USPEX SCHOOL 2020

Search for materials with optimal properties

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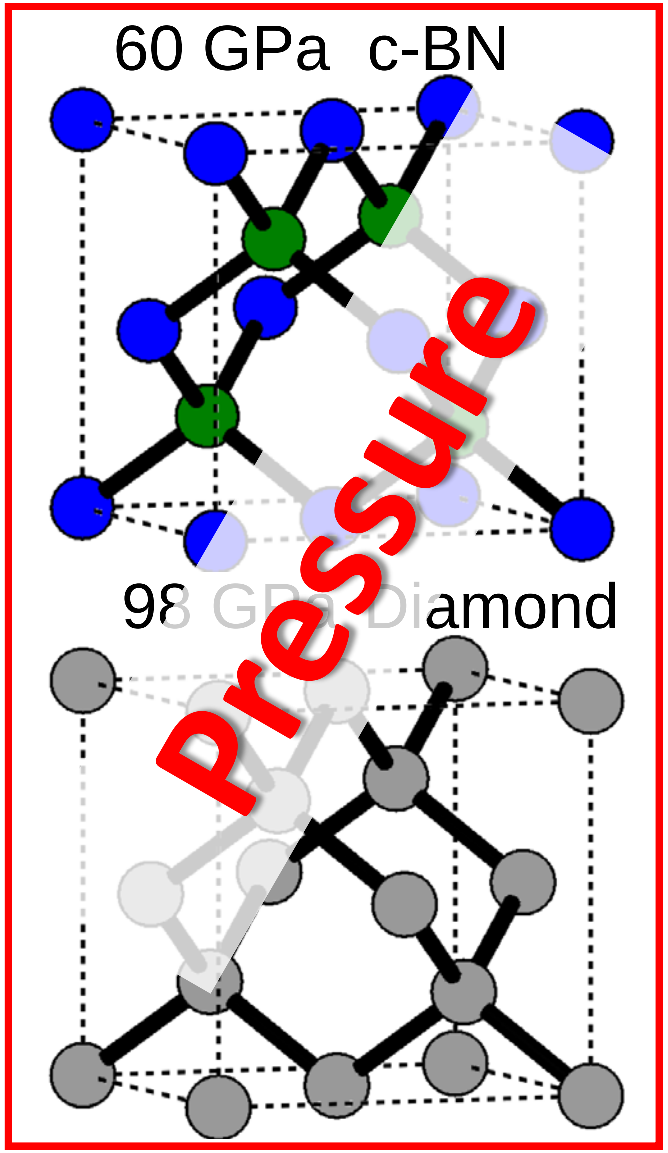
USPEX Computational Materials Discovery

