## **Supporting Information**

## Structure Determination of an Amorphous Compound AlB<sub>4</sub>H<sub>11</sub>

Xuenian Chen,<sup>a,b</sup> Yongsheng Zhang,<sup>c</sup> Yongli Wang,<sup>c</sup> Wei Zhou,<sup>d,e</sup> Douglas A. Knight,<sup>f</sup> Teshome B. Yisgedu,<sup>a</sup> Zhenguo Huang,<sup>a</sup> Hima K. Lingam,<sup>a</sup> Beau Billet,<sup>a</sup> Terrence J. Udovic,<sup>\*d</sup> Gilbert M. Brown,<sup>\*g</sup> Sheldon G. Shore,<sup>\*b</sup> Christopher Wolverton,<sup>\*c</sup> Ji-Cheng Zhao<sup>\*a</sup>

<sup>a</sup> Department of Materials Science and Engineering and <sup>b</sup> Department of Chemistry. The Ohio State University, Columbus, OH 43210, <sup>c</sup> Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, <sup>d</sup> NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, <sup>e</sup> Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, <sup>f</sup> Savannah River National Laboratory, Aiken SC 29808, <sup>g</sup> Oak Ridge National Laboratory, Oak Ridge, TN 37831

Figure S1. Special apparatus for sample collections during reaction from a reactor containing diborane (at 1.5 atm).

Figure S2. Simulated <sup>11</sup>B NMR spectra of AlB<sub>4</sub>H<sub>11</sub> based on the predicted Str-86.

Figure S3. Simulated <sup>11</sup>B NMR spectra of AlB<sub>4</sub>H<sub>11</sub> based on the predicted Str-108.

Figure S4. Simulated <sup>11</sup>B NMR spectra of AlB<sub>4</sub>H<sub>11</sub> based on the predicted Str-260.

Table S1. PEGS+DFT predicted AlB<sub>4</sub>H<sub>11</sub> structures: Str-0, Str-86, Str-108, Str-260, Str-400, and Str-640.

Table S2. Simulated chemical shifts (ppm) of boron atoms in <sup>11</sup>B NMR spectra of predicted Str-0, Str-86, Str-108, and Str-260.



*Figure S1*. Special apparatus for sample collections during reaction from a reactor containing diborane (at 1.5 atm).

