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STRUCTURAL CHARACTERIZATION OF LIGHT **METAL BOROHYDRIDES** BY DISPERSION-CORRECTED DENSITY FUNCTIONAL THEORY MODELLING

Mariana Derzsi,[1,3] **A. Starobrat,**[2,3] **T. Jaroń,**[3] **P. Malinowski**[3] **and W. Grochala**[3]

[1]*ATRI Institute Materal-Tech. Faculty, Slovak University of Technology in Bratislava*

[2]*College of Inter-Faculty Individual Studies in Math. and Natural Sciences, University of Warsaw*

[3]*Center of New Technologies, University of Warsaw*

mariana.derzsi@stuba.sk

ATRI Advanced Technologies Research Institute

STU MTF Slovak University of Technology in Bratislava Faculty of Materials Science and Technology in Trnava

EUROPEAN UNION
European Regional Development Fund
OP Integrated Infrastructure 2014 – 2020

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METAL BOROHYDRIDES

Importance

- H-rich systems with: potential hydrogen storage material

Challenges

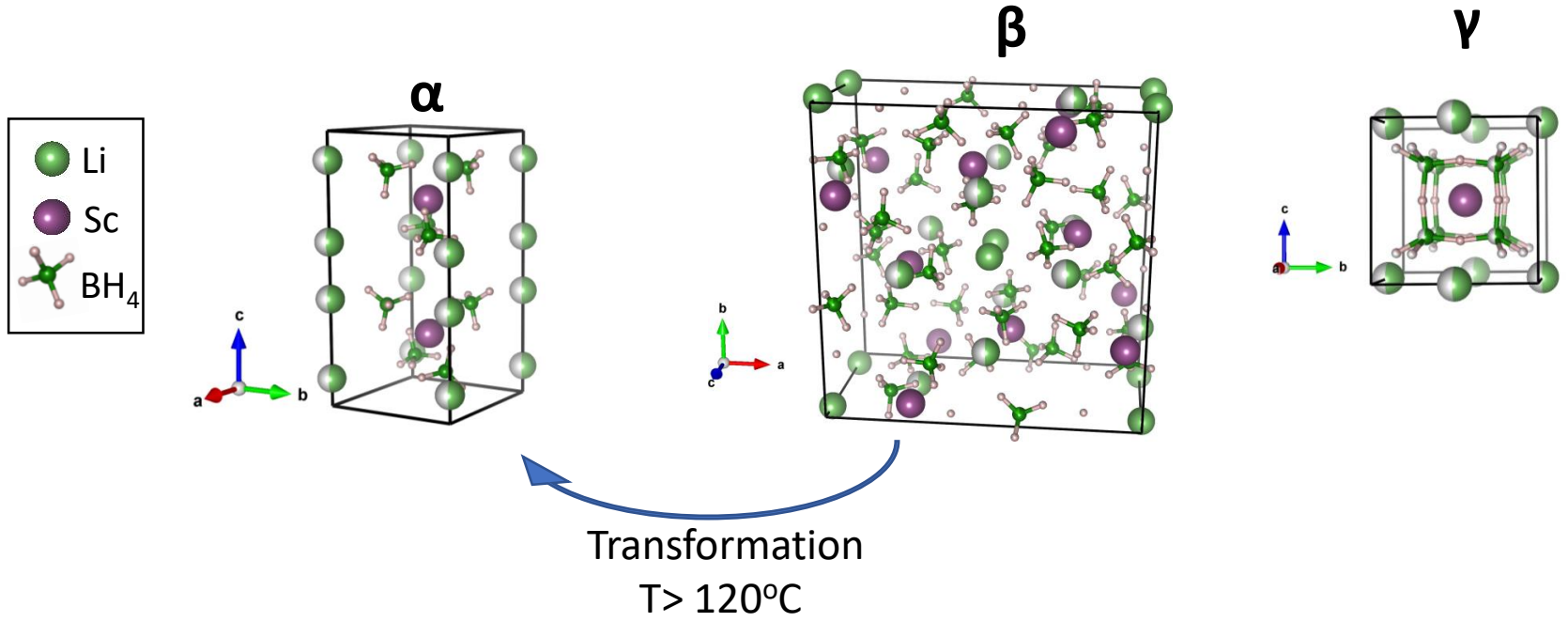
- Thermodynamic stability:
  - $Be(BH_4)_2$ with 20.7 wt.% ← immensely toxic
  - $Al(BH_4)_3$ 18.4 wt.% ← explosive
  - $Mg(BH_4)_2$ 14.8 wt.% ← overly-stable

Solutions

- Synthesis of multi-cation borohydrides.
- Structural systematics challenging: low crystallinity, poorly scattering atoms, frequent substitutional disorder.
- Computational modelling as a great aid to structure characterization.

