Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Na[Li(NH_2BH_3)$_2$] – the first mixed-cation amidoborane with unusual crystal structure

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Contents

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1. Study of thermal decomposition of lithium amidoborane

First step of thermal decomposition of $LiNH_2BH_3$ occurs in the temperature range of 45–100°C (TGA profile, Fig. S1). The major mass loss is observed in the range of 70–100°C with exothermic DSC peak at 92°C.[i] The observed mass loss is about 6.0%. Total mass loss of 10% was observed up to 250°C which is comparable with the value of 11% reported by Xiong *et al.*[ii] value. Mass spectroscopic analyses of gases evolved show emission of hydrogen substantially polluted with ammonia. Mass spectrum consists of peaks originating from H_2 (m/z = 2) and from NH_3 (m/z = 14, 15, 16, 17). Evolution of ammonia during thermal decomposition of LiAB was not mentioned in the previous works[i] but IT was observed in study on analogous NaAB.[iii] Lots of ammonia is evolved during the first step of decomposition of LiAB, preceding evolution of hydrogen (Fig. S1, region of evolution of pure ammonia marked with stripes) in a similar fashion as it is observed for NaAB.

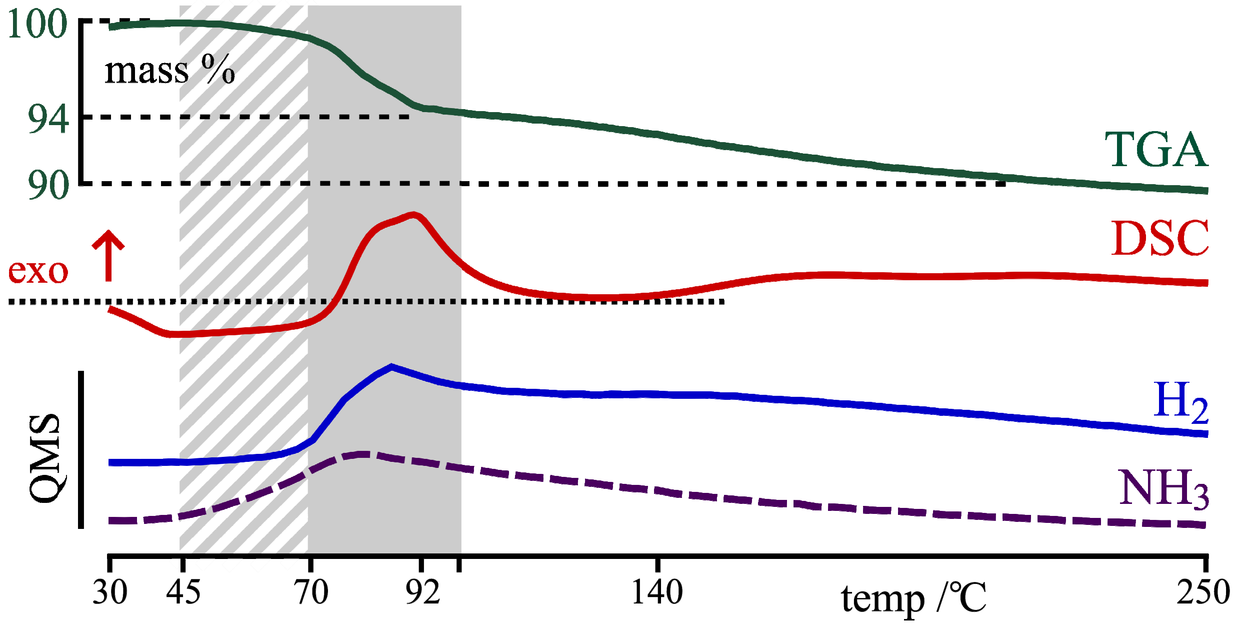
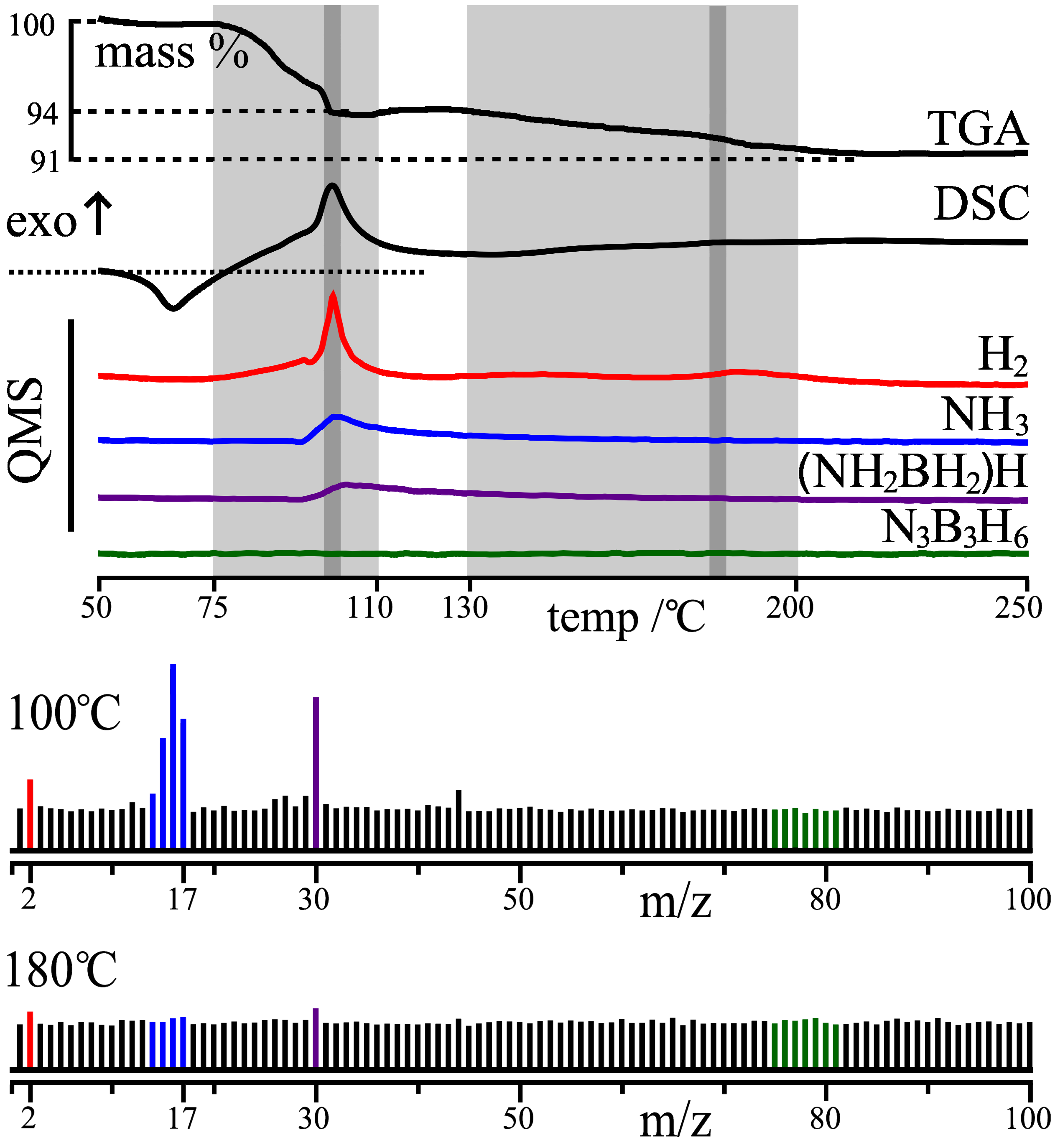


Fig. S1 Thermal decomposition of $LiNH_2BH_3$ at heating rate 10K/min: TGA and DSC profile (top), ion current of H_2 and NH_3 (bottom). First step of decomposition is marked, region where only MH_3 is evolved is striped.