System	Atom	Wyckoff site	Х	y	Z
Str-0	Al	1a	-0.44327	0.07529	0.44095
(P1)	Al	1a	0.25901	-0.40984	0.04455
a=7.117Å	В	1a	0.33880	0.20507	-0.38801
b=7.955Å	В	1a	0.47405	0.17428	-0.21548
c=6.907Å	В	1a	0.35658	0.36078	-0.15702
α=106.46	В	1a	0.43389	-0.18080	0.22807
β=80.58	В	1a	0.30656	-0.33644	0.36654
γ=104.90	В	1a	-0.43998	-0.22000	0.39979
	В	1a	-0.17581	0.21875	0.30673
	В	1a	0.01013	-0.35839	-0.04867
	Н	1a	0.43761	-0.48804	-0.17949
	Н	1a	0.46223	0.33136	-0.04371
	Н	1a	0.41879	0.28021	0.47733
	Н	1a	0.18214	0.10784	-0.42222
	Н	1a	-0.34855	0.20866	-0.22975
	Н	1a	0 39646	0.05862	-0.13024
	н	10	0.18977	0.34394	-0.06864
	ц	10	0.10777	0.28630	0 32443
	11	1a	-0.30447	-0.28030	0.32443
	п	1a	0.43013	-0.34//3	0.47748
	H	la	-0.481/4	-0.21488	0.05748
	Н	la	0.35053	-0.05857	0.25459
	Н	la	0.26511	-0.49904	0.28316
	Н	1a	0.17547	-0.28901	0.48311
	Н	1a	-0.40907	-0.11057	-0.43620
	Н	1a	-0.18196	0.13505	0.43871
	Н	1a	-0.33302	0.17114	0.22644
	Н	1a	-0.15023	0.37636	0.39042
	Н	1a	-0.05711	0.16436	0.17516
	Н	1a	0.00234	-0.43241	0.09403
	H H	1a 1a	0.00234 -0.02592	-0.43241 -0.21375	0.09403 0.02836
	H H H	1a 1a 1a	0.00234 -0.02592 0.18216	-0.43241 -0.21375 -0.32977	0.09403 0.02836 -0.13697
	H H H H	1a 1a 1a 1a	0.00234 -0.02592 0.18216 -0.08746	-0.43241 -0.21375 -0.32977 -0.46746	0.09403 0.02836 -0.13697 -0.17290
System	H H H H	la la la Wyckoff site	0.00234 -0.02592 0.18216 -0.08746	-0.43241 -0.21375 -0.32977 -0.46746	0.09403 0.02836 -0.13697 -0.17290
System	H H H Atom	la la la Wyckoff site	0.00234 -0.02592 0.18216 -0.08746 x 0.16965	-0.43241 -0.21375 -0.32977 -0.46746 <u>y</u> -0.25467	$ \begin{array}{r} 0.09403 \\ 0.02836 \\ -0.13697 \\ -0.17290 \\ \hline z \\ 0.39606 \\ \end{array} $
System Str-86 (P1)	H H H Atom Al Al	la la la Wyckoff site la la	0.00234 -0.02592 0.18216 -0.08746 <u>x</u> 0.16965 0.13917	-0.43241 -0.21375 -0.32977 -0.46746 <u>y</u> -0.25467 -0.48621	0.09403 0.02836 -0.13697 -0.17290 z 0.39606 -0.08570
System Str-86 (P1) a=6 193Å	H H H Atom Al Al B	la la la Wyckoff site la la la	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545	-0.43241 -0.21375 -0.32977 -0.46746 <u>y</u> -0.25467 -0.48621 -0.23402	0.09403 0.02836 -0.13697 -0.17290 z 0.39606 -0.08570 -0.25260
System Str-86 (P1) a=6.193Å b=6.220Å	H H H Atom Al Al B B B	la la la Wyckoff site la la la la	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321	-0.43241 -0.21375 -0.32977 -0.46746 <u>y</u> -0.25467 -0.48621 -0.23402 -0.32365	0.09403 0.02836 -0.13697 -0.17290 z 0.39606 -0.08570 -0.25260 -0.41054
System Str-86 (P1) a=6.193Å b=6.220Å c=10.044Å	H H H Atom Al Al B B B B	la la la Wyckoff site la la la la la la	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438	-0.43241 -0.21375 -0.32977 -0.46746 <u>y</u> -0.25467 -0.48621 -0.23402 -0.32365 -0.45940	0.09403 0.02836 -0.13697 -0.17290 z 0.39606 -0.08570 -0.25260 -0.41054 -0.28307
System Str-86 (P1) a=6.193Å b=6.220Å c=10.044Å α=79.98	H H H Atom Al Al B B B B B B B	la la la Wyckoff site la la la la la la la la	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102	-0.43241 -0.21375 -0.32977 -0.46746 <u>y</u> -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067	0.09403 0.02836 -0.13697 -0.17290 z 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420
System Str-86 (P1) a=6.193Å b=6.220Å c=10.044Å α=79.98 β=103.98	H H H Atom Al Al B B B B B B B B B B	la la la la Wyckoff site la la la la la la la la la	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744	-0.43241 -0.21375 -0.32977 -0.46746 <u>y</u> -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191	0.09403 0.02836 -0.13697 -0.17290 z 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420 0.20253
