Structure determination of an amorphous compound AlB4H11

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The amorphous nature of AlB$_4$H$_{11}$ and its insolubility in organic solvents prevent us from determining its structure using XRD, neutron diffraction, solution NMR, or mass spectrometry techniques. Solid-state NMR and vibrational spectra were found to be insufficient for even speculating on its structure. Instead, a novel combination of experimental measurements (NMR, IR, and neutron vibrational spectroscopy (NVS)) with a theoretical prediction method (the Monte-Carlo based prototype electrostatic ground state search (PEGS) with density functional theory (DFT) calculations) are used to identify local structures of this amorphous AlB$_4$H$_{11}$ phase as schematically depicted in Fig. 1.

We measured the vibrational spectra of AlB$_4$H$_{11}$ and in parallel used the PEGS + DFT method to predict the preliminary AlB$_4$H$_{11}$ structures and computed their phonon density of states (pDOS) from DFT. For each theoretical structure, we compared the calculated pDOS with the measured vibration spectra to determine the atomic arrangements represented in the amorphous structure. Based on these theoretical predictions, additional experiments were performed to confirm these atomic arrangements. The PEGS + DFT method was employed again to refine the low-energy structures, using experimentally and theoretically confirmed anion groups as input. This closely coupled, iterative experimental/theoretical procedure terminates when

† Electronic supplementary information (ESI) available: For details of the crystal structure information for structures Str-0, Str-86, Str-108, Str-260, Str-400, and Str-640, $^{11}$B NMR spectra information. See DOI: 10.1039/c2sc21100a

‡ This synthesis was reproduced about a quarter of a century later by Zhao et al. in search of high-capacity hydrogen storage materials.‡ AlB$_4$H$_{11}$ is an amorphous white solid at ambient temperature with several properties that are attractive for hydrogen storage: (1) a high hydrogen content of 13.5 mass %, (2) moderate stability with a decomposition temperature around 125 °C, (3) release of predominantly hydrogen in the desorbed gas, (4) endothermic desorption which is thermodynamically essential for rehydrogenation, and (5) partial rehydrogenation at moderate conditions (which is relatively rare for borane compounds).‡ These properties of AlB$_4$H$_{11}$, in contrast to those of other borane compounds, seem to suggest a completely unique structure.‡ A structure proposed by Himpsl and Bond based on the analogue to pentaborane (B$_5$H$_{11}$) is inconsistent with the IR and $^{11}$B NMR spectra of AlB$_4$H$_{11}$,‡‡ Hence, the determination of the AlB$_4$H$_{11}$ structure is significant for the understanding of its stability and hydrogenation/dehydrogenation properties.

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We measured the vibrational spectra of AlB$_4$H$_{11}$ and in parallel used the PEGS + DFT method to predict the preliminary AlB$_4$H$_{11}$ structures and computed their phonon density of states (pDOS) from DFT. For each theoretical structure, we compared the calculated pDOS with the measured vibration spectra to determine the atomic arrangements represented in the amorphous structure. Based on these theoretical predictions, additional experiments were performed to confirm these atomic arrangements. The PEGS + DFT method was employed again to refine the low-energy structures, using experimentally and theoretically confirmed anion groups as input. This closely coupled, iterative experimental/theoretical procedure terminates when
there is good agreement between experimental measurements and theoretical predictions (Fig. 1).

The structure prediction methodology utilized here, PEGS + DFT, has previously successfully predicted crystal structures of complex hydrides with anion groups like [BH₄]⁻, [B₃H₆]⁻², [B₅H₉]⁻³, and [B₁₂H₁₉]⁻³.⁴–⁶ However, the structural determination of AlB₄H₁₁ is significantly more challenging than these previous cases in two crucial aspects: (1) in these previously predicted structures, the cation and anion groups were known. For AlB₄H₁₁, we know only its stoichiometry and nothing of local geometries or the cationic and anionic units. (2) In all previous structural predictions, the compounds were perfectly crystalline. In order to overcome these barriers and predict low-energy AlB₄H₁₁ structures using PEGS + DFT, we first hypothetically split the AlB₄ stoichiometry into small fragments to make a fragment pool: Al, [AlH₄], [BH₄], [BH₃], and [BH]. In this pool, we chose different combinations (like Groups 1 and 2 in Fig. 2) as inputs to PEGS to build AlB₄H₁₁ and predicted its preliminary low-energy structures. By comparing the theoretically predicted local geometry with the structural information from experimental observations, we then refined our inputs for further PEGS predictions. Additional experimental measurements were performed to further define the structure. Our closely coupled theoretical and experimental approach gives an example of how to solve difficult structures such as AlB₄H₁₁. Our work also extends the application of the PEGS + DFT predictions to amorphous structures when certain structural fragments can be guessed or deduced from experimental information or chemical intuition.