2. Mass spectra of the gases evolved during thermal decomposition of NaLi(AB)$_2$



3. Temperature-resolved IR absorption spectra of NaLi(AB)$_2$

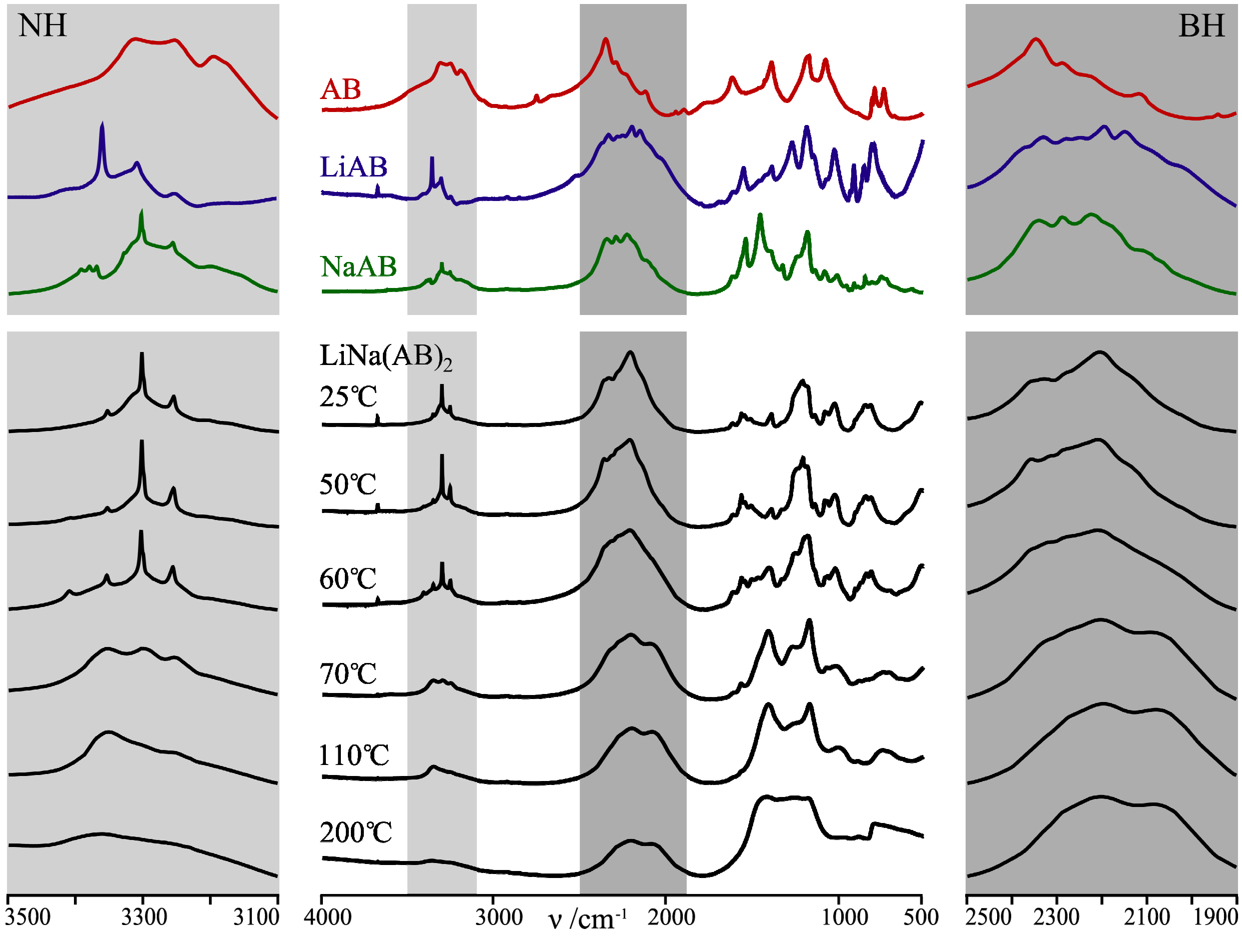


Fig. 4 Comparison of FTIR spectra of AB, LiAB, NaAB and LiNa(AB)$_2$ samples at room temperature and after thermal treatment. The ranges marked in grey are shown magnified on the sides.

