Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

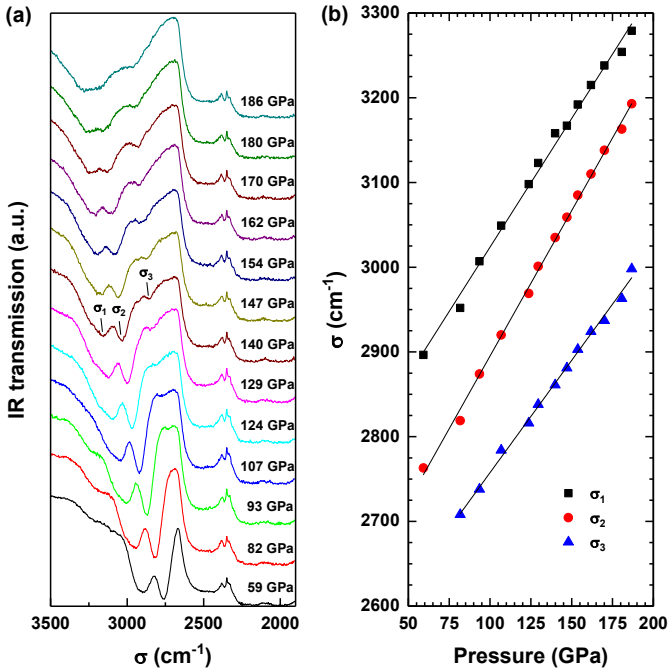


Figure S1 : a) IR transmission spectra of $NaBH_4$ at selected pressures and 300 K zoomed on regions of interest. (b) Evolution of the corresponding pressures of the three absorption bands related to B-H stretching vibrations