Mixed metal borohydride $LiSc(BH_4)_4$

- The first *tetragonal* **α** polymorph (*P*-42c, Z=2) was reported in 2008.
- In 2018, *tetragonal* **β** phase was observed (*I*4/m, Z=8).
- Recently, *cubic* **γ** polymorph (*P*-43m, Z=1) proposed.



Volume per FU:

V^{α} = 222.1 Å^3

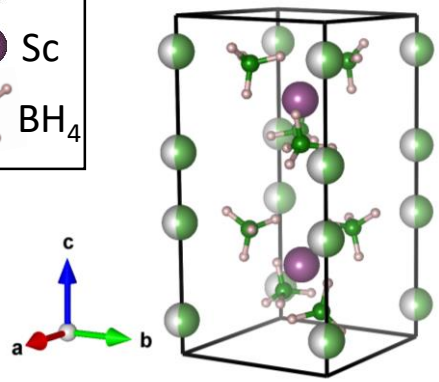
V^{β} = 188.1 Å^3 (85% α)

V^{γ} = 216.54 Å^3

α - $LiSc(BH_4)_4$

Li
Sc
BH_4

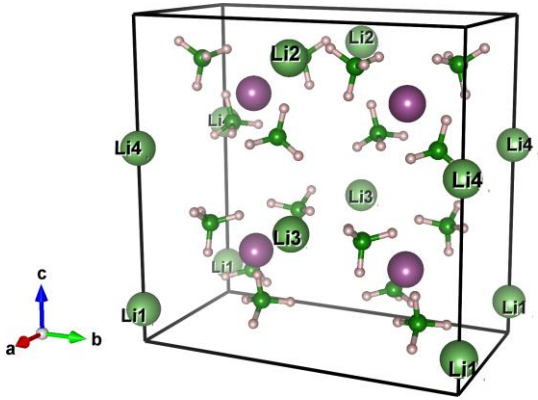
α (*P*-42*c*)



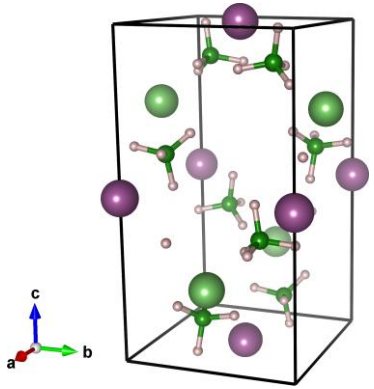
Synchrotron measurement

Hagemann et al., J. Phys. Chem. A (2008)

ordered α model ($P222_1$)



Predicted ground state (*I*-4)



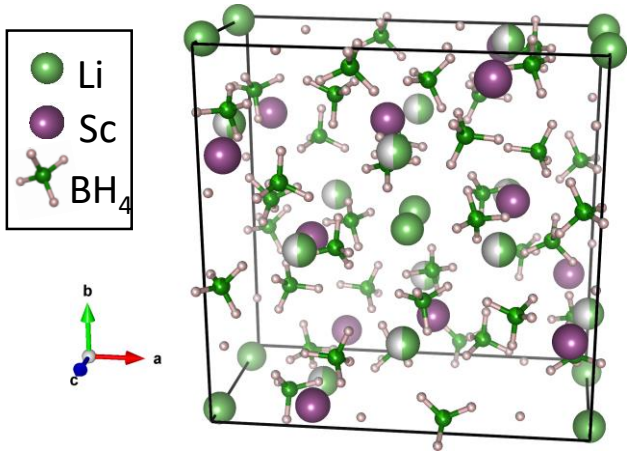
(PEG search)

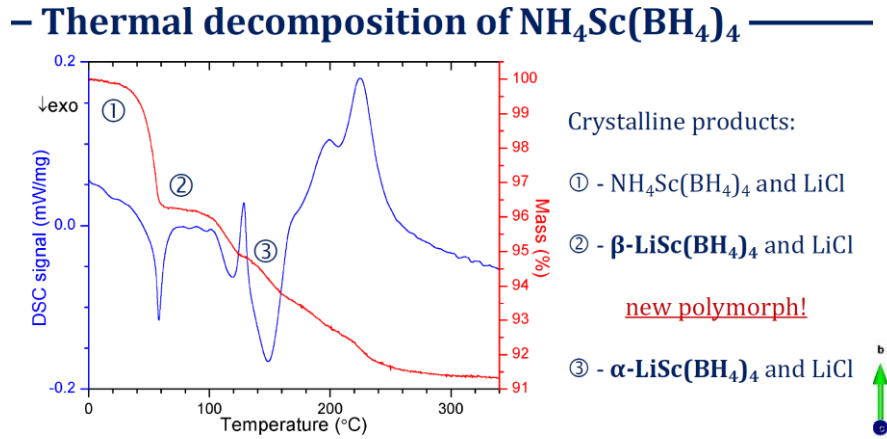
Kim et al., J. Phys. Chem. C (2009)