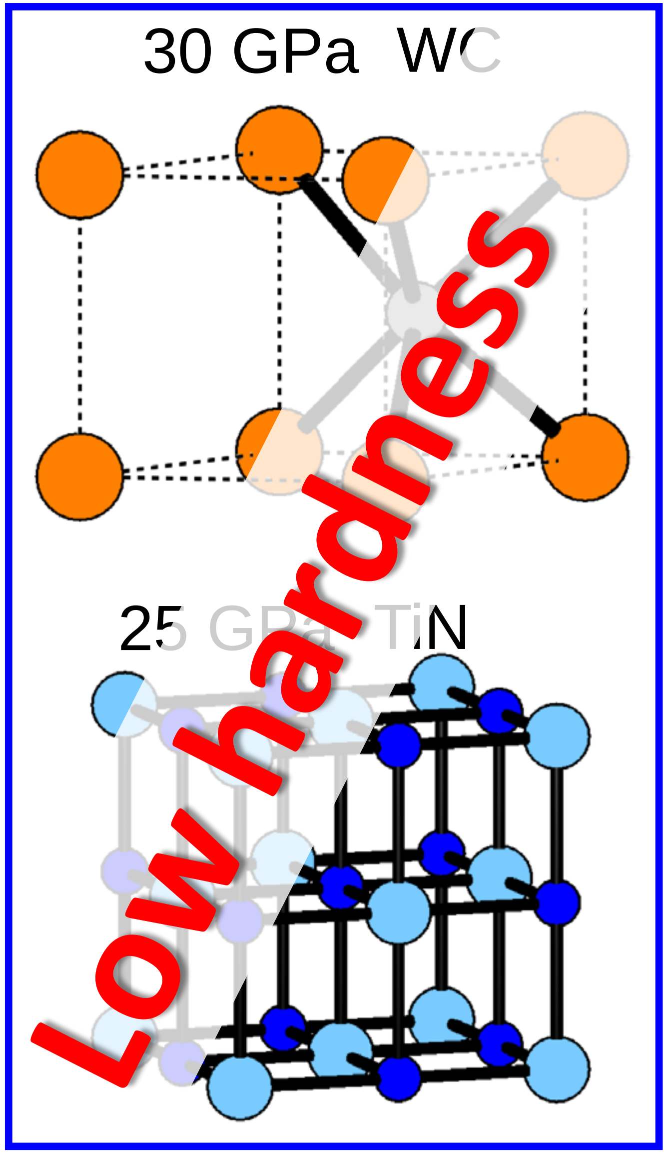
Outline

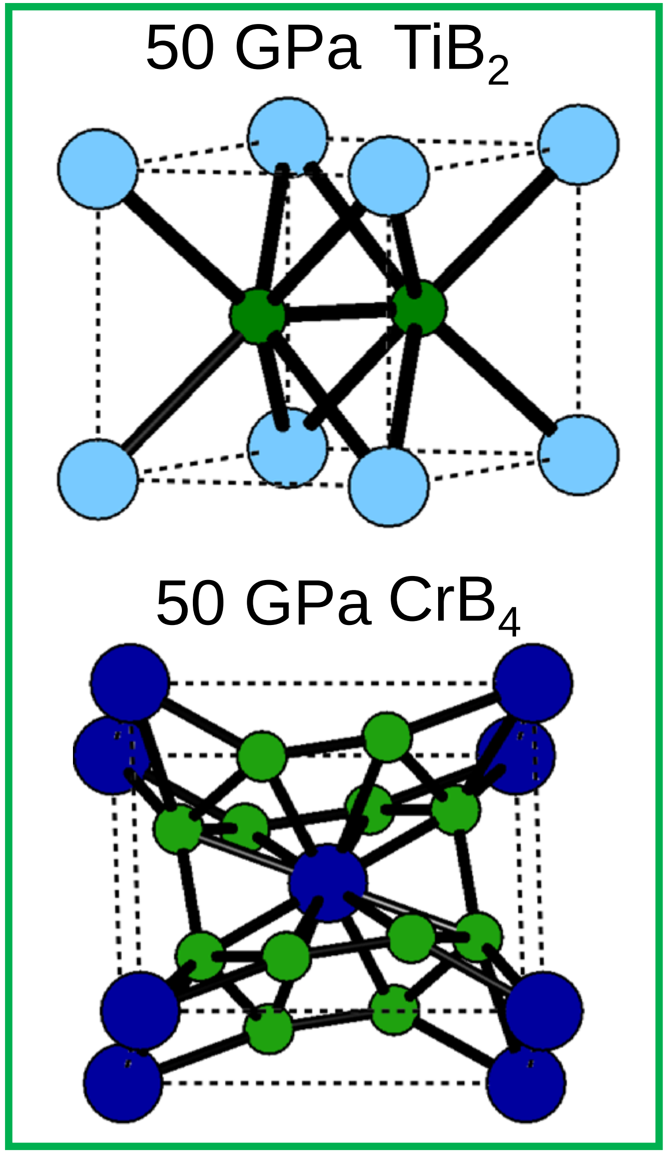
- Search for superhard materials with optimal hardness based on binary transition metal borides

- Hunt for superconducting compounds among the metal hydrides at high-pressures

Hard and Superhard materials







A.G. Kvashnin, et al., J. Appl. Phys., 126, 040901 (2019)

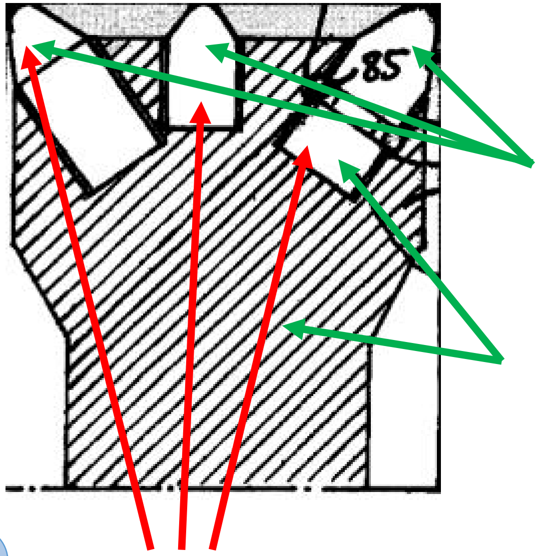
Superhard Materials

Ease in synthesis and production
High melting temperature
High hardness




The main direction of developments in this field of technology is replacement of traditional materials by new ones with improved properties





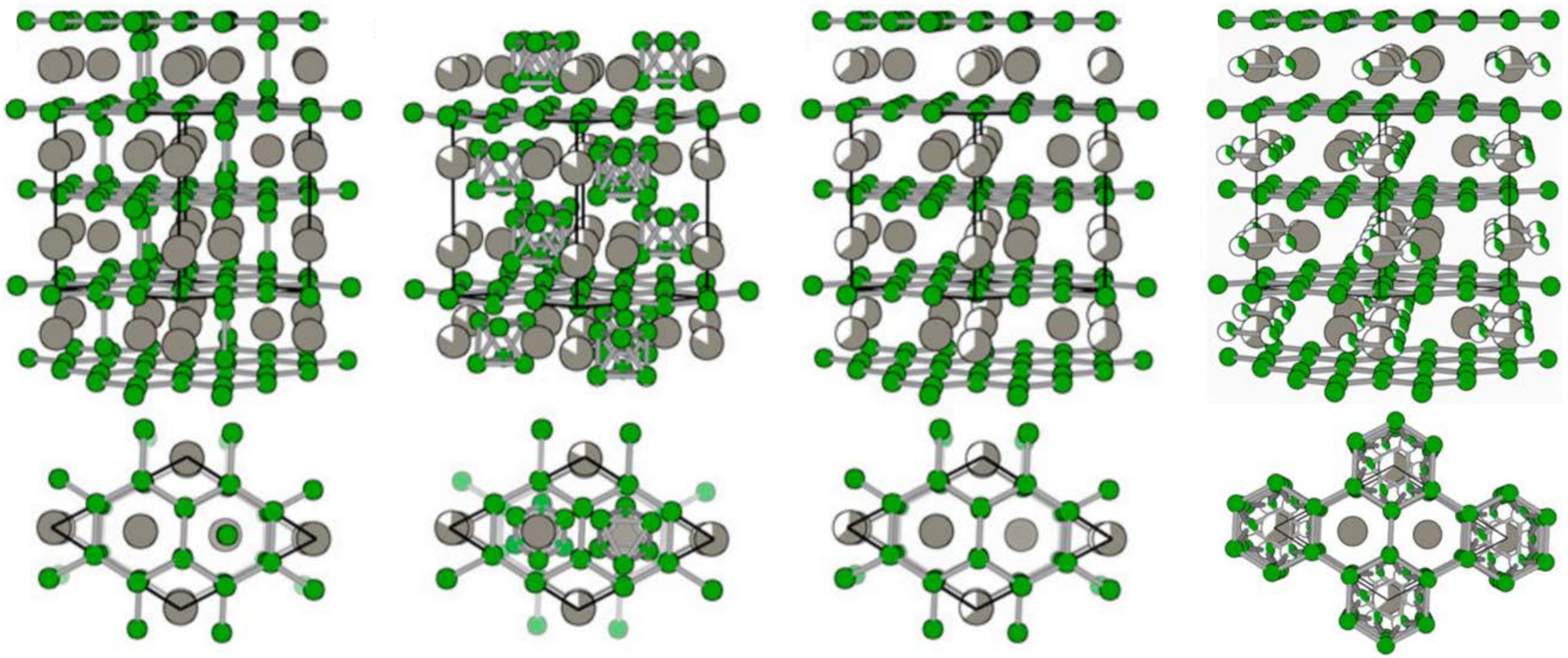
PCD, c-BN,
Mixture PCD/BN

Hard alloys of
WC, TiN etc.