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	H H H Atom Al Al B B B B B B B B B B B B B B B B B	la la la la Wyckoff site la la la la la la la la la la la	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744 0.03835	-0.43241 -0.21375 -0.32977 -0.46746 <u>y</u> -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191 -0.42480	0.09403 0.02836 -0.13697 -0.17290 z 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420 0.20253 0.09994
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	H H H Atom Al Al B B B B B B B B B B B B B B B B B	la la la la Wyckoff site la la la la la la la la la la la la	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744 0.03835 0.44313	-0.43241 -0.21375 -0.32977 -0.46746 <u>y</u> -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191 -0.42480 -0.02140	0.09403 0.02836 -0.13697 -0.17290 z 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420 0.20253 0.09994 0.40044
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	H H H Atom Al Al B B B B B B B B B B B B B B B B B	la la la la Wyckoff site la la la la la la la la la la la la la	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744 0.03835 0.44313 0.35602	-0.43241 -0.21375 -0.32977 -0.46746 <u>y</u> -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191 -0.42480 -0.02140 0.28745	0.09403 0.02836 -0.13697 -0.17290 z 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420 0.20253 0.09994 0.40044 -0.04608
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	H H H Atom Al Al B B B B B B B B B B B B B B B B B	la la la la Wyckoff site la la la la la la la la la la la la la	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744 0.03835 0.44313 0.35602 -0.09534	-0.43241 -0.21375 -0.32977 -0.46746 <u>y</u> -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191 -0.42480 -0.02140 0.28745 0.34684	0.09403 0.02836 -0.13697 -0.17290 2 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420 0.20253 0.09994 0.40044 -0.04608 -0.23609
$\begin{tabular}{ c c c c c c c } \hline System & \\ Str-86 & (P1) \\ a=6.193 \text{\AA} & \\ b=6.220 \text{\AA} & \\ c=10.044 \text{\AA} & \\ a=79.98 & \\ \beta=103.98 & \\ \gamma=99.84 & \\ \hline \end{tabular}$	H H H Atom Al Al B B B B B B B B B B B B B B B B B	la la la la Wyckoff site la la la la la la la la la la la la la	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744 0.03835 0.44313 0.35602 -0.09534 -0.11194	-0.43241 -0.21375 -0.32977 -0.46746 <u>y</u> -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191 -0.42480 -0.02140 0.28745 0.34684 -0.49141	0.09403 0.02836 -0.13697 -0.17290 2 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420 0.20253 0.09994 0.40044 -0.04608 -0.23609 -0.42004
$\frac{\text{System}}{\text{Str-86}} \\ (P1) \\ a=6.193\text{\AA} \\ b=6.220\text{\AA} \\ c=10.044\text{\AA} \\ \alpha=79.98 \\ \beta=103.98 \\ \gamma=99.84 \\ \end{cases}$	H H H Atom Al B B B B B B B B B B B B B B B B B B	la la la la Wyckoff site la la la la la la la la la la la la la	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744 0.03835 0.44313 0.35602 -0.09534 -0.11194 0.29418	-0.43241 -0.21375 -0.32977 -0.46746 <u>y</u> -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191 -0.42480 -0.02140 0.28745 0.34684 -0.49141 -0.25486	0.09403 0.02836 -0.13697 -0.17290 Z 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420 0.20253 0.09994 0.40044 -0.04608 -0.23609 -0.42004 -0.19701
$\frac{\text{System}}{\text{Str-86}} \\ (P1) \\ a=6.193 \text{\AA} \\ b=6.220 \text{\AA} \\ c=10.044 \text{\AA} \\ a=79.98 \\ \beta=103.98 \\ \gamma=99.84 \\ \end{cases}$	H H H Atom Al B B B B B B B B B B B B B B B B H H H H H H	la la la la Myckoff site la la la la la la la la la la la la la	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744 0.03835 0.44313 0.35602 -0.09534 -0.11194 0.29418 0.04181	-0.43241 -0.21375 -0.32977 -0.46746 <u>y</u> -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191 -0.42480 -0.02140 0.28745 0.34684 -0.49141 -0.25486 -0.06557	0.09403 0.02836 -0.13697 -0.17290 Z 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420 0.20253 0.09994 0.40044 -0.04608 -0.23609 -0.42004 -0.19701 -0.23762