2 Experimental and computational methodology

2.1 General comments

All manipulations were carried out on a standard high vacuum line, in a drybox or air bag under an atmosphere of nitrogen or argon. Ammonia (Matheson),⁷ sodium borohydride (GFS, Chemicals), iodine (GFS Chemicals), and anhydrous aluminum chloride (Aldrich) were used as received. Benzene and 1,2-dimethoxyethane were dried over sodium–benzophenone and freshly distilled prior to use. NVS of AlB₄H₁₁ was performed at 4 K with the Filter Analyzer Neutron Spectrometer a at NIST with 60° and 40° horizontal collimations before and after the CUT (2 2 0) monochromator, respectively. ¹¹B and ¹¹B[¹⁴H] NMR spectra were recorded on a Bruker AM-400 spectrometer at 128.4 MHz, and externally referenced to BF₃·OEt2 in C₆D₆ (δ = 0.00 ppm). ²⁷Al NMR spectra were obtained at 104.3 MHz for ²⁷Al nuclei using [Al(OH)₄]⁺ as reference (δ = 0.00 ppm). Infrared spectra were recorded on a Mattson-Polaris FT-IR spectrometer with 2 cm⁻¹ resolution.

2.2 Reaction of Al(BH₄)₃ with B₂H₆ monitored by ¹¹B and ¹¹B[¹⁴H] NMR

In order to investigate the formation mechanism of AlB₄H₁₁, the reaction between Al(BH₄)₃ and B₂H₆ was monitored using ¹¹B and ¹¹B[¹⁴H] NMR. Because the reaction must be performed at 100 °C under a positive diborane pressure (about 1.5 atm), a special apparatus was designed and connected to the top of a reactor to avoid diborane from escaping when samples were withdrawn (Fig. S1, † note stoppers 1 and 2 on the apparatus). In the reactor, 7.5 mmol Al(BH₄)₃ and 15.0 mmol B₂H₆, both freshly prepared using literature methods,⁸,⁹ were introduced. A sample of the reaction solution was withdrawn at three hour intervals for analysis. To withdraw a sample, the reactor was removed from an oil bath to an air bag. Stopper 2 was turned to an open position and the reactor was turned upside down to allow the reaction solution to fully fill the small space between stoppers 1 and 2. Then stopper 2 was closed and stopper 1 was turned open, and the sample was pipetted into an NMR tube. After the sample collection, stopper 1 was closed and the reactor was restored to initial reaction conditions. All collected samples were examined using ¹¹B and ¹¹B[¹⁴H] NMR.

2.3 Density-functional theory calculations

DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP) code with the projector augmented wave (PAW) scheme,¹⁰ and the generalized gradient approximation of Perdew and Wang¹¹ (GGA-PW91) for the electronic exchange-correlation functional. We used an energy cutoff for the plane wave expansion of 875 eV. We sampled Brillouin zones using Monkhorst–Pack¹² k-point meshes for all compounds with meshes chosen to give a roughly constant density of k-points (30 Å⁻¹) for all compounds. Tests show that our k-point meshes yield energies that are converged to within 0.01 eV per formula
unit (fu). Atomic positions and the unit cell were both relaxed until all the forces and components of the stress tensor were below 0.01 eV Å⁻¹ and 0.2 kbar, respectively. Phonons were calculated using the supercell force constant method as implemented in the program described by Wolverton et al. and the vibrational entropies and enthalpies were obtained by directly summing over the calculated phonon frequencies.

2.4 Structure prediction method

While DFT calculations are typically quite accurate for hydride systems, a direct prediction of unknown crystal structures from DFT is difficult due to the large configuration space which must be explored. For our crystal structure prediction task, we turned to the prototype electrostatic ground state (PEGS) search method in which the hydride system is described by a combination of electrostatic potential and soft sphere repulsion:

$$ E_{\text{PEGS}}^{\text{tot}} = \left( \sum_{i>j} \frac{Q_i Q_j}{d_{ij}} + \sum_{i>j} \frac{1}{d_{ij}^{12}} \right) \left( d_{ij} < (R_i + R_j) \right) $$