Substitution of traditional materials

W-B System. “WB_4” Structure

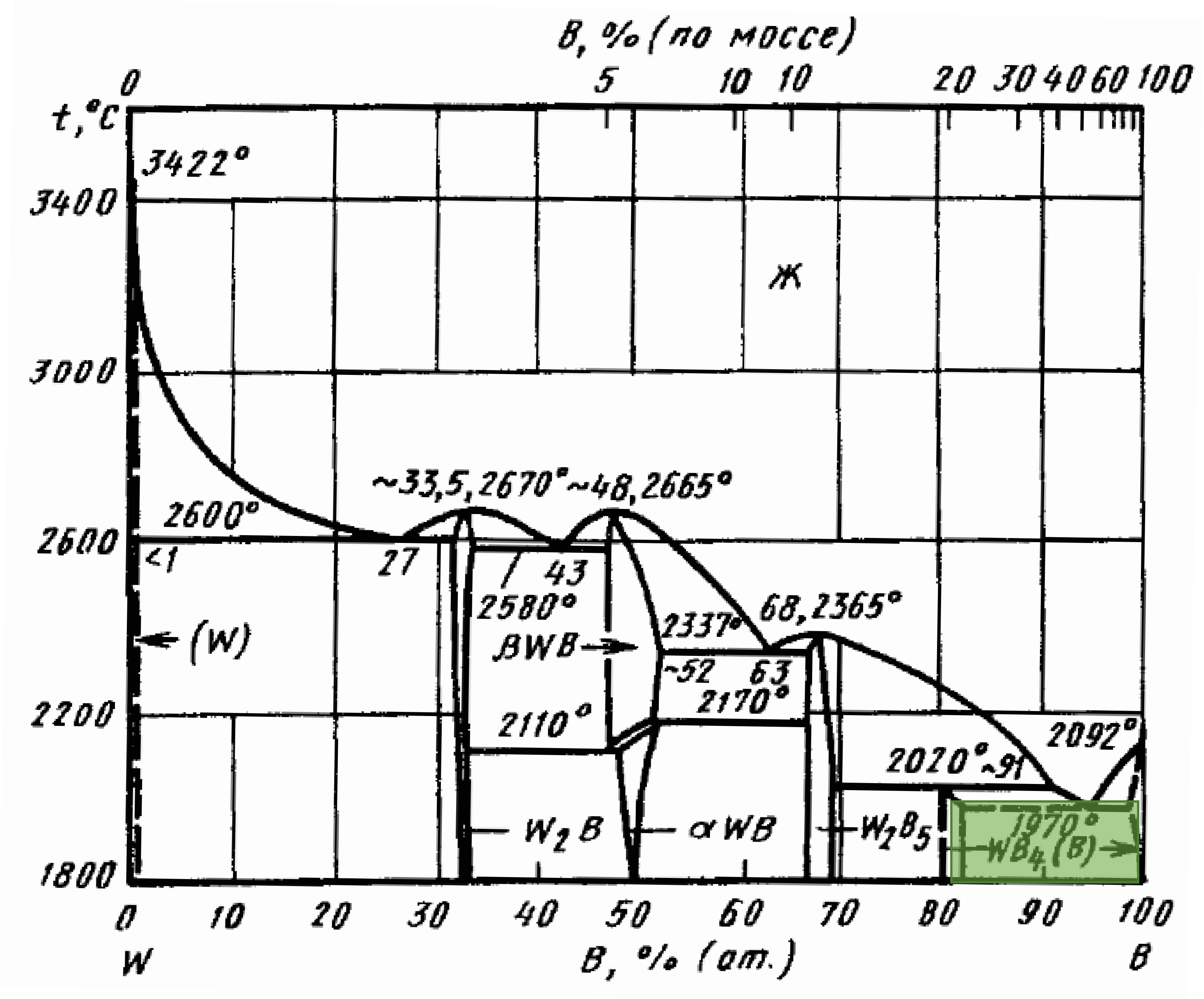
There are many experimental studies devoted to synthesis of superhard compound with preliminary composition of “WB_4”, but theoretical studies reported about the composition between WB_3 and WB_{12}



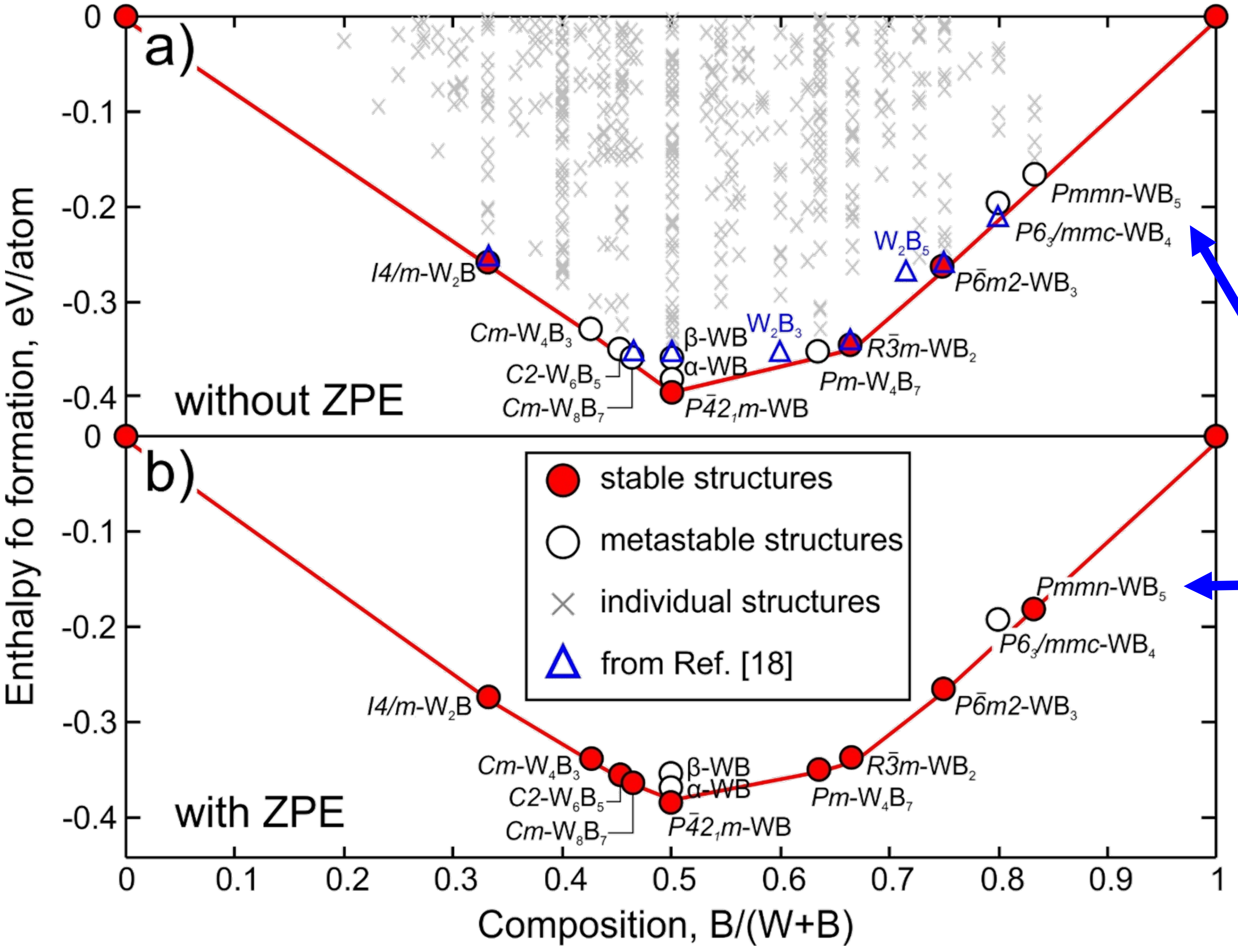
Controversial data about the crystal structure of higher tungsten boride leads to ambiguous conclusions about its properties.