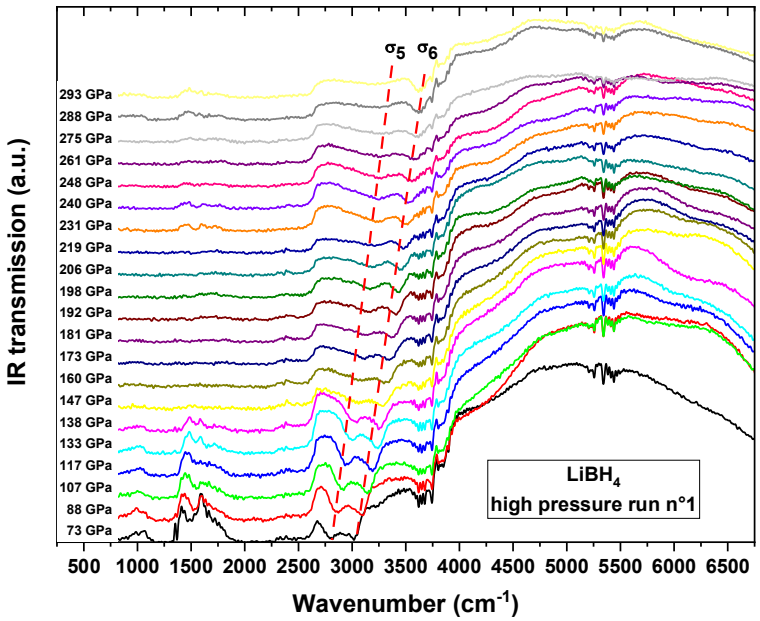
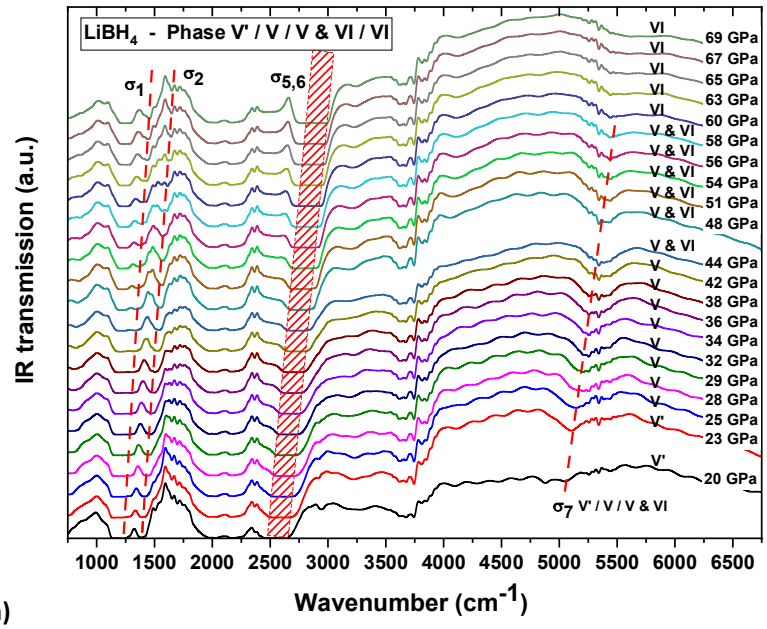
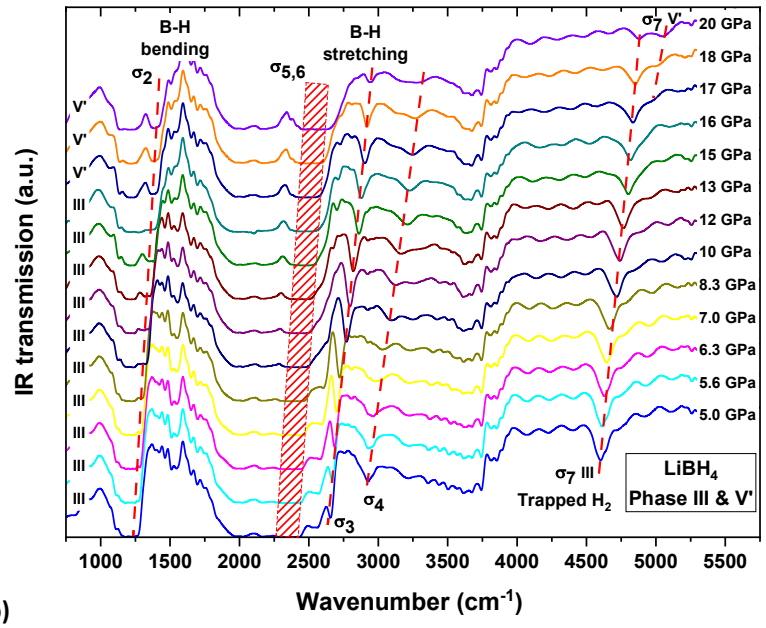


Figure S2 : IR transmission spectra of $LiBH_4$ for the high pressure run n°1 at 300 K. Followed absorption bands are indicated by red lines.



a)



b)

Figure S3 : IR transmission spectra of $LiBH_4$ at selected pressures and 300 K from (a) 20 to 69 GPa and from (b) 5 to 20 GPa (same diamond anvil cell). Followed absorption bands are indicated by red lines. Red rectangles indicate the saturated main stretching bands of $LiBH_4$.

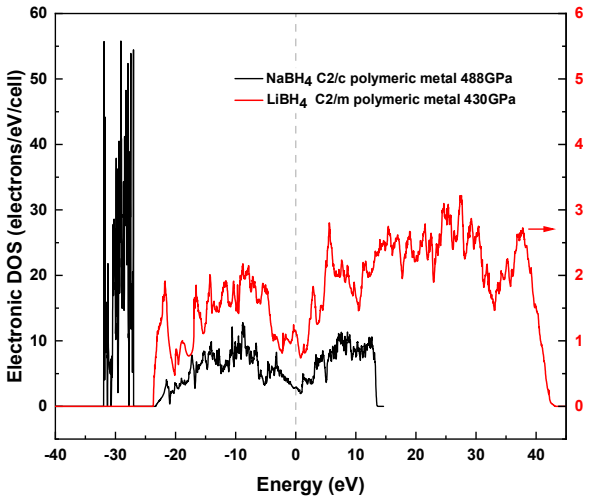


Figure S4 : Electronic density of states of metallic *C2/m* polymeric $LiBH_4$ at 430 GPa and of *C2/c* polymeric $NaBH_4$ at 488 GPa. The Fermi level is set at 0 eV.