$\frac{\text{System}}{\text{Str-86}} \\ (P1) \\ a=6.193\text{ Å} \\ b=6.220\text{ Å} \\ c=10.044\text{ Å} \\ a=79.98 \\ \beta=103.98 \\ \gamma=99.84 \\ \end{cases}$	H H H Atom Al B B B B B B B B B B B B B B B B H H H H H H H H	la la la la wyckoff site la la la la la la la la la la la la la	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744 0.03835 0.44313 0.35602 -0.09534 -0.11194 0.29418 0.04181 0.20442	-0.43241 -0.21375 -0.32977 -0.46746 y -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191 -0.42480 -0.02140 0.28745 0.34684 -0.49141 -0.25486 -0.06557 -0.40415	0.09403 0.02836 -0.13697 -0.17290 Z 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420 0.20253 0.09994 0.40044 -0.04608 -0.23609 -0.42004 -0.19701 -0.23762 -0.42399
$\begin{tabular}{ c c c c c c c } \hline System & \\ Str-86 & (P1) & \\ a=6.193 \text{\AA} & \\ b=6.220 \text{\AA} & \\ c=10.044 \text{\AA} & \\ a=79.98 & \\ \beta=103.98 & \\ \gamma=99.84 & \\ \hline \end{tabular}$	H H H Atom Al B B B B B B B B B B B B B B B B B B	la la la la wyckoff site la la la la la la la la la la la la la	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744 0.03835 0.44313 0.35602 -0.09534 -0.11194 0.29418 0.04181 0.20442 0.02418	-0.43241 -0.21375 -0.32977 -0.46746 y -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191 -0.42480 -0.02140 0.28745 0.34684 -0.02140 0.28745 0.34684 -0.49141 -0.25486 -0.06557 -0.40415 0.18647	0.09403 0.02836 -0.13697 -0.17290 Z 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420 0.20253 0.09994 0.40044 -0.23609 -0.42004 -0.19701 -0.23762 -0.42399 0.40212
$\begin{tabular}{ c c c c c }\hline\hline System \\ Str-86 \\ (P1) \\ a=6.193 Å \\ b=6.220 Å \\ c=10.044 Å \\ a=79.98 \\ \beta=103.98 \\ \gamma=99.84 \end{tabular}$	H H H Atom Al B B B B B B B B B B B B B B B B B B	la la la wyckoff site la la la la la la la la la la la la la	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744 0.03835 0.44313 0.35602 -0.09534 -0.11194 0.29418 0.04181 0.20442 -0.03418	-0.43241 -0.21375 -0.32977 -0.46746 y -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191 -0.42480 -0.02140 0.28745 0.34684 -0.02140 0.28745 0.34684 -0.49141 -0.25486 -0.06557 -0.40415 -0.18647	0.09403 0.02836 -0.13697 -0.17290 Z 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420 0.20253 0.09994 0.40044 -0.04608 -0.23609 -0.42004 -0.19701 -0.23762 -0.42399 0.49312 0.2025
$\begin{tabular}{ c c c c c c } \hline System & \\ Str-86 & (P1) & \\ a=6.193 \text{\AA} & \\ b=6.220 \text{\AA} & \\ c=10.044 \text{\AA} & \\ a=79.98 & \\ \beta=103.98 & \\ \gamma=99.84 & \\ \hline \end{array}$	H H H Atom Al B B B B B B B B B B B B B B B B B B	la la la la wyckoff site la la la la la la la la la la la la la	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744 0.03835 0.44313 0.35602 -0.09534 -0.11194 0.29418 0.04181 0.20442 -0.03418 -0.30085 0.21672	-0.43241 -0.21375 -0.32977 -0.46746 y -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191 -0.42480 -0.02140 0.28745 0.34684 -0.02140 0.28745 0.34684 -0.49141 -0.25486 -0.06557 -0.40415 -0.18647 -0.41891	0.09403 0.02836 -0.13697 -0.17290 Z 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420 0.20253 0.09994 0.40044 -0.04608 -0.23609 -0.42004 -0.19701 -0.23762 -0.42399 0.49312 -0.29626 0.27622
$\begin{tabular}{ c c c c c } \hline System & \\ Str-86 & (P1) & \\ a=6.193 \text{\AA} & \\ b=6.220 \text{\AA} & \\ c=10.044 \text{\AA} & \\ a=79.98 & \\ \beta=103.98 & \\ \gamma=99.84 & \\ \hline \end{tabular}$	H H H Atom Al B B B B B B B B B B B B B B B B B B	1a 1a 1a 1a 1a 1a 1a 1a 1a 1a 1a 1a 1a 1	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744 0.03835 0.44313 0.35602 -0.09534 -0.11194 0.29418 0.04181 0.20442 -0.03418 -0.30085 0.21853	-0.43241 -0.21375 -0.32977 -0.46746 y -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191 -0.42480 -0.02140 0.28745 0.34684 -0.02140 0.28745 0.34684 -0.49141 -0.25486 -0.06557 -0.40415 -0.18647 -0.41891 -0.33911	0.09403 0.02836 -0.13697 -0.17290 Z 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420 0.20253 0.09994 0.40044 -0.04608 -0.23609 -0.42004 -0.19701 -0.23762 -0.42399 0.49312 -0.29626 0.07003 2.6611