- Kim's models do not match the diffraction pattern of **α**

β - $LiSc(BH_4)_4$

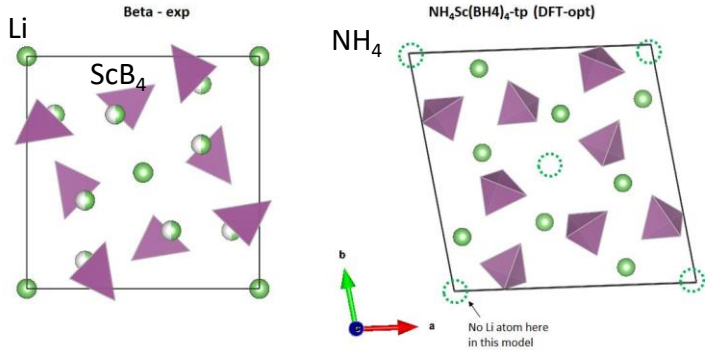
*I*4/m





Starobrat, T. Jaroń, W. Grochala, Dalton Trans. (2018)

Structural similarities with $NH_4Sc(BH_4)_4$ precursor



β - $LiSc(BH_4)_4$

a = 14.3 Å
c = 7.4 Å
β = 90.5°

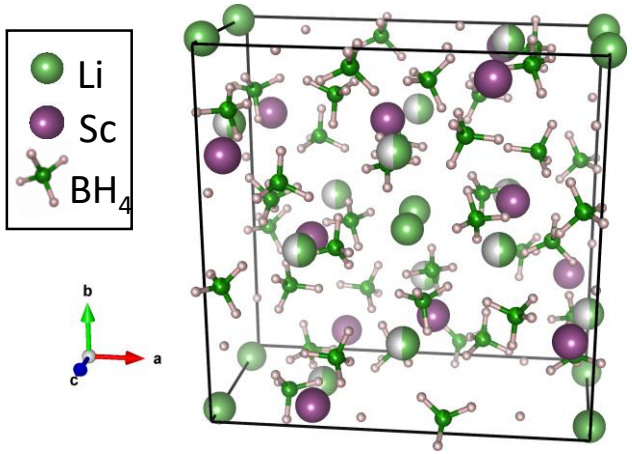
$NH_4Sc(BH_4)_4$

a = 15.7 Å
c = 7.9 Å
α = 89.5°
β = 90.5°
γ = 81.4°

(in β-$LiSc(BH_4)_4$ representation)