where each atom \( i \) is represented by a radius \( R_i \) and a charge \( Q_i \), and \( d_{ij} \) is the separation distance between atoms \( i \) and \( j \). The first term is the point charge electrostatic energy, while the second term is a repulsive soft-sphere potential. The Coulomb interactions are calculated for all pairs of atoms, regardless of distance, while the soft-sphere interactions are only non-zero when atomic spheres \( R \) overlap. The PEGS method requires the division of the solid into cationic and anionic units (which are treated as rigid units during Monte Carlo simulations, described below). In order to obtain preliminary structures of the amorphous AlB\textsubscript{4}H\textsubscript{11} phase, we arbitrarily chose two groups of cation and anion units to form AlB\textsubscript{4}H\textsubscript{11}: Al + [BH\textsubscript{4}] + [BH\textsubscript{3}] + 2[BH\textsubscript{2}] (Group 1 in Fig. 2) and [AlH\textsubscript{4}] + 3[BH\textsubscript{3}] + [BH\textsubscript{2}] (Group 2 in Fig. 2). We obtained the cation ionic radii of Al from standard sources \(( R = 0.5 \text{ Å})\), and its ionic charge was given a nominal value of +3e. The ionic radii and ionic charges of B, Al and H for anion groups [BH\textsubscript{2}]\textsuperscript{2-} and [AlH\textsubscript{4}]\textsuperscript{+} as well as the ionic radii of B and H for the [BH\textsubscript{3}]\textsuperscript{+}, [BH\textsubscript{2}]\textsuperscript{+}, and [BH\textsuperscript{2}] units were all taken from the literature.\textsuperscript{1,3} The anionic group charges for [BH\textsubscript{4}]\textsuperscript{-}, [BH\textsubscript{3}]\textsuperscript{-}, and [BH\textsubscript{2}] were unknown, and we used our chemical intuition to assign charges to B and H in the anion units such that the charges of [BH\textsubscript{3}]\textsuperscript{2-} and [BH\textsubscript{2}]\textsuperscript{2-} in Group 1 and [BH\textsubscript{3}]\textsuperscript{-} and [BH\textsubscript{2}]\textsuperscript{-} in Group 2 could balance the well-known charged units ([BH\textsubscript{4}]\textsuperscript{-} and Al\textsuperscript{3+} in Group 1, and [AlH\textsubscript{4}]\textsuperscript{-} in Group 2). For Group 3 (Fig. 2), the ionic radii of B and H in [BH\textsubscript{3}] were taken from the [BH\textsubscript{2}]\textsuperscript{-} unit in our previously published paper.\textsuperscript{4} The charges distributed on atoms in the [BH\textsubscript{2}]\textsuperscript{-} group ([BH\textsubscript{2}]\textsuperscript{-}) was set to -2 to balance the charges of Al\textsuperscript{3+} and [BH\textsubscript{4}]\textsuperscript{-} were computed by the GAMESS cluster code.\textsuperscript{17} All anion group parameters are given in Table 1.

<table>
<thead>
<tr>
<th>( R_{Ri} )</th>
<th>( R_{Hi} )</th>
<th>( Q_{BH4} )</th>
<th>( Q_{BH3} )</th>
<th>( Q_{BH2} )</th>
<th>( Q_{AlH4} )</th>
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</thead>
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<td>Al</td>
<td>0.93</td>
<td>0.93</td>
<td>0.93</td>
<td>0.93</td>
<td>1.8</td>
</tr>
<tr>
<td>B</td>
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<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.52</td>
</tr>
<tr>
<td>H</td>
<td>-0.7</td>
<td>-3</td>
<td>-3</td>
<td>-1</td>
<td>-3</td>
</tr>
</tbody>
</table>

With the PEGS output structures, the MC movements included cation atom displacements, anion group displacements, anion group rotations, cation/anion swaps, and unit cell vector distortions and volume changes.

Table 1: Cation and anion radii \(( R \) and charges \(( Q \)) in PEGS simulations. In the [BH\textsubscript{3}]\textsuperscript{2-} unit, the B charges are in the sequence of B\textsubscript{0}/B\textsubscript{1}/B\textsubscript{2}, and the H charges are in the sequence of bonding with B\textsubscript{0}/B\textsubscript{1}/B\textsubscript{2}, and a bridging H.

Although PEGS MC simulations provide many candidate structures, the calculated electrostatic potential is too crude to be used alone to predict quantitatively accurate crystal structures. Hence, accurate methods like DFT calculations are needed to carry out a full relaxation of the PEGS output structures. We performed DFT calculations on all structures that resulted from our PEGS outputs, and selected the compounds with the low DFT energies as candidates for the stable structure. We note that during the course of the DFT relaxation, energetically unfavorable anion groups can rearrange into more favorable groups, thus giving us information about preferred anionic units.

2.5 Simulation of vibration spectra based upon the predicted structure of AlB\textsubscript{4}H\textsubscript{11}

For comparison with NVS measurements, the phonon densities of states (pDOS) were calculated from the DFT-optimized structures using the supercell method \((2 \times 2 \times 2 \text{ cell size})\) with finite displacements\textsuperscript{18} and were appropriately weighted to take into account the H, B, and Al total neutron scattering cross sections.

2.6 Simulation of \( ^{11}\text{B} \) NMR spectra based upon the predicted structure of AlB\textsubscript{4}H\textsubscript{11}

The \( ^{11}\text{B} \) NMR shifts were calculated using the GIPAW method as implemented in the Quantum ESPRESSO package.\textsuperscript{19} The \( ^{11}\text{B} \) NMR GIPAW chemical shifts were referenced to B\textsubscript{2}H\textsubscript{6} (by ensuring that the theoretical \( ^{11}\text{B} \) chemical shift of B\textsubscript{2}H\textsubscript{6} coincided with its experimental value, \( \delta 16.6 \text{ ppm referenced to BF}_3\text{OEt}_2 \) in C\textsubscript{6}D\textsubscript{6} (\( \delta 0.00 \text{ ppm} \))).