4. Table of the IR absorption bands of AB, LiAB, NaAB and NaLi(AB)$_2$

Table S1. Absorption bands detected in IR spectra (wavenumber [cm^{-1}]) of AB, LiAB, NaAB and LiNa(AB)$_2$ samples at room temperature and after thermal treatment. Assignment of the bands for AB is according to Ref. 2. (ν = stretching, δ = deformation: bending and torsional modes)

				NaLi(AB)$_2$					
Band	AB	LiAB	NaAB	25°C	50°C	60°C	70°C	110°C	200°C
ν(NH)			3393 vw		3410 vw	3410 w	3410 sh		
			3380 vw						
			3369 vw						
		3360 s		3354 w	3354 w	3354 w	3353 w	3351 w	3360 vw
		3319 s							
	3311 vs		3303 m	3303 s	3303 m	3303 m	3303 w	3305 sh	3305 sh
	3253 vs	3251 s	3256 w	3256 m	3256 m	3256 w	3254 w	3255 vw	3260 sh
	3196 s	3199 sh	3200 vw	3205 sh	3205 sh	3205 sh	3200 sh	3200 sh	
		3175 sh		3170 sh	3170 sh				
ν(BH)				2355 sh	2357 s	2355 sh			
	2347 vs	2332 s	2340 s	2328 s	2315 sh	2315 sh	2320 sh	2320 sh	
	2289 s	2279 m	2289 s	2275 sh	2275 sh	2275 hs	2270 sh	2270 sh	2280 sh
		2243 m	2224 s	2202 vs	2209 vs	2209 vs	2203 vs	2197 s	2203 m
		2194 s							
	2118 m	2150 s	2120 sh	2140 sh	2140 sh		2094 s	2081 s	2083 m
		2035 sh		2025 sh	2025 sh				
ν(BN)		1478 vw	1448 vs			1461 m			
	1363 s	1379 vs	1385 m	1382 w	1383 w	1397 m	1402 vs	1401 vs	1407 vs
δ(NH)	1611 m	1607 s	1608 s	1609 vw	1606 w	1605 w	1605 vw	1605 sh	
				1557 w	1558 m	1558 m	1561 w	1560 sh	
		1545 s		1539 w	1541 w	1540 m			
		1505 m		1505 w	1503 w	1500 m			
δ(BH)		1305 sh	1317 m	1315 sh	1325 w	1323 m			
		1262 s	1232 m	1245 sh	1230 sh	1242 s	1259 s	1250 sh	1248 vs
		1178 vs	1198 vs	1199 vs	1199 vs	1198 vs			
				1185 sh	1185 sh	1187 vs			
	1163 vs	1162 vs	1173 s	1177 sh	1177 vs	1173 vs	1163 vs	1162 vs	1173 vs
		1136 m	1128 w	1130 w	1129 w	1130 sh			
	1067 s	1065 m	1074 w	1071 w	1072 w	1070 m			
				1056 w	1056 w	1065 m	1064 m	1070 sh	
		1017 s	999 w	1014 m	1014 m	1013 m	1007 m	996 m	968 m
other		902 m		915 vw	915 sh	915 vw			
				895 w	894 w	896 w			
				865 sh	865 sh	865 sh	871 vw	881 s	876 m
		842 m	837 w	834 m	832 m	831 m	830 vw		
		800 s	797 w	806 m	803 m	803 m			
		783 s	742 w				728 w	733 m	779 s

5. Comparison of the DFT-predicted and experimental unit cells of NaLi(AB)$_2$

Table 2. Comparison between the experimental and theoretical (DFT) unit cell parameters of NaLi(NH_2BH_3)$_2$. Uncertainties were omitted.