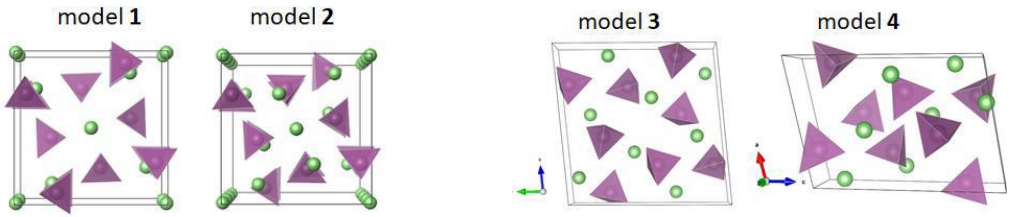
β - $LiSc(BH_4)_4$ – DFT results

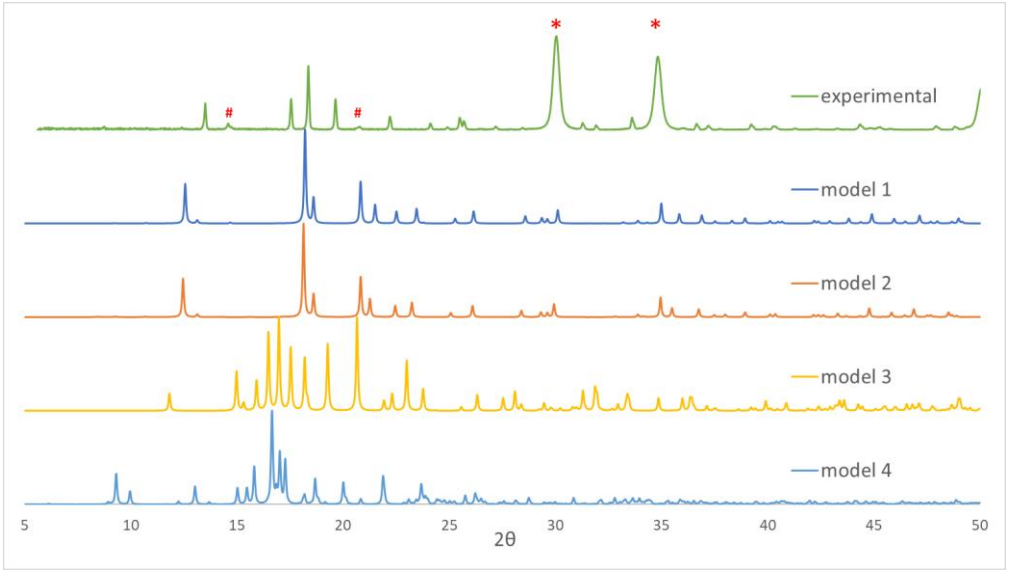
*I*4/m



1. Ordered β models

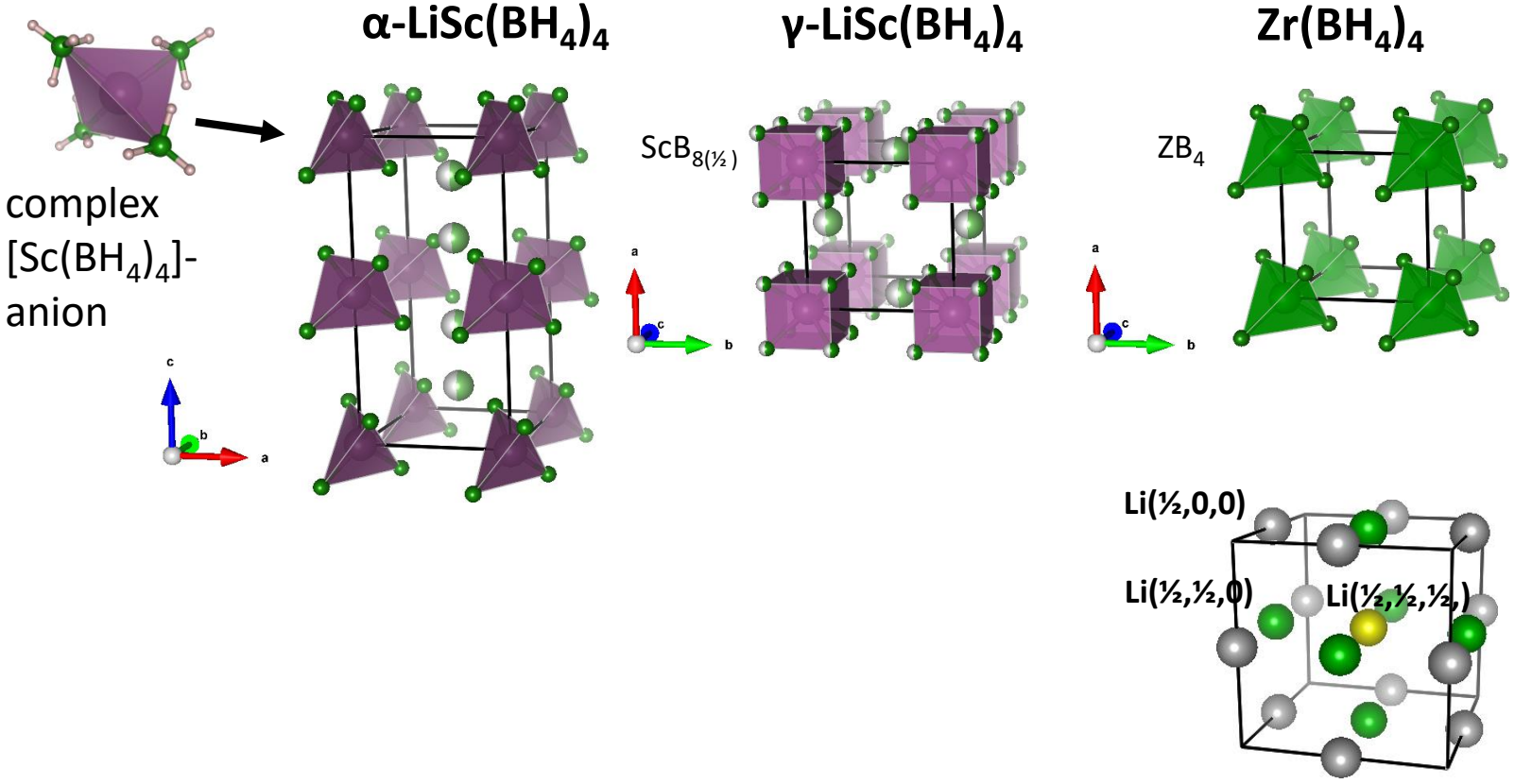
2. $NH_4Sc(BH_4)_4$ type models





- Many ordered models were tested.
- Our approach to describe β phase with ordered models has failed.