3 Results and discussion

3.1 Prediction of preliminary AlB\textsubscript{4}H\textsubscript{11} structures using two arbitrary groups

From PEGS + DFT predictions, Str-400 and Str-640 (Fig. 3) are the lowest-energy, one-formula-unit (fu) AlB\textsubscript{4}H\textsubscript{11} crystal structures derived from Groups 1 and 2 (Fig. 2), respectively. (The number in the nomenclature is the energy difference in meV relative to the theoretically predicted lowest-energy AlB\textsubscript{4}H\textsubscript{11} structure, e.g., Str-400 is 400 meV per formula unit higher in

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The B₃H₇ unit exhibits two types of geometries in borane compounds. One is a π-borallyl anion ligand [B₃H₇]²⁻ with a V-shaped geometry, an analogue of a π-allyl moiety C₃H₆²⁻, which is often coordinated to a metal to form a coordination compound.⁴⁶ Another geometry is a Lewis acid neutral ligand [B₃H₇]₂/C0 unit. Both Str-640 and Str-400 form a –[B₃H₇]–Al(BH₄)– chain (Fig. 3). This kind of polymer chain structure is likely to be the base of an amorphous phase, in agreement with the experimental observations.

The B₃H₇ unit in both Str-640 and Str-400 appeared to be triangular in shape but its formal oxidation state should be −2 to be consistent with the typical oxidation state of the Al³⁺ cation and BH₄⁻ anion in the AlB₄H₁₁ (Al(BH₄)(B₃H₇)) formula. The [B₃H₇]²⁻ unit in Str-640 contains two bridging H atoms while that in Str-400 contains only one bridging H atom (Fig. 3), which can be viewed as removing one bridging H atom from the [B₃H₇]⁺ unit.²⁴ The triangular [B₃H₇]⁻ geometry in Str-400 is the same as that in the NH₃B₃H₇ compound.²² The total energy of Str-400 is ~240 meV per fu lower than that of the Str-640 structure, indicating that the [B₃H₇]⁻ geometry in Str-400 is more favorable than that in Str-640.

### 3.2 Chemical composition information obtained from the reaction of AlB₄H₁₁ with liquid ammonia

Having obtained initial predictions of structure from theory, we turn to experimental measurement to further refine the structural information. Since the polymeric AlB₄H₁₁ compound did not dissolve in any organic solvent we tested and it completely decomposed in water, no spectroscopic information could be obtained from solution-based measurements. However, we found that when liquid ammonia was condensed onto the solid powder of AlB₄H₁₁, a clear solution emerged without any obvious bubble formation (no gaseous species). The ¹¹B NMR spectrum of AlB₄H₁₁ in liquid ammonia showed two sets of boron signals that are identified as [BH₄]⁻ and [B₃H₇]⁻ based on their chemical shifts and coupling with hydrogen (Fig. 4a).²⁴⁻²⁵ The observation of these species is consistent with the predicted structures and with the known reactions of aluminum borohydrides and aluminum hydrides with ammonia. The absence of hydrogen as a product and the absence of borane ammonia adducts are significant observations. The products indicate AlB₄H₁₁ reacts with liquid ammonia rather than simply dissolving in it. The aluminum borohydride Al(BH₄)₃ reacts with stoichiometric NH₃ to form Al(BH₄)(NH₃)₂ but with excess ammonia forms [Al(NH)(NH₃)₃]BH₄ which is soluble in liquid ammonia.²⁶ The hexamminealuminum and borohydride ions are both chemically stable in liquid ammonia. In contrast, AlH₃ reacts with liquid ammonia to evolve hydrogen (reaction eqn (1)).²⁷ The amido species, Al(NH₂)₃, rearranges to form imido and nitride species, Al(NH)(NH₃) and AlN.²⁷

\[
\text{AlH}_3 + 3\text{NH}_3 \rightarrow \text{Al(NH)}_2\text{Al(NH)}_3 + 3\text{H}_2 \tag{1}
\]

![Fig. 4](image-url) (a) ¹¹B and (b) ²⁷Al NMR spectra of AlB₄H₁₁ in liquid ammonia.
AlB₄H₁₁ + 6NH₃ → [Al(NH₃)₅(NH₂)]⁺ + BH₄⁻ + B₃H₈⁻ (2)

The absence of molecular hydrogen suggests AlB₄H₁₁ does not contain a terminal Al–H bond, and the [B₃H₇]⁻ ion could arise from H⁺ donation from NH₃ coordinated to Al(III) to coordinated B₃H₈⁻ (reaction eqn (2)).

The ²⁷Al NMR spectrum also showed two signals δ 9.2 and 7.6 ppm, indicating that two kinds of Al environments, a six-coordinated aluminum and other various coordinated environments, were present after AlB₄H₁₁ reacted with liquid ammonia (Fig. 4b). One explanation is that the amide complexes of aluminum in liquid ammonia begin to oligomerize and separate signals arise from monomer and dimer (amide bridged). An alternative explanation is that there are different types of Al-coordinated environments in AlB₄H₁₁, which when reacted with liquid ammonia produced two types of Al species. Although the analysis of ²⁷Al MAS NMR spectra primarily indicated that Al was considered as a single site in AlB₄H₁₁, the existence of Al with multiple chemical environments in this amorphous compound is possible considering the very broad Al signal in the solid ²⁷Al NMR spectra of AlB₄H₁₁, in contrast to the sharp Al signals in the solid of ²⁷Al NMR spectra of other amorphous compounds such as aluminates, glasses, or other non-crystalline components in mineral or ceramic systems.