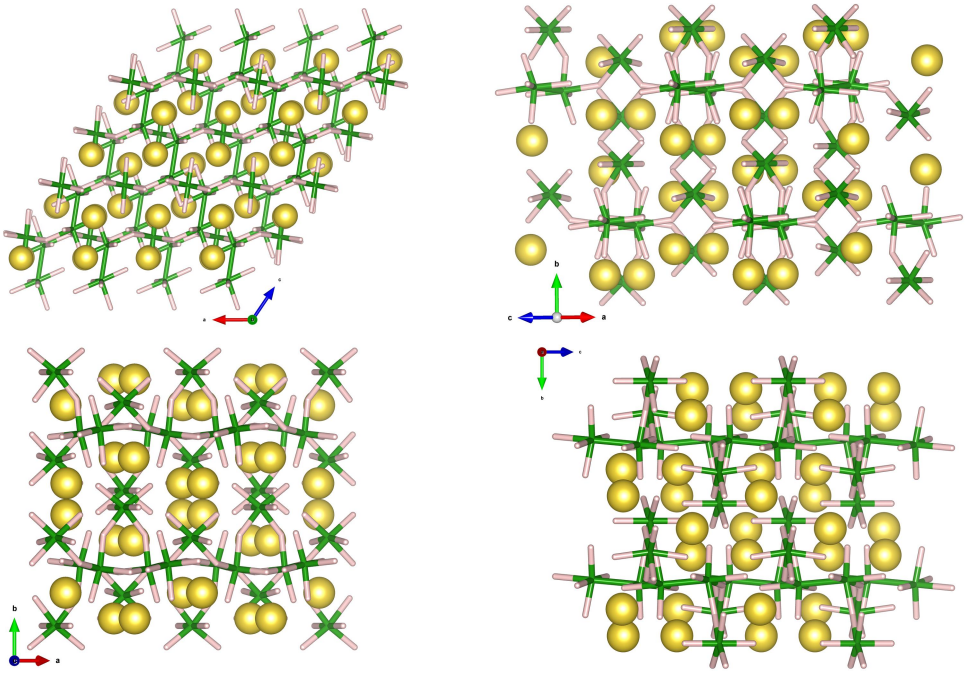


Figure S5 : Extended views of the predicted *C2/c* polymeric metallic $NaBH_4$ showing the layered feature.

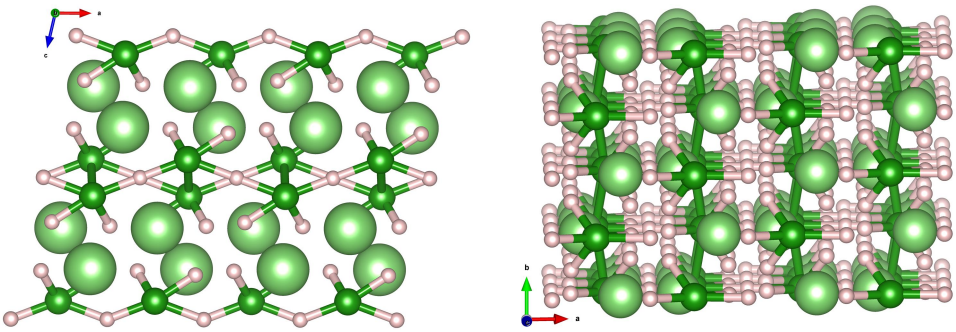


Figure S6 : Extended views of the *C2/m* polymeric metallic $LiBH_4$ predicted by Yao & Klug [1]

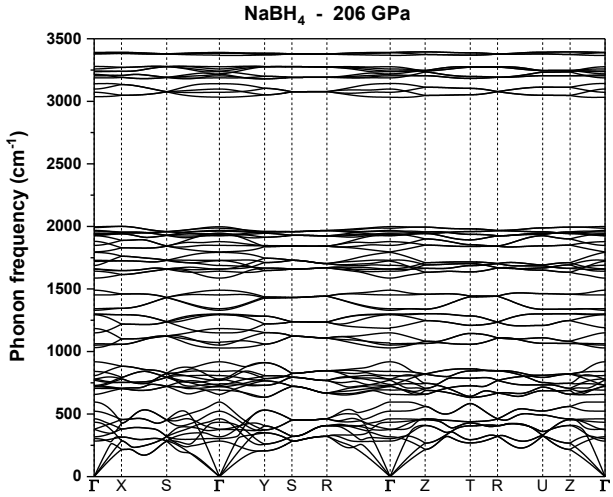


Figure S7 : Phonon band structure of *Pnma* $NaBH_4$ at 206 GPa.