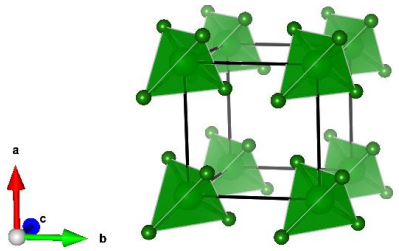
Common features of α and γ $LiSc(BH_4)_4$



- **α** and **γ** phase share simple cubic **Sc sublattice**
- Differ only in occupation of **interstitial** positions by Li
- $Zr(BH_4)_4$ prototype structure contains tetrahedral voids ready to host Li in:
  - Centre (½, ½, ½)
  - Face (½, ½,0)
  - Edge (½, ½, ½)

DFT Modelling $LiSc(BH_4)_4$ in $Zr(BH_4)_4$ type lattice

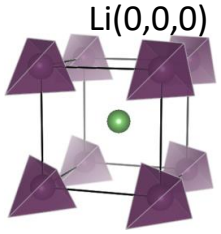
Modelling strategy



$Zr(BH_4)_4$

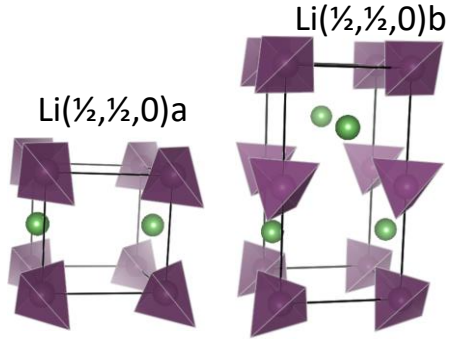
Sc → Zr substitution
Li → tetrahedral vacancy

Li in centre



DFT-D3: ΔE = 0 meV

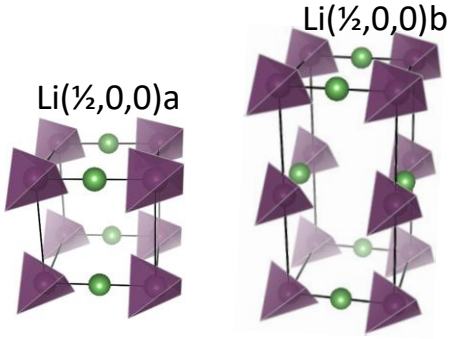
Li on face



-608 meV **-701 meV**

The most preferred position

Li on edge



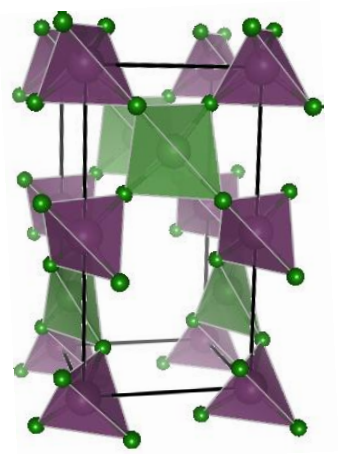
-275 meV -254 meV

DFT Modelling $LiSc(BH_4)_4$ in $Zr(BH_4)_4$ type lattice

Kim et al., J. Phys. Chem. C (2009)

Li on face

P-42c



ΔE = -701 meV

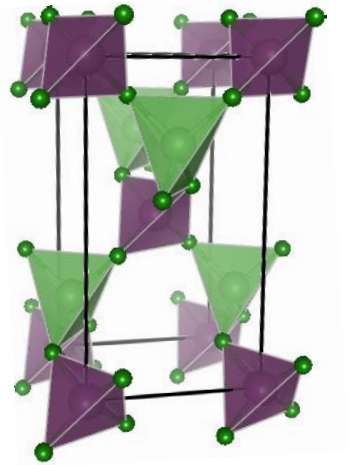
a = 5.851 Å, c = 11.827 Å

$d(H...H)_{inter}$ = 2.752 Å

DFT-D3 result

Kim's best model

I-4



-680 meV

a = 5.760 Å, c = 11.985 Å

$d(H...H)_{inter}$ = 2.800 Å

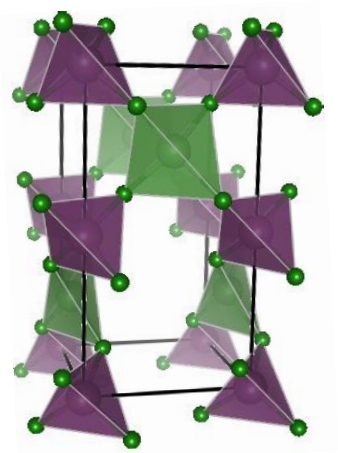
DFT-D3 result

- In the lowest-E models LiB_4 found in tetrahedral geometry
- The two models differ in Sc sublattice
- The model with simple cubic Sc sublattice with face-centred Li was found to be the ground state