3.3 Prediction of AlB₄H₁₁ structures using [BH₄]⁻ and [B₃H₇]²⁻ units

Based on the structural information obtained from the NMR experiments, we subsequently further refined the theoretically predicted structures. Structures such as Str-0 and Str-640 predicted from PEGS + DFT using one formula unit have only one type of Al chemical environment because there is only a single Al in the formula unit (fu). When the PEGS + DFT calculations were extended to larger cells with two formula units (now using the experimentally confirmed [BH₄]⁻ and [B₃H₇]²⁻ anionic units), the predicted 2-fu structures of AlB₄H₁₁ indeed exhibited two distinct Al environments (the neighboring [BH₄]⁻ and [B₃H₇]²⁻ units had different orientations). Furthermore, these 2-fu structures have much lower energy than that of the 1-fu structures. Fig. 3 shows four predicted low-energy AlB₄H₁₁ structures: Str-0, Str-86, Str-108 and Str-260, each of which contains 2-fu. Among them, Str-0 is the lowest-energy structure, which is 86, 108, and 260, 400, and 640 meV per fu lower than Str-86, Str-108, and Str-260, and the previously predicted 1-fu Str-400 and Str-640, respectively. The low-energy 2-fu AlB₄H₁₁ structures (Str-0, Str-86, Str-108 and Str-260 in Fig. 3) still maintain the same [B₃H₇]⁻–Al(BH₄)⁻ polymer chain as in both Str-640 and Str-400, but the two BH₄ units are now twisted relative to each other perpendicular to the chain direction, thus requiring a longer repeating unit: -[B₃H₇]⁻–Al(BH₄)⁻-[B₃H₇]⁻–Al(BH₄)⁻.

3.4 Comparison of pDOS with experimental spectra

In order to assess the correctness of predicted structures, we compare the calculated phonon density of states (pDOS) of the predicted structures of Str-0, Str-86, Str-108, Str-260 and Str-400 from PEGS + DFT with the experimental spectra, NVS from 250 to 1750 cm⁻¹ and IR spectra from 1500 to 2750 cm⁻¹ (Fig. 5). For the calculated pDOS of Str-400, there is a discrepancy below 750 cm⁻¹ in the NVS where the peak positions of the computed pDOS are ~100 cm⁻¹ lower than experimental measurements. The peak positions in this region are dominated by the vibration of the heavy atom (Al). Hence, we find that the pDOS of the predicted 2-fu low-energy AlB₄H₁₁ structures (especially Str-0, Str-86, Str-108 in Fig. 3) with two Al environments is in better agreement with the experimental results in the low-frequency region (<500 cm⁻¹) than Str-400 that contains only one Al environment (Fig. 5).

All predicted structures possess vibrational modes associated with B–H bonds in the region between 2000 and 2750 cm⁻¹, which is in general agreement with the experimental IR spectra. The comparison of the pDOS of the 2-fu Str-0, Str-86 and Str-108 with 2-fu Str-260 and 1-fu Str-400 shows a difference in the region of 1500 to 1750 cm⁻¹: the pDOS of Str-260 and Str-400 do not have a peak at ~1610 cm⁻¹ that is present in the pDOS of other 2-fu AlB₄H₁₁ structures. Str-0, Str-86 and Str-108 contain two [B₃H₇]²⁻ units and the B–H bond lengths involving bridging H are 1.29 and 1.44 A in one unit and 1.32 and 1.34 A in the other. These B–H bond lengths agree well with those in the [B₃H₇] cluster of an experimentally determined NH₃·B₃H₇ compound. The bond lengths of the bridging H with nearby B are 1.324 and 1.324 A in a monomer and are changed to 1.294 and 1.362 A in a dimer. The eigenvectors/eigenvalues obtained via
direct diagonalization of the dynamical matrix of the AlB3H11 structures (Str-0, Str-86 and Str-108) show that the bridging H vibrations in the first [B3H3] unit contribute to modes with frequencies of ~1267 and ~2143 cm\(^{-1}\) while the other unit vibrates at a frequency in the region from 1500 to 1750 cm\(^{-1}\) (~1618 cm\(^{-1}\)) which is in good agreement with the NH3B3H7 IR measurement (1599 cm\(^{-1}\)).\(^\text{23a}\) Note that the 2-fu Str-260 (ref. 29) has two [B3H7]\(^{2-}\) units, but the B–H bond lengths involving bridging H in the two units are the same: 1.29 and 1.44 Å; thus, it produces a peak in the region from 1500 to 1750 cm\(^{-1}\) that is associated with the 1.32 and 1.34 Å values in Str-0, Str-86, and Str-108.