Method	a /Å	b /Å	c /Å	α /^{o}	β /^{o}	γ /^{o}	V /Å^3	d /gcm^{-3}	xyz_{N1}	xyz_{N2}	xyz_{B1}	xyz_{B2}
Exp.	5.020	7.120	8.920	103.0	102.2	103.6	289.98	1.027	-0.001, 0.272, 0.378	0.707, 0.253, 0.655	0.850, 0.201, 0.200	0.484, 0.647, 0.252
DFT	5.035	7.102	8.768	102.5	102.7	105.1	282.58	1.054	0.029, 0.280, 0.385	0.646, 0.260, 0.654	0.871, 0.186, 0.198	0.515, 0.628, 0.246

Method	xyz_{HN11}	xyz_{HN12}	xyz_{HN21}	xyz_{HN22}	xyz_{HB11}	xyz_{HB12}	xyz_{HB13}	xyz_{HB21}	xyz_{HB22}	xyz_{HB23}	xyz_{Na}	xyz_{Li}
Exp.	-0.009, 0.168, 0.441	0.246, 0.327, 0.402	0.658, 0.264, 0.543	0.654, 0.107, 0.648	0.609, 0.093, 0.178	0.966, 0.095, 0.127	0.868, 0.343, 0.144	0.238, 0.267, 0.745	0.628, 0.432, 0.899	0.464, 0.523, 0.710	0.323, 0.231, 0.024	0.909, 0.550, 0.363
DFT	0.112, 0.181, 0.407	0.141, 0.407, 0.402	0.520, 0.183, 0.537	0.689, 0.148, 0.703	0.620, 0.081, 0.176	0.990, 0.076, 0.129	0.872, 0.323, 0.131	0.293, 0.228, 0.735	0.642, 0.412, 0.890	0.487, 0.503, 0.710	0.344, 0.232, 0.018	0.975, 0.557, 0.364