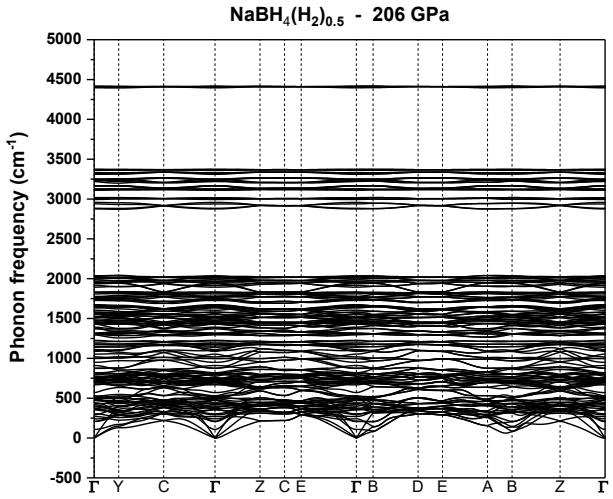


Figure S8 : Phonon band structure of the predicted $NaBH_4(H_2)_{0.5}$ at 206 GPa.

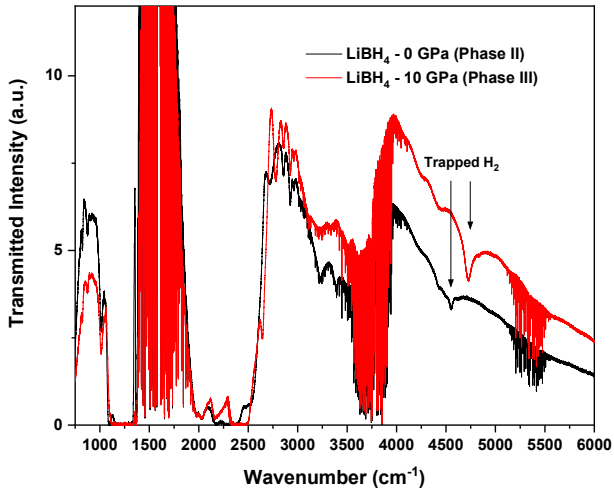


Figure S9 : IR transmission spectra of $LiBH_4$ before and after the phase transition II/III.

All CIF below were generated by FINDSYM [2] from the ABINIT code output. Unique axis *b* was taken for monoclinic cell. Cell lengths are given in ångström.

CIF file of phase II $P4_2/nmc$ $NaBH_4$ computed at 5.9 GPa

```
# CIF file created by FINDSYM, version 7.0

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_audit_creation_method FINDSYM

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_cell_length_c        5.55754
_cell_angle_alpha    90.0000
_cell_angle_beta     90.0000
_cell_angle_gamma 90.0000
_cell_volume     91.9761

_symmetry_space_group_name_H-M "P 42/n 21/m 2/c (origin choice 2)"
_symmetry_Int_Tables_number 137
_space_group.reference_setting '137:-P 4ac 2a'
_space_group.transform_Pp_abc a,b,c;0,0,0

loop_
_space_group_symop_id
_space_group_symop_operation_xyz
1 x,y,z
2 x+1/2,-y,-z
3 -x,y+1/2,-z
4 -x+1/2,-y+1/2,z
5 -y,-x,-z+1/2
6 -y+1/2,x,z+1/2
7 y,-x+1/2,z+1/2
8 y+1/2,x+1/2,-z+1/2
9 -x,-y,-z
10 -x+1/2,y,z
11 x,-y+1/2,z
12 x+1/2,y+1/2,-z
13 y,x,z+1/2
14 y+1/2,-x,-z+1/2
15 -y,x+1/2,-z+1/2
16 -y+1/2,-x+1/2,z+1/2

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_fract_symmform
```

```
Na1   Na   2 a    0.75000    0.25000    0.75000    1.00000   0,0,0
B1    B    2 b    0.75000    0.25000    0.25000    1.00000   0,0,0
H1    H    8 g    0.25000    0.50530    0.62484    1.00000   0,Dy,Dz

# end of cif
```