Some H atoms from the [BH\(_4\)] and [B3H7] units are located very close to the Al atoms or bridged with B and Al. Although they lead to the Al–H (bridging) stretching that is characteristic of Al–H vibrational frequencies around 1500 cm\(^{-1}\) as observed in Al(BH\(_4\))\(_3\),\(^\text{30}\) they do not lead to the formation of [AlH\(_4\)] units. If AlB\(_4\)H\(_11\) contained an [AlH\(_4\)] cluster, which has short Al–H bond lengths, the stretching of the Al–H bond would exhibit frequencies at ~1780 cm\(^{-1}\).\(^\text{31}\) The absence of a peak at ~1780 cm\(^{-1}\) in both experimental measurements and theoretical pDOS calculations further corroborates our previous conclusion that there is no terminal Al–H in AlB\(_4\)H\(_11\), which is consistent with the observation of no hydrogen release when AlB\(_4\)H\(_11\) reacted with liquid ammonia.

Although overall good agreement is observed between the pDOS of the theoretically predicted low-energy AlB\(_4\)H\(_11\) structures (Str-0, Str-86 and Str-108) and the experimental vibrational measurements (NVS and IR), some small discrepancies in peak positions and intensities exist (Fig. 5), which may be related to several factors. The experimental IR and NVS spectra were obtained from the amorphous AlB\(_4\)H\(_11\) phase, while the theoretical pDOS were calculated using crystalline AlB\(_4\)H\(_11\) structures.\(^\text{32}\) The –[B3H7]–Al(BH\(_4\))– polymer chain in the amorphous AlB\(_4\)H\(_11\) may be twisted or reoriented like the different orientations in Str-0, Str-86, and Str-108, thus shifting the frequencies. It is also important to note that the degree of agreement between experimental NVS and simulated spectra is compound-dependent and is based on the ability to accurately model the various types of bonding interactions that are present. As such, agreement for any given compound, even if the crystal structure is known, can be less than perfect, especially in the low-frequency region, where significant shifts have been reported.\(^\text{33}\) Nonetheless, the overall good agreement between theoretical and experimental vibrational modes in the present case suggests that DFT describes the bonding interactions fairly well, and is consistent with an AlB\(_4\)H\(_11\) amorphous phase containing distinct [BH\(_4\)]

\[ \text{[BH}_4\text{]} \]

and [B3H7]\(^{2-}\) units within a –[B3H7]–Al(BH\(_4\))– polymer chain structure.

### 3.5 Comparison between simulated and experimental \(^{11}\)B NMR spectra

To further evaluate the predicted structures, the \(^{11}\)B NMR chemical shifts were simulated using the GIPAW method as implemented in the Quantum ESPRESSO package.\(^\text{34}\) In the simulated \(^{11}\)B NMR, two sets of signals are separately located at higher and lower fields, which is consistent with the solid \(^{11}\)B NMR spectrum of AlB\(_4\)H\(_11\) (Table S2†). The simulated chemical shifts vary from structure to structure but are generally comparable with the experimental AlB\(_4\)H\(_11\) solid-state spectrum that has two broad signals located at around \(\delta = 38.8\) and –51.0 ppm at a roughly 2 : 1 respective ratio.\(^\text{35}\) Three boron signals for the lowest-energy structure (Str-0) are located at higher field (\(\delta = 58.48, -60.96,\) and –61.82 ppm) and five boron signals at lower field (\(\delta = 33.45, -41.29, -46.50, -46.61,\) and –47.61 ppm).

The ratio of the two sets of signals (5 : 3) is close to the experimental value (2 : 1). Two broad peaks created by stacking together the two sets of simulated NMR signals closely resemble the experimental solid-state \(^{11}\)B NMR spectrum of AlB\(_4\)H\(_11\) with the peaks positions only differing by about 8–10 ppm (higher field) (Fig. 6).

Two sets of boron signals are predicted for Str-86 with one set (two signals) located at \(\delta = 59.41\) and –70.40 ppm and the other set (six boron signals) at \(\delta = 30.5\) to –44.13 ppm. The intensity ratio of the two sets is 3 : 1. Both Str-108 and Str-260 have four boron signals at higher field and four boron signals at lower field with the integrated peak intensity ratio of 1 : 1 (see ESI† for details). A comparison of the simulated \(^{11}\)B NMR spectra of these structures with the solid-state \(^{11}\)B NMR spectrum of AlB\(_4\)H\(_11\) indicates that the lowest-energy structure (Str-0) has the best merit in terms of both peak shapes and the peak intensity ratio. Thus we believe Str-0 is the best representation of the AlB\(_4\)H\(_11\) structure.

Both simulated and experimental spectra show the chemical shifts of all boron atoms at a range from \(\delta = -30\) to –70 ppm, which supports the triangle-shaped B\(_5\) unit rather than a V-shaped \(\pi\)-borallyl anion ligand [B\(_3\)H\(_7\)]\(^{2-}\) in which the two terminal boron signals would appear at about \(\delta \geq 8\) ppm and the central boron at about \(\delta < 20\) ppm.\(^\text{36}\) The \(^{11}\)B chemical shift of the Lewis acid B\(_5\)H\(_7\) is very dependent on the coordinated Lewis base, and the observed \(^{11}\)B NMR shift, ranging from at least \(\delta + 8\) to –53 ppm,\(^\text{37}\) is consistent with the triangular boron unit.