DFT Modelling $LiSc(BH_4)_4$ in $Zr(BH_4)_4$ type lattice

Li on face

P-42c



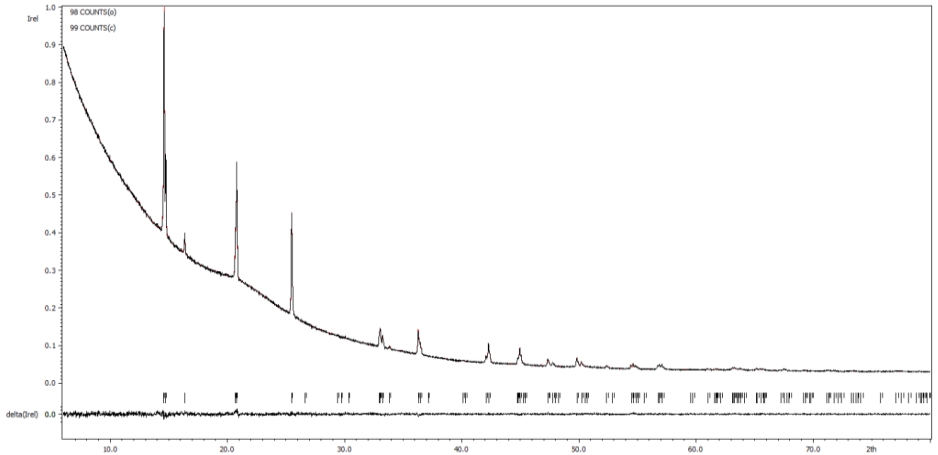
ΔE = -701 meV

a = 5.851 Å, c = 11.827 Å

$d(H...H)_{inter}$ = 2.752 Å

DFT-D3 result

Rietveld refinement of α-phase with ordered *P*-42c model



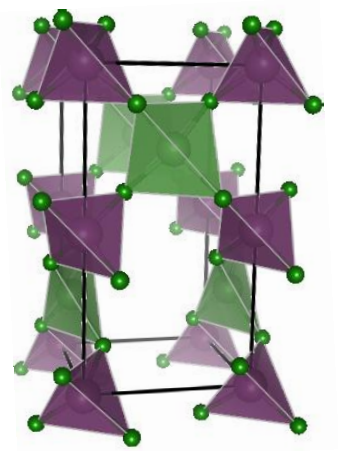
Comparison of XRD parameters:

	ordered model	disordered model
SPGR	P-42c	P-42c
wRp [%]	1.17	1.44
cRp [%]	28.63	32.21
a [Å]	6.0670(5)	6.0710(8)
c [Å]	12.0147(10)	12.0233(16)

DFT Modelling $LiSc(BH_4)_4$ in $Zr(BH_4)_4$ type lattice

Li on face

P-42c



ΔE = -701 meV

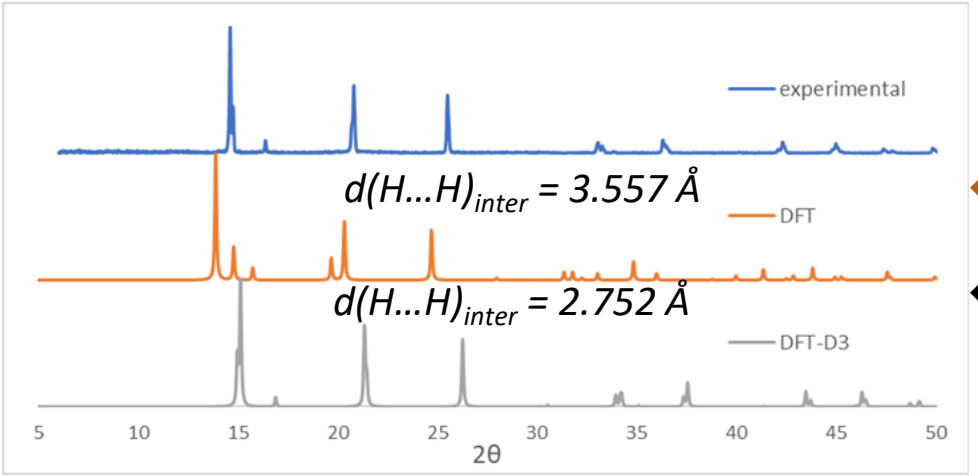
a = 5.851 Å, c = 11.827 Å

$d(H...H)_{inter}$ *= 2.752 Å*

DFT-D3 result

Importance of dispersion-corrected DFT (D3)