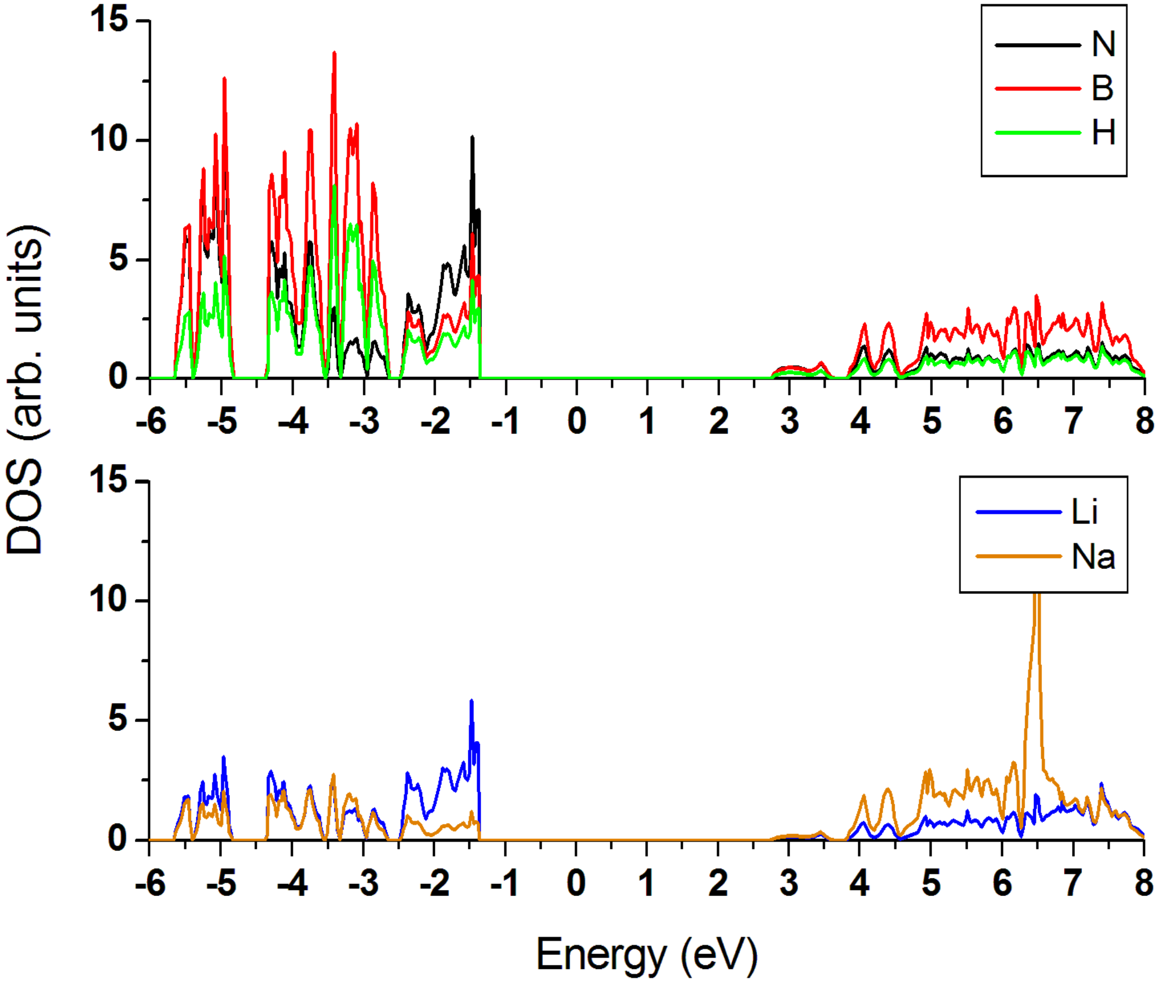
6. R factors from structural refinement

The entire multi phase Rietveld refinement:
R_{exp} = 2.040%
R_{wp} = 2.505%
R_{p} = 1.913%
GooF = 1.228
Structure 1: LiNa(NH2BH3)2 R_{Bragg} = 2.07%
Structure 2: WC R_{Bragg} = 1.66%
Phase 1: a=4.736(2), b=4.298(3), c=4.023(4), α=87.3(7)^o, β=112.7(3)^o, γ=115.7(9)^o
The volume of the unit cell of the unidentified P1 phase is unusually small, *ca.* 67.4 Å^3 (*cf.* for example volume of NaH per FU, 30.9 Å^3) which suggests that at least one unit cell vector should be doubled. The doubled volume of P1 cell of 134.8 Å^3 is reminiscent of that of volume per FU of NaLi(AB)$_2$ (145 Å^3) thus suggesting possibility of polymorphism. Note, LiAB has two polymorphic forms.

7. Atomic fractional coordinates for NaLi(AB)$_2$

Na1	0.67700	0.76860	0.97640
Li1	0.09100	0.45000	0.63700
N1	0.99900	0.27200	0.37800
N2	0.70700	0.25300	0.65500
B1	0.85000	0.20100	0.20000
B2	0.51600	0.35300	0.74800
H1	1.11206	0.18064	0.40695
H2	1.14093	0.40699	0.40159
H3	0.86756	0.34294	0.14392
H4	0.96628	0.09478	0.12701
H5	0.60860	0.09283	0.17786
H6	0.65361	0.10655	0.64775
H7	0.65754	0.26355	0.54319
H8	0.29311	0.22832	0.73503
H9	0.64240	0.41235	0.89022
H10	0.48747	0.50291	0.70982

8. DFT-calculated atomic DOS for NaLi(AB)$_2$



It is clear that there is a larger contribution from Li than from Na to the valence band (from -5.5 eV to -1.4 eV) and a smaller contribution from Li than from Na to the conduction band (from +2.7 eV to +8.0 eV) which implies more ionic character of bonding for Na^+ than for Li^+. Among nonmetals, contribution from B to conduction band is the largest in agreement with Lewis acid character of B^{3+} in amidoborane anion. Thus, in a simplified picture, NH_2^- and H^- serve as Lewis bases, while B^{3+}, Na^+ and Li^+ as Lewis acids in this compound.

References

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[i] Z. Xiong, C. K. Yong, G. Wu, P. Chen, W. Shaw, A. Karkamkar,T. Autrey, M. O. Jones, S. R. Johnson, P. P. Edwards and W. I. F. David, *Nat. Mater.*, 7 (2008) 138.

[ii] 11% mass loss was observed during 19 hours heating in temperature 91°C while our scan lasted only 40 minutes.

[iii] K. J. Fijalkowski and W. Grochala, *J. Mater. Chem.*, 19 (2009) 2043.