Chretien, A. & Helgorsky, J. *CR Acad Sci Paris* **252**, 742–744 (1961)
Romans, P. A. & Krug, M. P. *Acta Crystallographica* **20**, 313–315 (1966)
Nowotny, H., Haschke, H. & Benesovsky, F. *Monatshefte für Chemie,* **98**, 547–554 (1967)
Lundström, T. & Rosenberg, I. *Journal of Solid State Chemistry* **6**, 299–305 (1973)

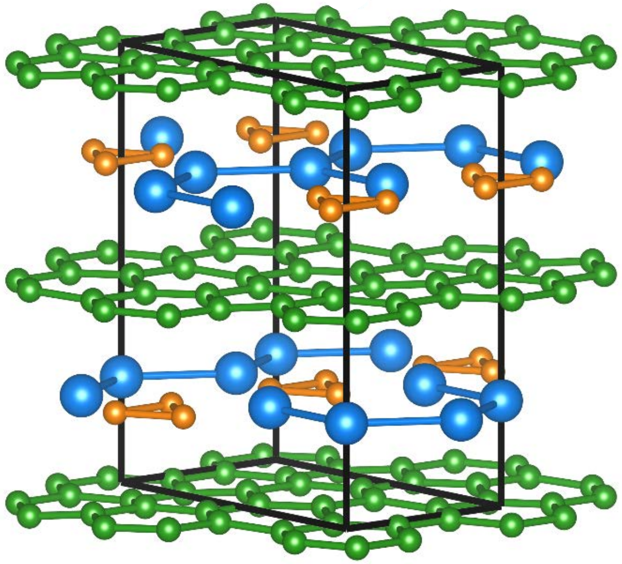
W-B System. WB_5 Structure



W-B System. WB_5 Structure



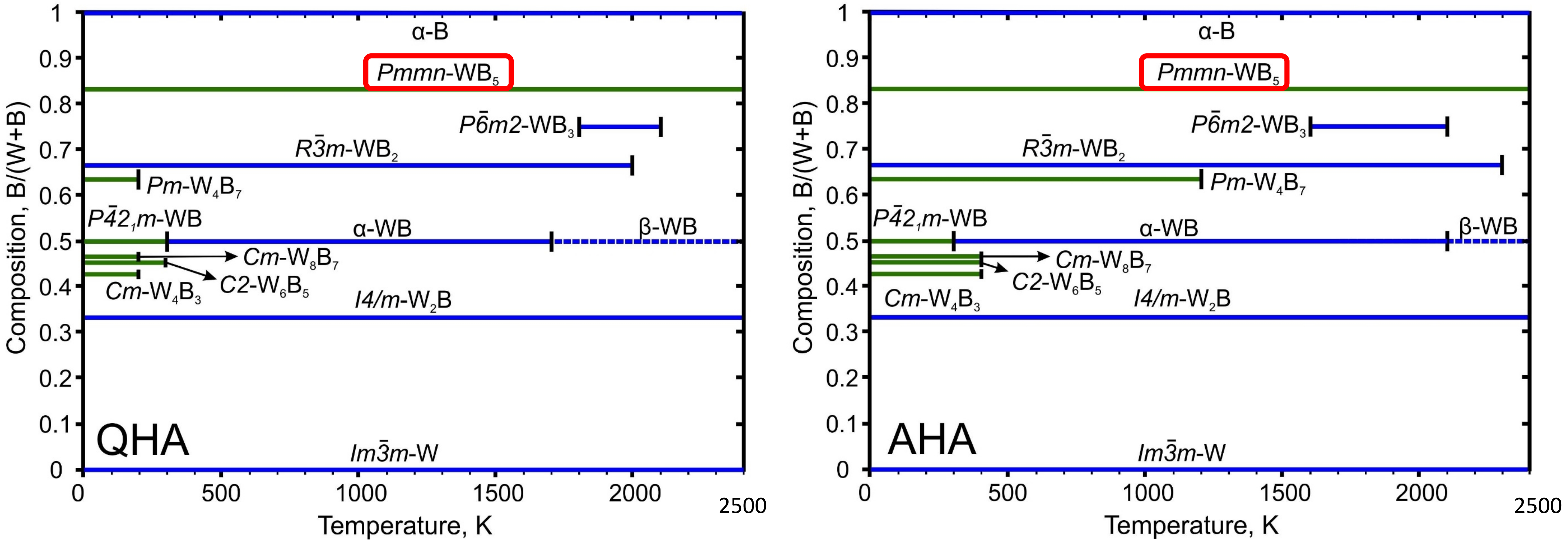
New higher boride WB_5 was predicted, which has unique mechanical properties and potentially can be used instead of traditional hard alloys