### 3.6 Formation mechanism of AlB\(_4\)H\(_11\)

Based on the identified structure of AlB\(_4\)H\(_11\), we performed a preliminary study of its formation mechanism. The reaction of Al(BH\(_4\))\(_3\) and diborane was monitored by \(^{11}\)B and \(^{11}\)B{\(^1\)H}
Al(BH₄)₃ + B₂H₆ → 1/n[HAi(BH₄)₂]₁₋₉-B₂H₇ + H₂ → 
1/n[Al(B₂H₇)(BH₄)]ₙ + ½ B₂H₆ + H₂

Scheme 1 The formation mechanism of AlB₄H₁₁.

formed; and (3) a –[B₂H₇]–Al(BH₄)– polymer chain was formed as shown in Scheme 1.

The mechanism is supported by the observation that Al(BH₄)₃ reacts with CO at ambient temperature to form [HAi(BH₄)₂]ₙ; the CO molecule pulls a BH₃ moiety from Al(BH₄)₃ to produce CO·BH₃.³⁴ε It is reasonable to assume that B₂H₆ performs the same function as CO to react with a BH₃ group of Al(BH₄)₃ to form a B₂H₆ unit and [HAi(BH₄)₂]. For the room-temperature reaction of Al(BH₄)₃ with CO, two signals of BH₄⁻ were detected at δ = 38.0 and –43.3 ppm probably due to the formation of two states of aggregation of [HAi(BH₄)₂]ₙ (n = 1 and 2). This explanation is supported by the formation of both monomer and dimer compounds, [HGa(BH₄)₂] and [HGa(BH₄)₂], in a similar reaction of Ga(BH₄)₃ with CO.³⁶ Thus, at an elevated temperature, reaction of Al(BH₄)₃ with B₂H₆ might have led to higher oligomers of [HAi(BH₄)₂]ₙ, and the small peaks observed at δ = 33.4 to –44.7 ppm are likely representing polymeric [HAi(BH₄)₂]ₙ with more than two different states of oligomers. The initially formed polymer species probably had limited solubility in the reaction solution, so these peaks in their ¹¹B NMR spectra gradually diminished as the reaction proceeded (Fig. 7).

While one set of signals at lower field from δ = 33.4 to –44.7 ppm is reasonably assigned to the intermediate of HAl(BH₄)₂, another set of signals at high field from δ = –52.6 and –53.8 ppm is considered to be related to one of the boron atoms in the B₃H₇ unit which is produced from the reaction of B₂H₆ with a BH₃ group. This reaction has been investigated extensively both theoretically and experimentally.³⁸ The boron signals appearing at such a high field region of ¹¹B NMR spectra is unusual – only when boron atoms are located at unique environments, especially in an open-skeleton structure.³⁷ One boron signal in several Lewis-acid–base adducts of triborane, L·B₃H₇, appeared at this high field region.³⁵ The three B atoms in B₂H₆ display two NMR signals over a wide range. The chemical shifts depend heavilyp on the properties of the coordinated Lewis base. The coordinated B is distinguishable from the other two in the adduct, L·B₂H₆.³⁵ In THF·B₂H₆, the coordinated boron signal was located at δ = 12.8 and the other two B at δ = 44.4 ppm.³⁵ In contrast, the coordinated boron signal in the Lewis adduct pH₃·B₂H₆ appeared at δ = –51.3 ppm, which is close to the small ¹¹B NMR peaks observed in the current experiment, and the other two B signals appeared at δ = –10.2 ppm.³⁵ The exact state of B₂H₆ in the reaction system is unknown and seems to be interacting with [HAi(BH₄)₂]ₙ, as indicated in the predicted structures where each B₂H₆ unit is connected to an Al atom through a bridge hydrogen. Thus, we assumed the small peaks at δ = –52.6 and –53.1 ppm were associated with a B₂H₆ group that is interacting with [HAi(BH₄)₂]ₙ in some way. At an initial stage, these species had some solubility in the solution so they could be detected in ¹¹B NMR spectra. This explanation is consistent with the simulated ¹¹B NMR spectra in which the chemical shifts of B in the B₂H₆ group in Str-0 are distributed over a wide range from δ = –33.45 to –61.82 ppm.