Simulated XRD patterns of α

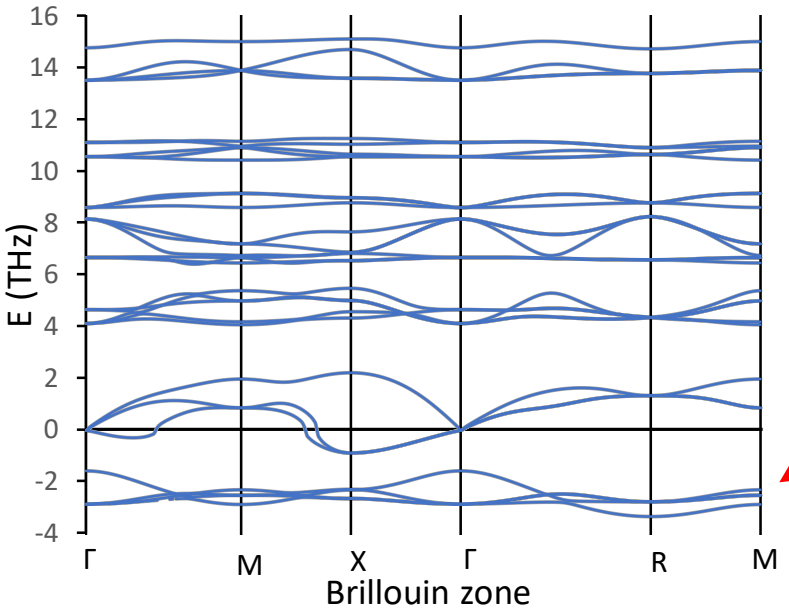


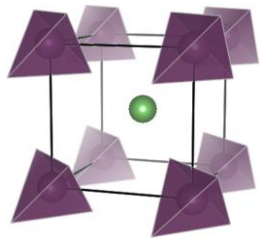
← basic DFT method fails

← Qualitative agreement reached only with dispersion-corrected DFT (DFT-D3)

Modelling $LiSc(BH_4)_4$ – lattice dynamics approach

Phonon dispersion curves (DFT)

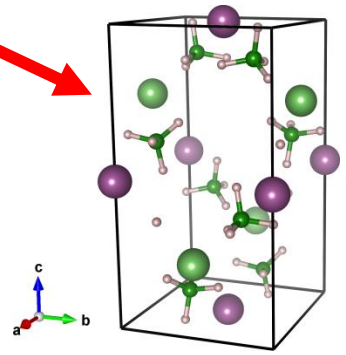




Li(½,½, ½)