Vickers hardness is 45 GPa

A.G. Kvashnin, et al., J. Phys. Chem. Lett., 9, 3470–3477 (2018)

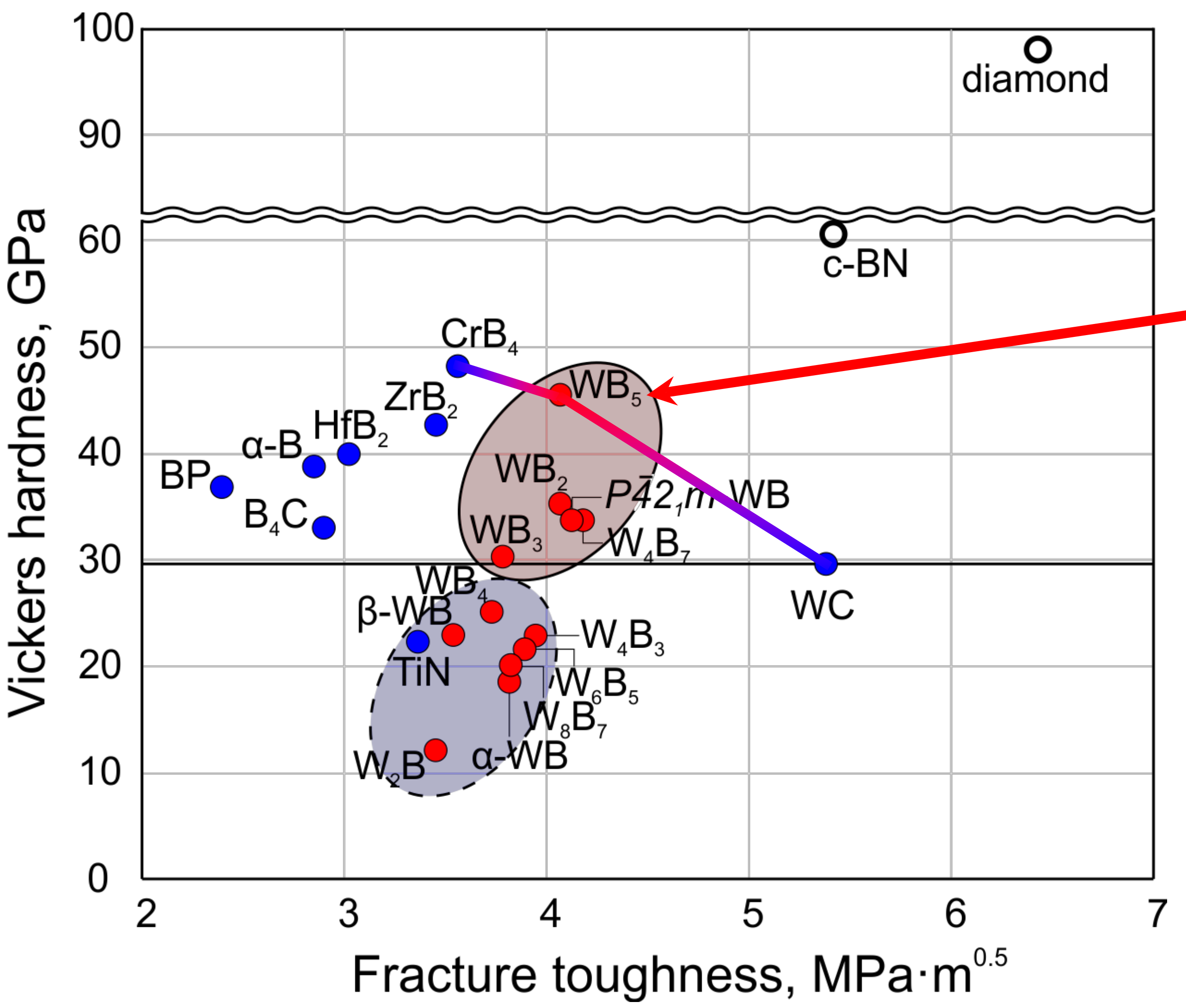
Temperature stability

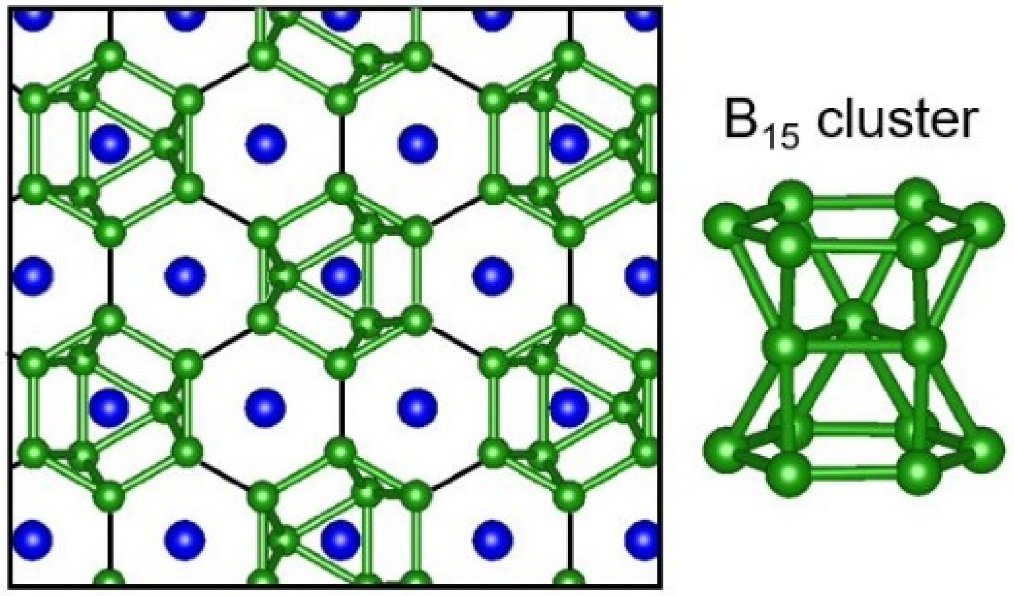


Wide temperature range of stability of WB$_5$ makes it a perspective material for big number of potential applications in industry

A.G. Kvashnin, et al., J. Phys. Chem. Lett., 9, 3470–3477 (2018)