$\frac{\text{System}}{(P1)} \\ a=6.193\text{ Å} \\ b=6.220\text{ Å} \\ c=10.044\text{ Å} \\ a=79.98 \\ \beta=103.98 \\ \gamma=99.84 \\ \end{cases}$	H H H Atom Al B B B B B B B B B B B B B B B B B B	1a 1a 1a 1a 1a 1a 1a 1a 1a 1a 1a 1a 1a 1	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744 0.03835 0.44313 0.35602 -0.09534 -0.11194 0.29418 0.04181 0.20442 -0.03418 -0.30085 0.21853 -0.07825	-0.43241 -0.21375 -0.32977 -0.46746 y -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191 -0.42480 -0.02140 0.28745 0.34684 -0.02140 0.28745 0.34684 -0.49141 -0.25486 -0.06557 -0.40415 -0.18647 -0.41891 -0.33911 -0.26228	0.09403 0.02836 -0.13697 -0.17290 Z 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420 0.20253 0.09994 0.40044 -0.04608 -0.23609 -0.42004 -0.19701 -0.23762 -0.42399 0.49312 -0.29626 0.07003 0.06011
$\frac{\text{System}}{(P1)} \\ a=6.193\text{ Å} \\ b=6.220\text{ Å} \\ c=10.044\text{ Å} \\ a=79.98 \\ \beta=103.98 \\ \gamma=99.84 \\ \end{cases}$	H H H Atom Al B B B B B B B B B B B B B B B B B B	1a         1a	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744 0.03835 0.44313 0.35602 -0.09534 -0.11194 0.29418 0.04181 0.20442 -0.03418 -0.30085 0.21853 -0.07825 0.27522	-0.43241 -0.21375 -0.32977 -0.46746 y -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191 -0.42480 -0.02140 0.28745 0.34684 -0.02140 0.28745 0.34684 -0.06557 -0.40415 -0.18647 -0.41891 -0.33911 -0.26228 -0.47871	$\begin{array}{c} 0.09403\\ 0.02836\\ -0.13697\\ -0.17290\\ \hline z\\ \hline 0.39606\\ -0.08570\\ -0.25260\\ -0.41054\\ -0.28307\\ 0.27420\\ 0.20253\\ 0.09994\\ 0.40044\\ -0.04608\\ -0.23609\\ -0.42004\\ -0.19701\\ -0.23762\\ -0.42399\\ 0.49312\\ -0.29626\\ 0.07003\\ 0.06011\\ 0.32523\\ \end{array}$
$\frac{\text{System}}{(P1)} \\ a=6.193\text{ Å} \\ b=6.220\text{ Å} \\ c=10.044\text{ Å} \\ a=79.98 \\ \beta=103.98 \\ \gamma=99.84 \\ \end{cases}$	H H H Atom Al Al B B B B B B B B B B B B B B B B B	1a         1a	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744 0.03835 0.44313 0.35602 -0.09534 -0.11194 0.29418 0.04181 0.20442 -0.03418 -0.30085 0.21853 -0.07825 0.27522 -0.02240	-0.43241 -0.21375 -0.32977 -0.46746 y -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191 -0.42480 -0.02140 0.28745 0.34684 -0.02140 0.28745 0.34684 -0.06557 -0.40415 -0.18647 -0.41891 -0.33911 -0.26228 -0.47871 0.32008	0.09403 0.02836 -0.13697 -0.17290 Z 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420 0.20253 0.09994 0.40044 -0.04608 -0.23609 -0.42004 -0.19701 -0.23762 -0.42399 0.49312 -0.29626 0.07003 0.06011 0.32523 0.32118
$\begin{tabular}{ c c c c c c } \hline System & \\ Str-86 & (P1) & \\ a=6.193 \text{\AA} & \\ b=6.220 \text{\AA} & \\ c=10.044 \text{\AA} & \\ a=79.98 & \\ \beta=103.98 & \\ \gamma=99.84 & \\ \hline \end{array}$	H H H Atom Al Al B B B B B B B B B B B B B B B B B	1a         1a	0.00234 -0.02592 0.18216 -0.08746 x 0.16965 0.13917 0.09545 0.04321 -0.11438 0.07102 -0.08744 0.03835 0.44313 0.35602 -0.09534 -0.11194 0.29418 0.04181 0.20442 -0.03418 -0.30085 0.21853 -0.07825 0.27522 -0.02240 -0.02183	-0.43241 -0.21375 -0.32977 -0.46746 y -0.25467 -0.48621 -0.23402 -0.32365 -0.45940 0.49067 -0.29191 -0.42480 -0.02140 0.28745 0.34684 -0.02140 0.28745 0.34684 -0.02140 0.28745 0.34684 -0.06557 -0.40415 -0.18647 -0.41891 -0.33911 -0.26228 -0.47871 0.32008 -0.09643	0.09403 0.02836 -0.13697 -0.17290 Z 0.39606 -0.08570 -0.25260 -0.41054 -0.28307 0.27420 0.20253 0.09994 0.40044 -0.04608 -0.23609 -0.42004 -0.19701 -0.23762 -0.42399 0.49312 -0.29626 0.07003 0.06011 0.32523 0.32118 0.21388

