the hydrogen storage requirements due to its outstanding volumetric and gravimetric hydrogen density [1,2], however, it's still in the basic and technological research.

Sodium borohydride is an ionic crystal consisting of positively charged Na^+ ions and negatively charged BH_4^- ions. Its hydrogen atom is covalently bound and arranged in subunits. The four hydrogen atoms surround the central boron atom and form a regular tetrahedron [3,4]. To better understand the structural, electronic and thermodynamic properties of sodium borohydride in both stable and metastable states under various temperatures and pressures, a variety of methods, both experimental and theoretical, have been applied, including heat capacity measurements [5,6], X-ray and neutron diffraction [7,8], neutron scattering [9,2,10], Raman spectroscopy [7], nuclear magnetic resonance (NMR) [8,11–14] and density functional theory (DFT) [3,9,15,16].

From the inelastic neutron scattering spectra, Allis et al. [9,16] found $NaBH_4$ holds a cubic structure at high temperature (HT), and can transform into the low-temperature (LT) phase with tetragonal symmetry on cooling at 190 K. Its phase transition has been interpreted as a disorder-order transition involving the orientations of the tetrahedral BH_4^- ions [5]. However, the transition path is still unclear so far. We designed all possible orientations

of BH_4^- tetrahedra and the rotational barriers were calculated with first-principles calculations. The potential energy landscape revealed the transition path of $NaBH_4$.

Additionally, Kim et al. [17] have proposed that $NaBH_4$ is a quasi-molecular solid for which van der Waals (vdW) interactions should be important. Bil et al. [18] have demonstrated that the vdW interactions indeed play a critical role in another metal borohydride - $Mg(BH_4)_2$. There have been not any relevant calculations of the vdW interactions in the study of $NaBH_4$ so far. In order to figure out the role of van der Waals corrections in describing the system of $NaBH_4$, especially in describing phase transition, we considered the vdW interactions in this compound through the DFT-D2 [19] method and the vdW-DF [20–23] method.

2. Computational details

Our calculations were performed using the plane-wave basis set with the projector augmented wave (PAW) [24,25] effective potentials, as implemented in the Vienna Ab-initio Simulation Package (VASP) code [26,27]. The equilibrium geometry and the potential energy surface calculations were carried out with both standard DFT, DFT-D2 and vdW-DF methods. The Perdew-Burke-Ernzerhof (PBE) [28] generalized gradient approximation (GGA) [29] exchange-correlation functional was used here. The Brillouin zone (BZ) integration was carried out using the special k-point sampling of the Monkhorst-Pack [30] type. Our tests show that a plane-wave cutoff energy of 950 eV and Monkhorst-Pack k meshes of $9 \times 9 \times 9$ give an excellent convergence for total energy and the geometry of the investigated system. The chosen plane-wave cutoff and the number of k points were carefully checked to ensure the total

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energy converged to better than 1 meV per formula unit (f.u.). Meanwhile, geometries were relaxed toward equilibrium until the forces have become less than 10^{-3} eV/Å. Experimentally established structural data were used as input for the geometrical optimization calculations. Total energies calculations along the atom migration paths are used to map out the possible pathways.

3. Results and discussions

3.1. HT or LT-phase structures

The HT-phase of $NaBH_4$ has a face-centered cubic structure while the LT-phase has a body centered tetragonal structure [5,13] (Fig. 1(a) and (b)). The HT-phase crystallizes into a cubic structure with disordered orientations of BH_4^- anions. The Na^+ cations and BH_4^- anions form a NaCl-type arrangement with symmetry Fm-$3m$ [31]. In this structure Na occupies the (4a), (0,0,0) sites, B the (4b), (0.5,0.5,0.5) sites and the hydrogen atoms are statistically distributed over two (16c) sites, occupying the 8 corners of a cube around B atom with 50% occupancy. This implies a random distribution of BH_4^- tetrahedra in two different orientations [31–33].

For the HT-phase, the centrosymmetric model is intrinsically disordered, showing two alternative orientations of the BH_4^- tetrahedra, as the BH_4^- tetrahedra are not fixed but rapidly change among the two different orientations, and therefore only a statistically average structure can be defined [31–33]. As shown in Fig. 1 (a), each tetrahedron possesses two different alternative orientations. Bindzus et al. [34] have proposed several instantaneous representations of the orientational disorder. Inspired by their previous work, we hypothesize that each tetrahedron has a fixed orientation. Thus, for the disordered Fm-$3m$, there are three different configurations in principle to verify all possible permutations. That is to say, this Fm-$3m$ HT-phase can be expressed as a statistical average of three substructures, which are described as A-, B- and C-$NaBH_4$ (Fig. 1(c)–(e)). The space groups of A-, B- and C-$NaBH_4$ are F-$43m$, P-$43m$, and $P4_2/nmc$, respectively. The ordered

LT-phase crystallizes into a tetragonal structure with $P4_2/nmc$ symmetry [35].