Mechanical properties



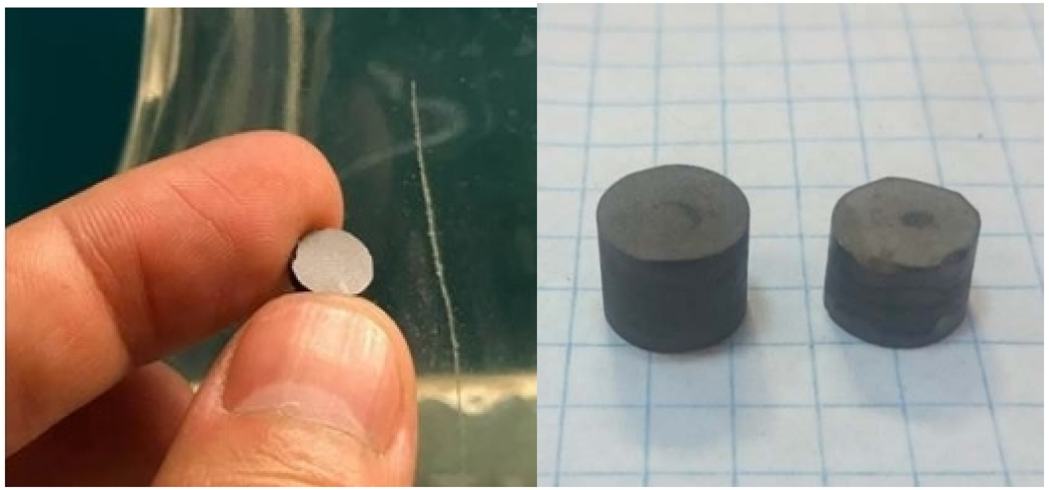


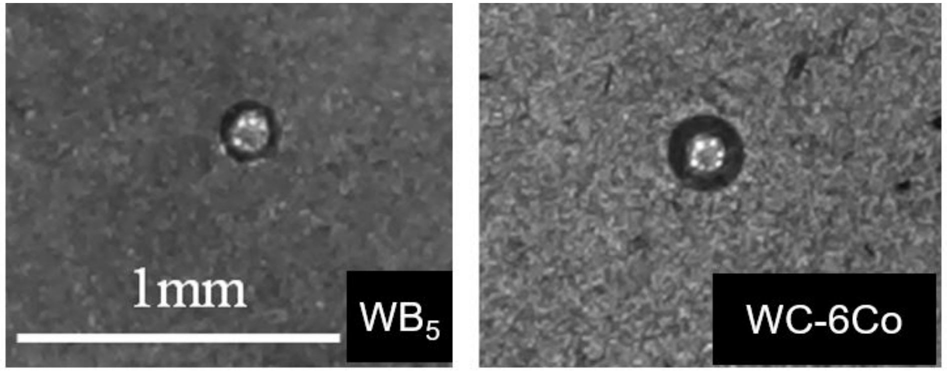
New compound with unique combination of hardness and fracture toughness was predicted

A.G. Kvashnin, et al., J. Phys. Chem. Lett., 9, 3470–3477 (2018)

Synthesis and properties of higher tungsten boride

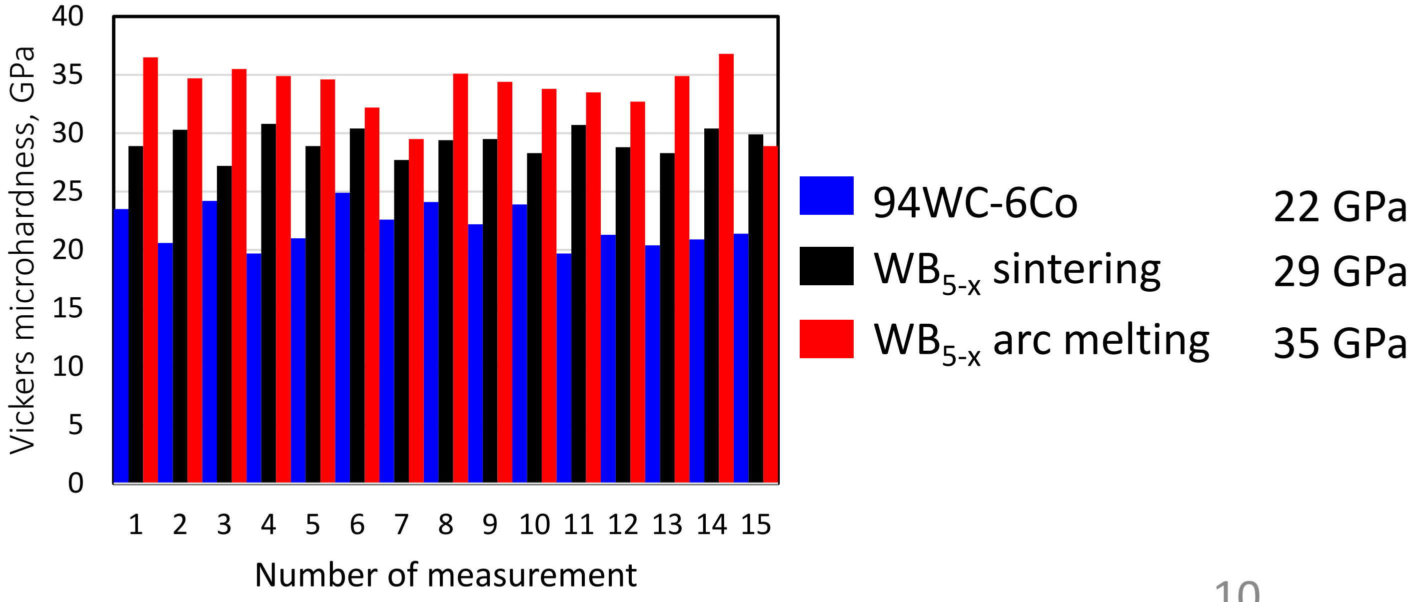
Using high-temperature sintering of boron and tungsten nanometer-size powders the highest tungsten boride was synthesized