CIF file of *P-42$_1$c* $NaBH_4$ computed at 5.9 GPa (not stable)

```
# CIF file created by FINDSYM, version 7.0

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_cell_angle_beta     90.0000
_cell_angle_gamma 90.0000
_cell_volume      91.9761

_symmetry_space_group_name_H-M "P -4 21 c"
_symmetry_Int_Tables_number 114
_space_group.reference_setting '114:P -4 2n'
_space_group.transform_Pp_abc a,b,c;0,0,0

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_space_group_symop_operation_xyz
1 x,y,z
2 x+1/2,-y+1/2,-z+1/2
3 -x+1/2,y+1/2,-z+1/2
4 -x,-y,z
5 y+1/2,x+1/2,z+1/2
6 y,-x,-z
7 -y,x,-z
8 -y+1/2,-x+1/2,z+1/2

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_fract_symmform
Na1   Na   2 b    0.00000    0.00000    0.50000    1.00000   0,0,0
B1    B    2 a    0.00000    0.00000    0.00000    1.00000   0,0,0
H1    H    8 e    0.00014    0.75530    0.87484    1.00000   Dx,Dy,Dz
```

end of cif

CIF file of phase III *Pnma* $NaBH_4$ computed at 206 GPa

```
# CIF file created by FINDSYM, version 5.1.0

data_NaBH4 / Phase III / 206 GPa / DFT
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_cell_angle_beta       90.0000
_cell_angle_gamma      90.0000

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_symmetry_Int_Tables_number 62
_space_group.reference_setting '062:-P 2ac 2n'
_space_group.transform_Pp_abc a,b,c;0,0,0

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_space_group_symop_operation_xyz
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2 x+1/2,-y+1/2,-z+1/2
3 -x,y+1/2,-z
4 -x+1/2,-y,z+1/2
5 -x,-y,-z
6 -x+1/2,y+1/2,z+1/2
7 x,-y+1/2,z
8 x+1/2,y,-z+1/2

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
Na1   Na   4 c   0.83379   0.25000   0.79722   1.00000
B1    B    4 c   0.41871   0.25000   0.19985   1.00000
H1    H    4 c   0.58850   0.25000   0.05307   1.00000
H2    H    4 c   0.23820   0.25000   0.07472   1.00000
H3    H    8 d   0.40806   0.51046   0.36350   1.00000

# end of cif
```

CIF file of $P2_1/c$ $NaBH_4(H_2)_{0.5}$ computed at 206 GPa

```
# CIF file created by FINDSYM, version 5.1.0

data_NaBH4(H2)0.5 / 206 GPa / DFT
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_cell_angle_beta       99.3611
_cell_angle_gamma      90.0000

_symmetry_space_group_name_H-M "P 1 21/c 1"
_symmetry_Int_Tables_number 14
_space_group.reference_setting '014:-P 2ybc'
_space_group.transform_Pp_abc a,b,c;0,0,0

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_space_group_symop_operation_xyz
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2 -x,y+1/2,-z+1/2
3 -x,-y,-z
4 x,-y+1/2,z+1/2

loop_
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_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
Na1   Na   4 e   0.87115   0.74995   0.87377   1.00000
Na2   Na   4 e   0.35775   0.74993   0.88396   1.00000
B1    B    4 e   0.36748   0.75008   0.14151   1.00000
B2    B    4 e  -0.09160   0.75003   0.13689   1.00000
H1    H    4 e   0.62153   0.53508   0.78458   1.00000
H2    H    4 e   0.37846   0.46476   0.71542   1.00000
H3    H    4 e   0.74777   0.75008   0.18624   1.00000
H4    H    4 e   0.10841  -0.01877  -0.05640   1.00000
H5    H    4 e   0.89157   0.01874   0.55641   1.00000
H6    H    4 e   0.52234   0.75011   0.08778   1.00000
H7    H    4 e   0.20532   0.75006   0.05601   1.00000
H8    H    4 e   0.07049   0.74996   0.72626   1.00000
H9    H    4 e   0.35122   0.13628   0.02985   1.00000
H10   H    4 e   0.64873   0.86395   0.47003   1.00000

# end of cif
```