*Table S1*: PEGS+DFT predicted AlB<sub>4</sub>H<sub>11</sub> structures: Str-0, Str-86, Str-108, Str-260, Str-400, and Str-640.

## Electronic Supplementary Material (ESI) for Chemical Science This journal is The Royal Society of Chemistry 2012

	i.				
	Н	1a	-0.28432	-0.33921	0.19757
	Н	1a	-0.07319	0.43305	0.03017
	Н	1a	-0.40564	0.12232	0.42544
	Н	1a	0.40096	-0.06681	0.28230
	Н	1a	0.48083	-0.19180	0.48282
	Н	1a	0.27068	0.03748	0.41987
	Н	1a	0.47520	0.14875	0.00046
	Н	1a	0.32169	0.33768	-0.17193
	Н	1a	0.17001	0.21970	-0.01435
	Н	1a	0.43565	0.45646	0.00909
System	Atom	Wyckoff site	x	V	Z.
Str-108	Al	1a	0.43120	0.44856	-0.46516
(P1)	Al	1a	0.13889	0.03663	0.04353
a=7.779Å	В	1a	0.31947	-0.27472	-0.33388
b=7.344Å	В	1a	0.21151	-0.21815	-0.16773
c=7.893Å	В	1a	0.19105	-0.44388	-0.34374
α=108.47	В	1a	0.30516	0.23432	0.27406
β=112.83	B	1a	0.28865	0.45622	0.22369
$\gamma = 74.30$	B	la	0.31796	0.22940	0.05536
	В	la	-0.12045	0.02117	0.0/192
	В	la	-0.2/438	0.32836	-0.32779
	Н	la	0.03/46	-0.45064	-0.46141
	H	la	0.13554	-0.35666	-0.17634
	Н	la	0.25799	-0.17753	-0.44808
	Н	1a	0.49222	-0.29783	-0.25788
	Н	1a	0.07318	-0.08823	-0.20628
	Н	1a	0.32110	-0.18595	-0.00165
	Н	1a	0.26981	0.40188	-0.29870
	Н	1a	0.46063	0.14413	0.02463
	Н	1a	0.31146	0.41083	0.05558
	Н	1a	0.44585	0.14862	0.37245
	Н	1a	0.15992	0.23060	0.29709
	Н	1a	0.42356	-0.45678	0.31188
	Н	1a	0.13772	-0.44083	0.20208
	Н	1a	0.17485	0.20020	-0.08590
	Н	1a	-0.16118	0.11775	0.20915
	Н	1a	-0.10180	0.14151	-0.00403
	Н	1a	0.03823	-0.08488	0.13399
	Н	1a	-0.22179	-0.08443	-0.05239
	Н	1a	-0.18200	0.43071	-0.18871
	Н	1a	-0.41340	0.31253	-0.29193
	Н	1a	-0.32814	0.41520	-0.45907
	Н	1a	-0.20432	0.16525	-0.38809
System	Atom	Wvckoff site	X	V	Z
Str-260	Al	1a	0.31640	-0.46829	-0.11083
(P1)	Al	1a	0.46445	-0.01467	0.44132
a=6.700Å	В	1a	0.23310	0.15864	0.35678
b=7.746Å	В	1a	0.31265	0.35257	0.16516
c=8.150A	B	1a	0.46040	0.29217	0.35525
$\alpha = 67.80$	B	la	0.42474	-0.17344	-0.25340
p=8/./0	В	1a 1-	-0.32611	-0.0/982	-0.33827
γ=96.16	B	1a	-0.3/913	-0.51584	-0.1/813
	D	1a 1a	0.08007	0.42383	-0.23903
	D	1a 1-	-0.45100	-0.13428	0.20389
	Н	1a	0.45620	0.38130	0.44058
	Н	1a	0.48248	0.45/21	0.1816/
	H	1a	0.09534	0.15656	0.45540
	Н	la	0.22111	0.01827	0.31796