P-43m

unstable modes



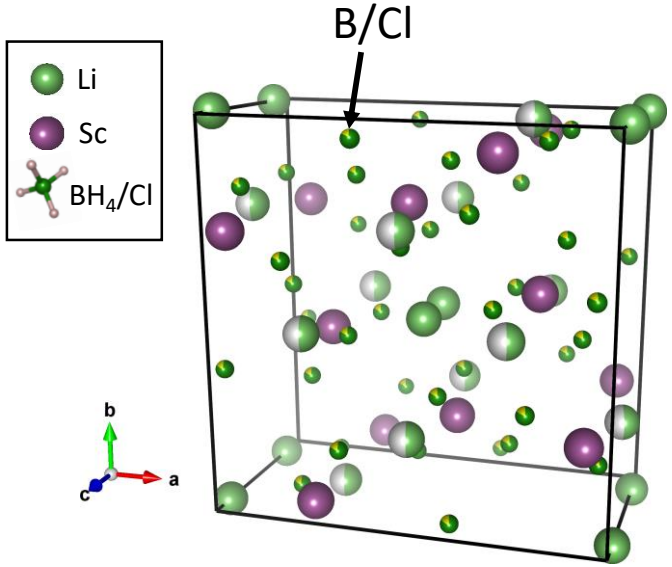
The lowest-E

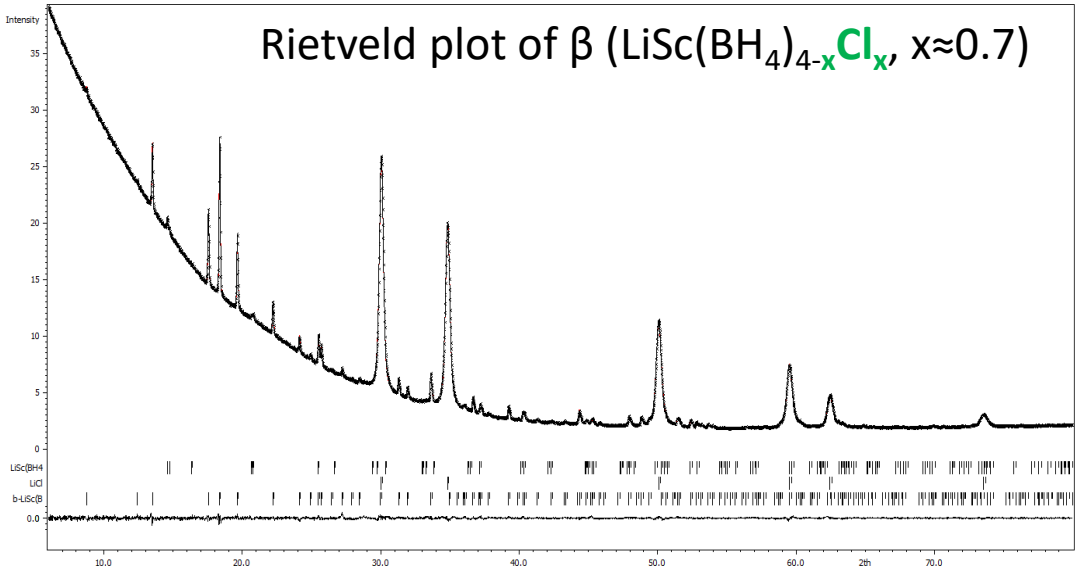
Kim's 'ground state'(*I*-4)

Kim et al., J. Phys. Chem. C (2009)

- Searched for lower-energy solutions by distorting the structure along the atomic displacements of ALL unstable modes.
- Four optical modes are being instable:
  - Li displacement,
  - BH_4 reorientation and translation.
- Computed close to 100 structures.

β phase = $LiSc(BH_4)_{4-x}Cl_x$, x≈0.7

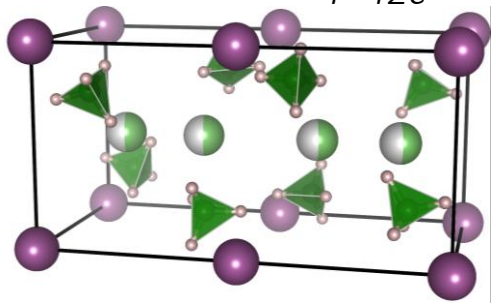




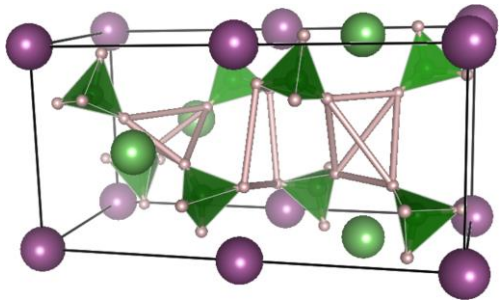
$LiSc(BH_4)_{4-x}Cl_x$	x=0	x≈0.7
wRp [%]	0.98	0.97
cRp [%]	8.78	8.66

SUMMARY

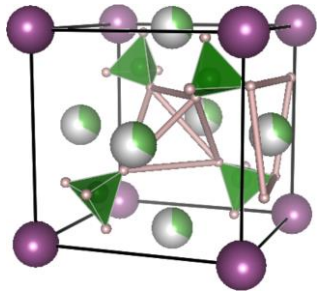
α (disordered)
Hagemann et al. 2008
P-42c



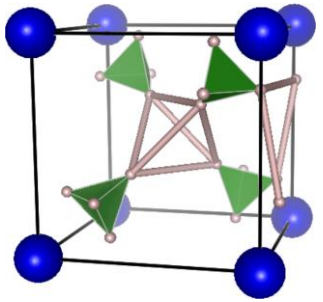
α (ordered)
Derzsi et al. 2020
P-42c



γ (α, Li in all faces)
Derzsi et al. 2020
P-43c



$Zr(BH_4)_4$
P-43m



- We have been able to **resolve the old standing problem** of the structure and stability of the α polymorph.
- **α** is best described by the ordered *P*-42c model.
- **α** is confirmed to be the ground state (only) polymorph of $LiSc(BH_4)_4$.
- **γ** can be interpreted as **α** with substantial Li disorder.
- **β** redetermined as **mixed anion** BH_4-Cl **phase**: $LiSc(BH_4)_{4-x}Cl_x$, where x≈0.7.

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THANK YOU FOR YOUR ATTANTION