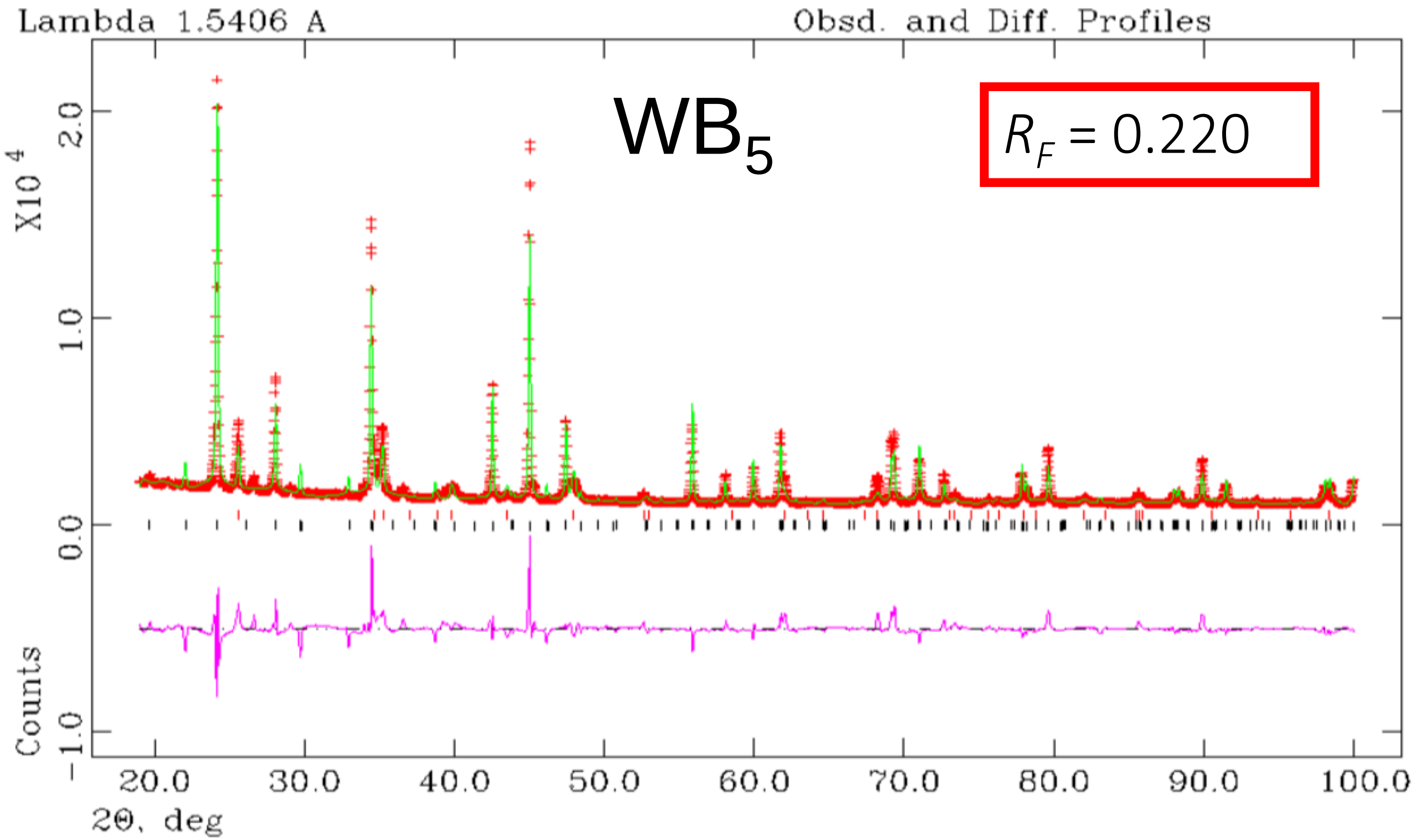
Imprint left by the diamond cone in the Rockwell hardness test

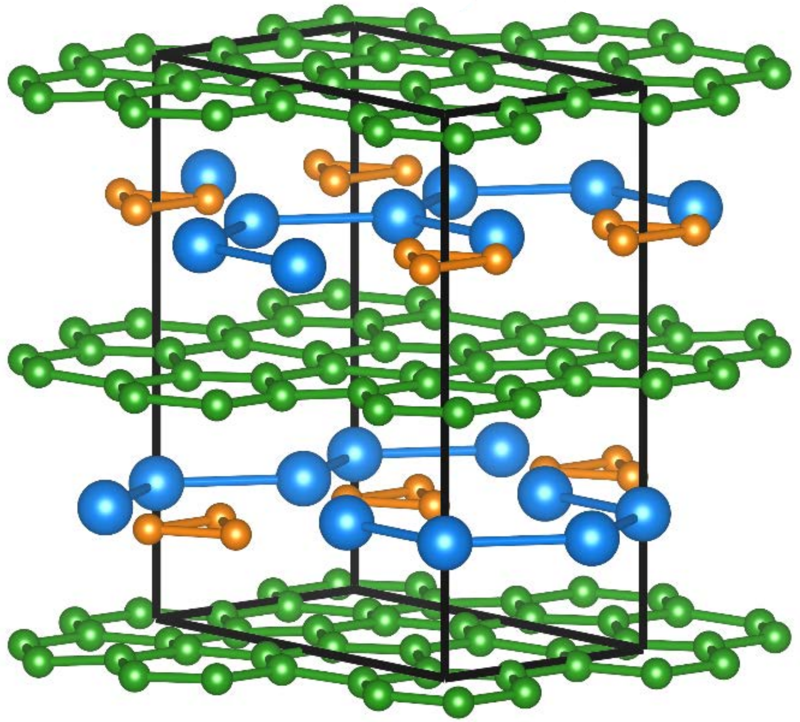
Measurements of Vickers microhardness of synthesized WB_{5-x} samples show that they 30-50% harder (depending on synthesis conditions) than 94WC-6Co, which confirms our predictions



A.G. Kvashnin, et al., Adv. Sci., 2000775 (2020)