CIF file of metallic *C*2/c $NaBH_4$ computed at 488 GPa

```
# CIF file created by FINDSYM, version 7.0

data_NaBH4 / C2/c metal / 488 GPa / DFT
_audit_creation_method FINDSYM

_cell_length_a       5.42036
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_cell_length_c       5.33356
_cell_angle_alpha   90.0000
_cell_angle_beta    124.09675
_cell_angle_gamma 90.0000
_cell_volume     212.6499

_symmetry_space_group_name_H-M "C 1 2/c 1"
_symmetry_Int_Tables_number 15
_space_group.reference_setting '015:-C 2yc'
_space_group.transform_Pp_abc a,b,c;0,0,0

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_space_group_symop_operation_xyz
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2 -x,y,-z+1/2
3 -x,-y,-z
4 x,-y,z+1/2
5 x+1/2,y+1/2,z
6 -x+1/2,y+1/2,-z+1/2
7 -x+1/2,-y+1/2,-z
8 x+1/2,-y+1/2,z+1/2

loop_
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_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_fract_symmform
Na1  Na  8 f  0.07010  0.15344  -0.04719  1.00000  Dx,Dy,Dz
Na2  Na  8 f  0.42387  0.05835   0.55562  1.00000  Dx,Dy,Dz
B1    B  8 f  0.32172  0.24221   0.66953  1.00000  Dx,Dy,Dz
B2    B  4 e  0.00000  0.64194   0.25000  1.00000  0,Dy,0
B3    B  4 e  0.00000  0.03097   0.25000  1.00000  0,Dy,0
H1    H  8 f  0.54299  0.22947  -0.06354  1.00000  Dx,Dy,Dz
H2    H  8 f  0.37632  0.15978  -0.00443  1.00000  Dx,Dy,Dz
H3    H  8 f  0.81065  0.04801   0.70291  1.00000  Dx,Dy,Dz
H4    H  8 f  0.60541  0.46894  -0.00166  1.00000  Dx,Dy,Dz
H5    H  8 f  0.34767  0.36720   0.71850  1.00000  Dx,Dy,Dz
H6    H  8 f  0.17495  0.26220   0.77630  1.00000  Dx,Dy,Dz
H7    H  8 f  0.25898  0.12652   0.67897  1.00000  Dx,Dy,Dz
```

```
H8    H    8 f   0.17699   0.44101   0.78805   1.00000   Dx,Dy,Dz

# end of cif
```

CIF file of phase II *Pnma* $LiBH_4$ computed at 0 GPa

```
# CIF file created by FINDSYM, version 7.0

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_cell_length_a       7.51975
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_cell_angle_gamma 90.0000
_cell_volume     214.7249

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_symmetry_Int_Tables_number 62
_space_group.reference_setting '062:-P 2ac 2n'
_space_group.transform_Pp_abc a,b,c;0,0,0

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2 x+1/2,-y+1/2,-z+1/2
3 -x,y+1/2,-z
4 -x+1/2,-y,z+1/2
5 -x,-y,-z
6 -x+1/2,y+1/2,z+1/2
7 x,-y+1/2,z
8 x+1/2,y,-z+1/2

loop_
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_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_fract_symmform
Li1  Li   4 c   0.15395   0.25000   0.11109   1.00000   Dx,0,Dz
B1   B    4 c   0.32124   0.25000   0.41342   1.00000   Dx,0,Dz
H1   H    4 c  -0.08729   0.25000  -0.06920   1.00000   Dx,0,Dz
H2   H    4 c   0.41379   0.25000   0.25768   1.00000   Dx,0,Dz
H3   H    8 d   0.22451   0.02548   0.41010   1.00000   Dx,Dy,Dz
```

```
# end of cif
```