		Н	1a	0.19633	0.47167	0.13130
		Н	1a	0.35010	0.29345	0.04708
		Н	1a	-0.37034	0.25255	0.33360
		Н	1a	-0.32897	-0.33832	-0.03302
		Н	1a	-0.21817	-0.22271	-0.28935
		Н	1a	0.34143	-0.10033	-0.16901
		Н	1a	0 30980	-0 22012	-0 34962
		Н	1a	-0.25118	0.03592	-0.28831
		н	1a	-0 27017	-0.04354	-0.49520
		н	10	-0.38666	-0.45870	-0.21160
		н	10	0.04054	-0.43070	-0.38187
		ц	10	0.04034	0.41402	0.25021
		и П	10	0.27342	0.41492	-0.23921
		п	1a	0.03570	-0.49137	-0.15585
		п	la 1	0.00317	0.20341	-0.10327
		H	la	-0.29490	-0.21929	0.27456
		H	la	-0.40636	0.01842	0.22912
		Н	la	0.43664	-0.16740	0.15683
		Н	la	0.45016	-0.23637	0.41350
	System	Atom	Wyckoff site	X	У	Z
	Str-400	Al	la	0.44213	0.34031	-0.01863
	(P1)	B	la	0.24063	0.16418	0.23529
	a=5.96/A	B	1a 1-	-0.4106/	-0.2/126	0.04/82
	D=5.0/3A	B	1a	-0.44920	0.07029	-0.13947
	a = 69.76	Б	1a 1a	0.33448	-0.20440	-0.13774
	$\beta = 100.43$	H	1a 1a	0.13701	0.25407	0.31319
	$\gamma = 93.39$	Н	1a	0 19104	-0.08106	0.29766
	1 20.03	Н	1a	0.45615	0.17486	0.26079
		Н	1a	-0.28869	-0.46210	0.04566
		Н	1a	-0.41682	-0.28536	0.22310
		Н	1a	-0 34039	0 16778	-0.30003
		Н	1a	0.37601	0.00478	-0 29864
		н	1a	0.16163	-0 17488	-0.08330
		н	10	0.30340	-0.35518	-0.25116
		н	10	-0.26244	-0.09001	-0.03597
:	S	11	Ta Wheelesff site	-0.20244	-0.07001	-0.03377
-	System Str-640			X	y 0.38552	Z
	(P1)	B	10	-0.41784	0.29967	-0.21890
	a=5 112Å	B	1a	0 29355	0 29463	-0.31465
	b=6.070Å	B	1a	0.12034	-0.37324	0.26592
	c=6.563Å	В	1a	-0.40022	0.16507	-0.44080
	α=84.23	Н	1a	-0.27808	0.24215	0.37433
	β=74.23	Н	1a	0.33597	0.19933	-0.48615
	γ=94.50	Н	1a	0.16284	0.42367	0.27443
		Н	1a	-0.04702	-0.33765	0.43910
		Η	1a	-0.31625	0.49655	-0.23385
		Η	1a	-0.43303	0.19526	-0.05087
		Н	1a	0.27924	0.49398	-0.36775
		Н	1a	0.10054	0.19066	-0.18248
		Н	1a	0.33415	-0.26617	0.25193
		Н	1a	0.00412	-0.34171	0.13101
		Н	1a	-0.42380	-0.03454	-0.41228

Atoms	Str-0	Str-86	Str-108	Str-260
B1	-60.96	-59.41	-54.14	-59.18
B2	-33.45	-43.64	-55.22	-45.64
B3	-58.48	-30.50	-40.23	-39.01
B4	-61.82	-70.40	-59.57	-58.94
B5	-46.61	-39.31	-44.40	-39.77
B6	-46.50	-41.55	-42.76	-45.65
B7	-47.61	-35.66	-38.88	-56.25
B8	-41.29	-44.13	-51.24	-55.80

*Table S2*. Simulated chemical shifts (ppm) of boron atoms in <sup>11</sup>B NMR spectra of predicted Str-0, Str-86, Str-108, and Str-260.



*Figure S2*. Simulated <sup>11</sup>B NMR spectra of AlB<sub>4</sub>H<sub>11</sub> based on the predicted Str-86.



*Figure S3*. Simulated <sup>11</sup>B NMR spectra of AlB<sub>4</sub>H<sub>11</sub> based on the predicted Str-108.



*Figure S4*. Simulated <sup>11</sup>B NMR spectra of AlB<sub>4</sub>H<sub>11</sub> based on the predicted Str-260.