3.2. Structure relaxation

The structures of the three configurations and the LT-structure were optimized, using the experimental data [8,33] as initial values, and the results are listed in Table 1. From these results, the DFT calculations have 3–5% volume reduction compared to experimental values. The DFT-D2 calculations underestimate lattice parameters and cell volume significantly, giving a volume 14%–21% smaller than experimental values. Compared with the DFT and DFT-D2 results, the results based on the vdW-DF method are obviously in good agreement with the experimental value, resulting in about 1% difference in volume. Our results conform to the conclusion made by Bil et al. [18]. They have reported that the vdW-DF method leads to a good agreement with experiment while the DFT-D2 method results in more compact structures. Our results show that vdW interaction plays an important role in reproducing the experimental structural parameters of $NaBH_4$, but need to choose an accurate simulation method.

The optimized structures of A- and B-$NaBH_4$ are still the cubic structures with the lattice constants $a = b = c$. While for the optimized structure of C-$NaBH_4$, there is a tiny difference between the lattice constants a and c. The space groups of the A- and B-$NaBH_4$ are F-$43m$ and P-$43m$, belong to the cubic system, however the C-$NaBH_4$ with $P4_2/nmc$ symmetry belongs to the tetragonal system. In order to study the phase transition of these three substructures, we need to reconstruct the model as discussed in the following subsection.

3.3. C-$NaBH_4$

Most interestingly, we found that the C-$NaBH_4$ has the same space group as the LT-phase. So it seems that there exists some relationship between the two structures. As explained previously, C-NaBH4 is obtained from the cubic HT-phase and still retains
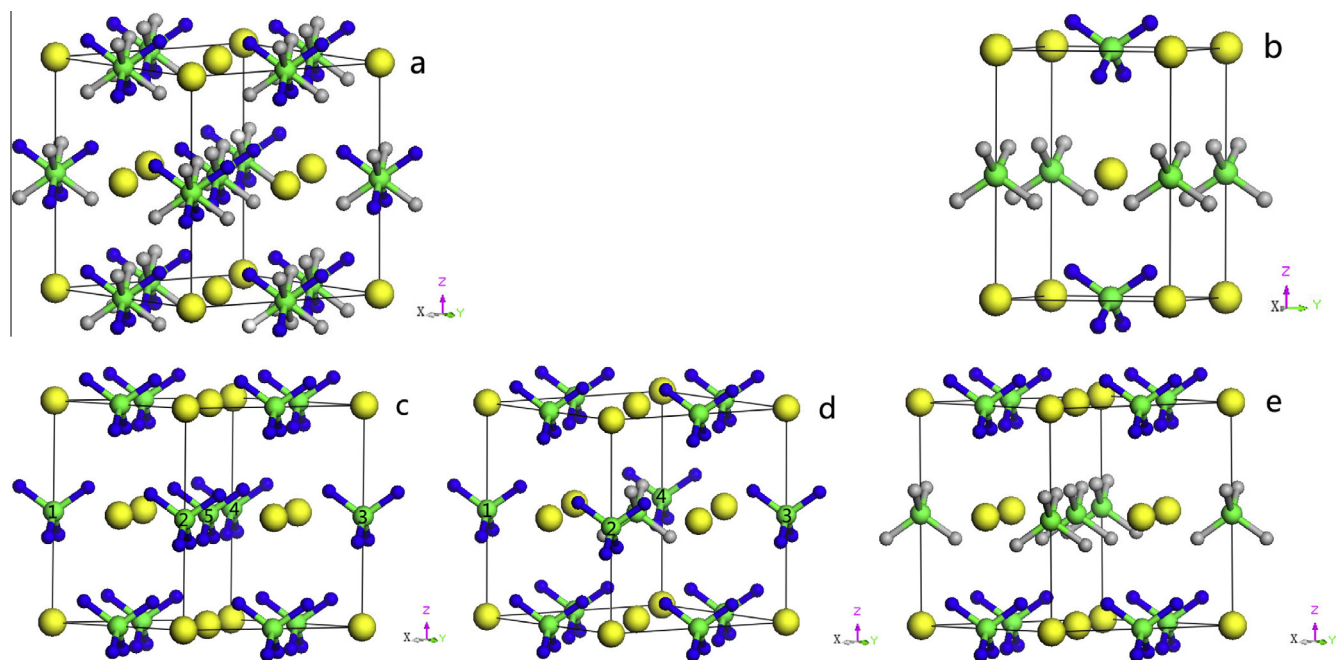

Fig. 1. $NaBH_4$ structures (a) HT-structure, (b) LT-structure, (c) A-$NaBH_4$, (d) B-$NaBH_4$, (e) C-$NaBH_4$ (The yellow spheres represent Na atoms, the green spheres represent B atoms, the gray and the blue spheres represent H atoms). Two orientations of the disordered BH_4^- group in the cubic phase are shown by gray and blue colors. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)