NMR. Each of the starting materials alone, Al(BH₄)₃ or B₂H₆, is found to be stable at 100 °C in benzene solution. The ¹¹B and ¹³B(¹H) NMR spectra of the mixture of Al(BH₄)₃ and B₂H₆ show that when the reaction started, two sets of small peaks simultaneously appeared at δ = 33.4, –36.89, –38.1, –43.6, and –44.7 ppm and at δ = –52.6 and 53.8 ppm (Fig. 7). These peak positions are close to, but not identical to, the two broad peaks observed in the solid ¹¹B NMR spectra of AlB₄H₁₁.² The low-field peaks at around δ = –33.4 to –44.7 ppm are likely related to an intermediate [HAi(BH₄)₂]ₚ with different states (n) of aggregation,³⁴ε and the high-field peaks at δ = –52.6 and –53.8 ppm might be related to a boron hydride species such as B₂H₇ that does not exist alone but interacts with [HAi(BH₄)₂]ₚ or Al₂B₄H₁₄.³³ Nöth showed that diborane dissociates in THF solution to form THF·B₂H₆ and the equilibrium among Al(BH₄)₃, HAi(BH₄)₂, and THF·B₂H₆ is dynamic.³⁴ε Maybury and Larabee measured the kinetics of deuterium and boron exchange between Al(BH₄)₃ and B₂D₆ (and ¹⁰B₂D₃) in the gas phase,³⁵ and proposed a mechanism involving thermal dissociation of both Al(BH₄)₃ and B₂D₆ followed by a rate-limiting reaction between BH₃ (formed from Al(BH₄)₃ dissociation) and B₂D₆. These experimental results led us to propose a formation mechanism of AlB₄H₁₁ as: (1) reaction of B₂H₆ with a BH₃ unit from Al(BH₄)₃ formed [HAi(BH₄)₂]ₚ and B₂H₆ with one H₂ being eliminated; (2) two intermediates of [HAi(BH₄)₂]ₚ and B₂H₆ interacted once they
Al(BH₄)₃ → HAl(BH₄)₂ + BH₃
BH₃ + B₂H₆ → B₂H₆
B₂H₆ + HAl(BH₄)₂ → Al(B₂H₆)(BH₄)₂ + H₂
Al(B₂H₆)(BH₄)₂ → 1/2[Al(B₂H₆)(BH₄)₆] + BH₃ + H₂
BH₃ → ½ B₂H₆

The sequence of reactions in Scheme 2 adds up to the net reaction for the formation of AlB₄H₁₁.

Al(BH₄)₃ + ½ B₂H₆ → AlB₄H₁₁ + 2 H₂

Scheme 2  An alternative formation mechanism for AlB₄H₁₁.

An alternative mechanism involved B₂H₆ reacting with BH₃ from Al(BH₄)₃ dissociation to form B₂H₆. This species reacts with HAl(BH₄)₂ with the elimination of H₂ to form a coordinated B₃H₇⁻ anion. A second mole of H₂ is eliminated as a second BH₃ (from coordinated BH₄⁻) evolves from the intermediate in a reaction of coordinated B₃H₈⁻ with coordinated BH₄⁻. The proposed reaction sequence is shown in Scheme 2.

This alternative mechanism is supported by reports reviewed by Beall et al. in which the formation of a stable B₃H₇⁻ anion from a reaction of diborane with a metal borohydride was observed. It was suggested that B₂H₇⁻ is a possible intermediate. Gaines et al. noted that the triborohydride ion can be prepared by reaction of metal borohydrides with diborane in ether solutions at 100 °C. These authors note that the preparation of B₂H₆⁻ from B₂H₆ and a metal borohydride requires a temperature of about 100 °C to proceed at a reasonable rate. The elimination of H₂, either before the B₂H₆ species is formed or after, is most likely the rate-limiting step. In this alternative reaction sequence, this intermediate may account for the unusually high field resonances at δ -52.6 and -53.8 ppm in which both a monomer and bridged dimer monohydride are initially formed.

We are confident to conclude from the overall good agreement between theoretical and experimental vibrational modes that the AlB₄H₁₁ amorphous phase contains distinct [BH₄] and [B₂H₆] units and also likely two Al environments, and it forms a −[B₂H₆]−Al(BH₄)− polymer chain. The lowest-energy structure (Str-0) has the best merit based not only on the computed ground-state energy, but also on the best observed agreement with NMR and NMR. The slight discrepancy found between the predicted properties of Str-0 and the experimental observations may be due to some twisting or reorientation of the −[B₂H₆]−Al(BH₄)− polymer chain as the chain gets longer.

4. Conclusions

The structure of amorphous AlB₄H₁₁ was predicted theoretically and then assessed experimentally, and the formation mechanism of AlB₄H₁₁ was also proposed. The predicted structures explicitly show a −[B₂H₆]−Al(BH₄)− polymer chain in which B₂H₆ exists in a triangular shape rather than as a V-shaped π-borallyl anion ligand. The BH₄⁻ and B₂H₆ moieties in AlB₄H₁₁ were converted to BH₄⁻ and B₂H₆⁺ in liquid ammonia, which was identified using ¹¹B NMR spectra. Two Al signals were also observed in $^{27}$Al NMR of the AlB₄H₁₁ in liquid ammonia, which is consistent with the predicted lowest-energy structures (Str-0 and Str-86). The computed phonon densities of states of the predicted structures are in good agreement with the experimental vibrational measurements over a wide range of frequencies. The calculated ¹¹B NMR chemical shifts for the predicted structures fall within the range of the experimentally measured values, especially for Str-0, whose simulated NMR peaks agree well with the experimental result. Preliminary study of the formation mechanism of AlB₄H₁₁ using ¹¹B NMR spectroscopy provides two possible pathways for the formation of AlB₄H₁₁.

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Notes and references

7 The mention of all commercial suppliers in this paper is for clarity. This does not imply our recommendation or endorsement of these suppliers.


29 Although the pDOS of Al2B14H30-Str400 has no peaks in the region of 1500–2000 cm⁻¹, we ignore the discussion of the structure in text because it has significantly higher energy than Str-0, and it does not contain the experimentally suggested two and two Al environments.