CIF file of phase III $I4_1/acd$ $LiBH_4$ computed at 11.8 GPa

```
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loop_
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2 x+1/2,-y+1/2,-z
3 -x+1/2,y,-z
4 -x,-y+1/2,z
5 -y+1/4,-x+1/4,-z+1/4
6 -y+1/4,x+3/4,z+1/4
7 y+3/4,-x+3/4,z+1/4
8 y+3/4,x+1/4,-z+1/4
9 -x,-y,-z
10 -x,y,z+1/2
11 x,-y+1/2,z+1/2
12 x,y+1/2,-z
13 y+1/4,x+1/4,z+1/4
14 y+3/4,-x+1/4,-z+3/4
15 -y+1/4,x+1/4,-z+3/4
16 -y+3/4,-x+1/4,z+1/4
17 x+1/2,y+1/2,z+1/2
18 x,-y,-z+1/2
19 -x,y+1/2,-z+1/2
20 -x+1/2,-y,z+1/2
21 -y+3/4,-x+3/4,-z+3/4
22 -y+3/4,x+1/4,z+3/4
23 y+1/4,-x+1/4,z+3/4
24 y+1/4,x+3/4,-z+3/4
25 -x+1/2,-y+1/2,-z+1/2
26 -x+1/2,y+1/2,z
27 x+1/2,-y,z
```

```
28 x+1/2,y,-z+1/2
29 y+3/4,x+3/4,z+3/4
30 y+1/4,-x+3/4,-z+1/4
31 -y+3/4,x+3/4,-z+1/4
32 -y+1/4,-x+3/4,z+3/4

loop_
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_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_fract_symmform
Li1   Li  8 a   0.00000   0.25000   0.37500   1.00000   0,0,0
Li2   Li  8 b   0.00000   0.25000   0.12500   1.00000   0,0,0
B1    B  16 e   0.45841   0.00000   0.25000   1.00000   Dx,0,0
H1    H  32 g   0.60941   0.60223   0.00221   1.00000   Dx,Dy,Dz
H2    H  32 g   0.24744   0.31580   0.41943   1.00000   Dx,Dy,Dz

# end of cif
```

CIF file of phase VI *Pnma* $LiBH_4$ computed at 100 GPa

```
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_cell_angle_gamma 90.0000
_cell_volume     78.7243

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_symmetry_Int_Tables_number 62
_space_group.reference_setting '062:-P 2ac 2n'
_space_group.transform_Pp_abc a,b,c;0,0,0

loop_
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_space_group_symop_operation_xyz
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2 x+1/2,-y+1/2,-z+1/2
3 -x,y+1/2,-z
4 -x+1/2,-y,z+1/2
5 -x,-y,-z
```

```
6 -x+1/2,y+1/2,z+1/2
7 x,-y+1/2,z
8 x+1/2,y,-z+1/2

loop_
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_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_fract_symmform
Li1  Li  4 c  0.83205  0.25000  0.29948  1.00000  Dx,0,Dz
B1   B   4 c  0.42347  0.25000  0.69623  1.00000  Dx,0,Dz
H1   H   8 d  0.59058  0.47770  0.14367  1.00000  Dx,Dy,Dz
H2   H   4 c  0.60419  0.25000  0.56626  1.00000  Dx,0,Dz
H3   H   4 c  0.24995  0.25000  0.55012  1.00000  Dx,0,Dz

# end of cif
```

CIF file of *C2/c* $LiBH_4$ computed at 300 GPa

```
# CIF file created by FINDSYM, version 7.0

data_LiBH4 / C2/c Yao & Klug / 300 GPa / DFT
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_cell_angle_alpha    90.0000
_cell_angle_beta     122.0053
_cell_angle_gamma 90.0000
_cell_volume     213.8642

_symmetry_space_group_name_H-M "C 1 2/c 1"
_symmetry_Int_Tables_number 15
_space_group.reference_setting '015:-C 2yc'
_space_group.transform_Pp_abc a,b,c;0,0,0

loop_
_space_group_symop_id
_space_group_symop_operation_xyz
1 x,y,z
2 -x,y,-z+1/2
3 -x,-y,-z
4 x,-y,z+1/2
5 x+1/2,y+1/2,z
6 -x+1/2,y+1/2,-z+1/2
7 -x+1/2,-y+1/2,-z
```

```
8 x+1/2,-y+1/2,z+1/2

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_fract_symmform
Li1   Li  8 f   0.12717   0.12453   0.00830   1.00000   Dx,Dy,Dz
Li2   Li  8 f   0.36886   0.08577   0.50117   1.00000   Dx,Dy,Dz
B1    B   8 f   0.22850   0.23018   0.69902   1.00000   Dx,Dy,Dz
B2    B   4 e   0.00000   0.57310   0.25000   1.00000   0,Dy,0
B3    B   4 e   0.00000   0.02316   0.25000   1.00000   0,Dy,0
H1    H   8 f   0.53937   0.25598  -0.02886   1.00000   Dx,Dy,Dz
H2    H   8 f   0.39898   0.12924   0.03071   1.00000   Dx,Dy,Dz
H3    H   8 f   0.84327   0.06176   0.72913   1.00000   Dx,Dy,Dz
H4    H   8 f   0.60236   0.43079  -0.01836   1.00000   Dx,Dy,Dz
H5    H   8 f   0.36061   0.33003   0.71974   1.00000   Dx,Dy,Dz
H6    H   8 f   0.15465   0.24366   0.85411   1.00000   Dx,Dy,Dz
H7    H   8 f   0.37342   0.13747   0.74487   1.00000   Dx,Dy,Dz
H8    H   8 f   0.16665   0.49818   0.75860   1.00000   Dx,Dy,Dz

# end of cif
```

CIF file of metallic *C2/m* $LiBH_4$ computed at 488 GPa

```
# CIF file created by FINDSYM, version 7.0

data_LiBH4 / C2/m metallic Yao & Klug / 488 GPa / DFT
_audit_creation_method FINDSYM

_cell_length_a        4.58861
_cell_length_b        2.77723
_cell_length_c        3.46473
_cell_angle_alpha    90.0000
_cell_angle_beta     102.8044
_cell_angle_gamma 90.0000
_cell_volume     43.0554

_symmetry_space_group_name_H-M "C 1 2/m 1"
_symmetry_Int_Tables_number 12
_space_group.reference_setting '012:-C 2y'
_space_group.transform_Pp_abc a,b,c;0,0,0

loop_
_space_group_symop_id
_space_group_symop_operation_xyz
1 x,y,z
```

```
2 -x,y,-z
3 -x,-y,-z
4 x,-y,z
5 x+1/2,y+1/2,z
6 -x+1/2,y+1/2,-z
7 -x+1/2,-y+1/2,-z
8 x+1/2,-y+1/2,z

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_fract_symmform
Li1   Li   4 l   0.64950   0.00000   0.35546   1.00000   Dx,0,Dz
B1    B    4 i   0.27549   0.00000   0.12878   1.00000   Dx,0,Dz
H1    H    2 a   0.00000   0.00000   0.00000   1.00000   0,0,0
H2    H    2 b   0.00000   0.50000   0.00000   1.00000   0,0,0
H3    H    4 i   0.09681   0.00000   0.31428   1.00000   Dx,0,Dz
H4    H    8 j   0.40128   0.28125   0.34126   1.00000   Dx,Dy,Dz

# end of cif
```

References

[1] Y. Yao and D. D. Klug, "High-pressure phases of lithium borohydride LiBH4: A first-principles study," *Phys. Rev. B*, vol. 86, no. 6, p. 064107, Aug. 2012.

[2] H. T. Stokes and D. M. Hatch, "FINDSYM : program for identifying the space-group symmetry of a crystal," *J. Appl. Crystallogr.*, vol. 38, no. 1, pp. 237–238, Feb. 2005.