Structure of higher boride

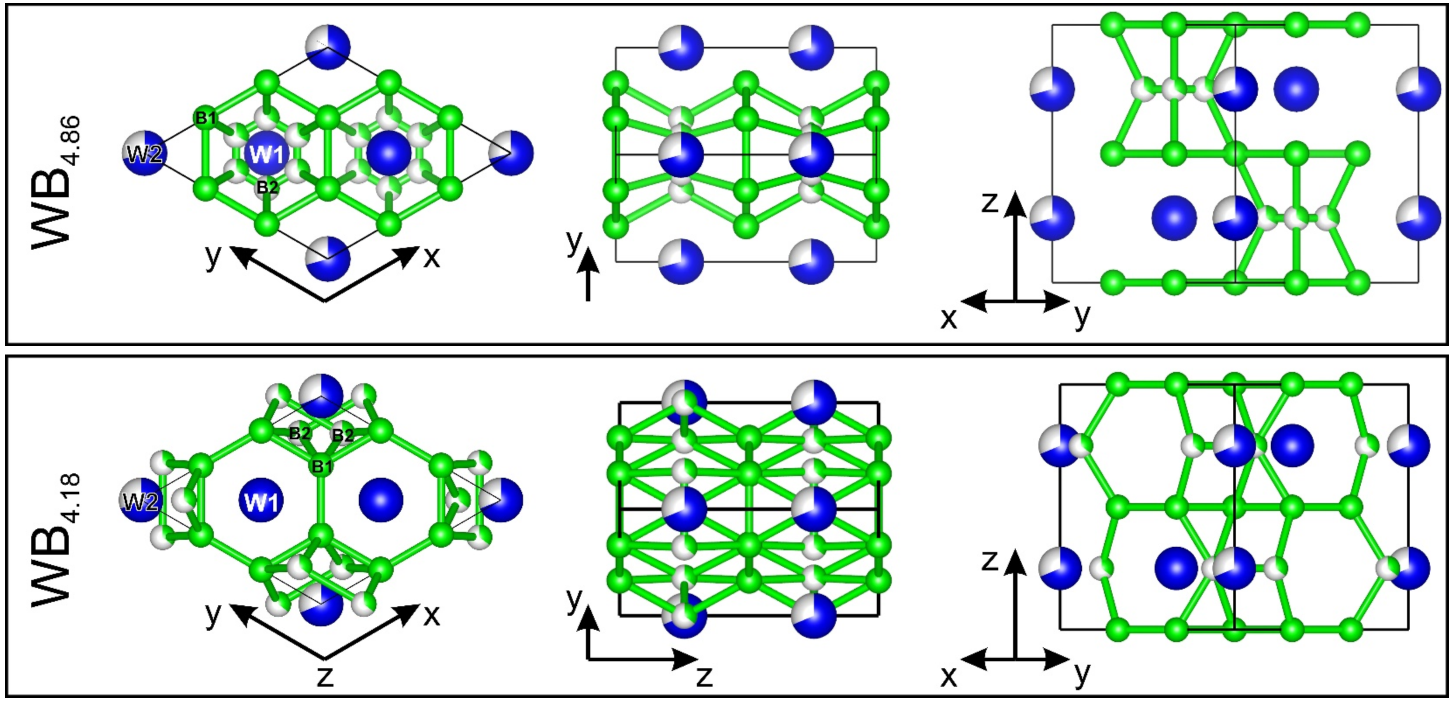




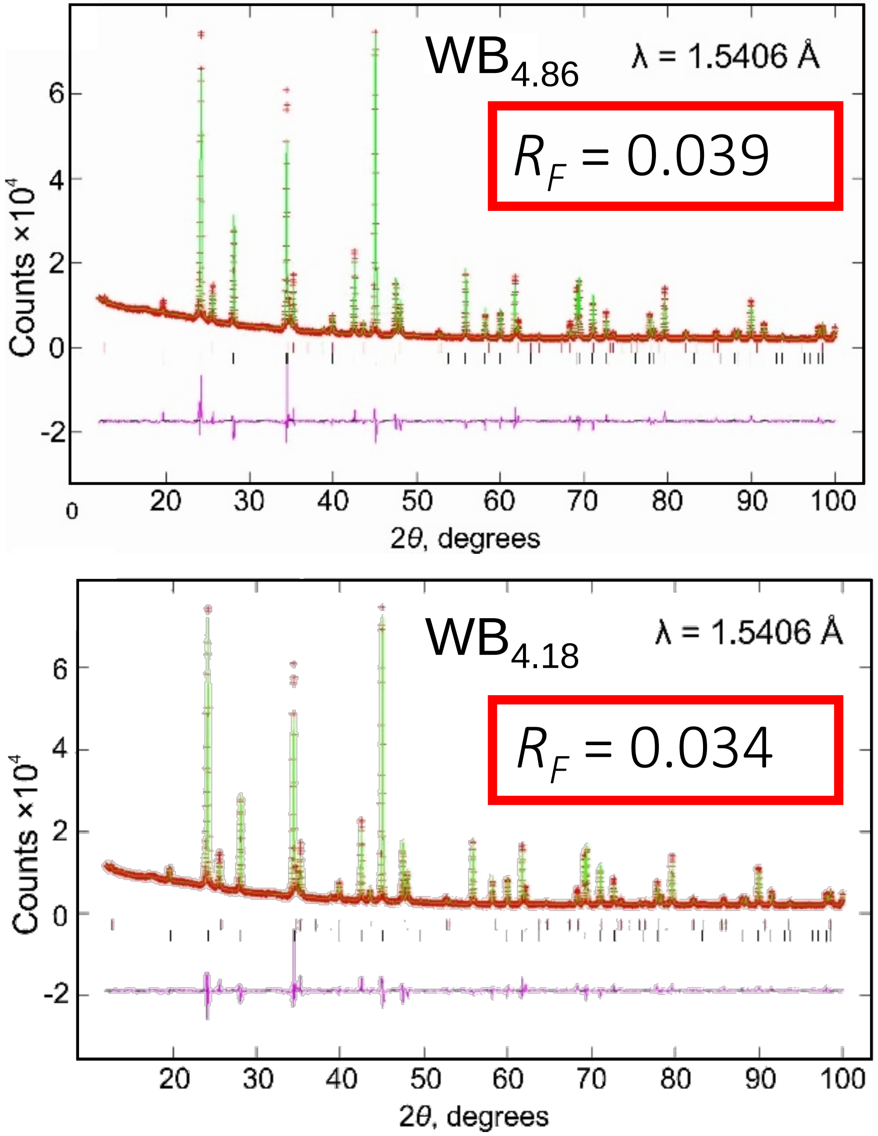
Synthesized compound has higher symmetry compared to predicted one ($P6_3/mmc$) and does not have WB_5 composition. Non-stoichiometric disordered structures need to be considered

Refinement of structure

Synthesized compound is WB_{5-x}
Models for structure refinement were proposed

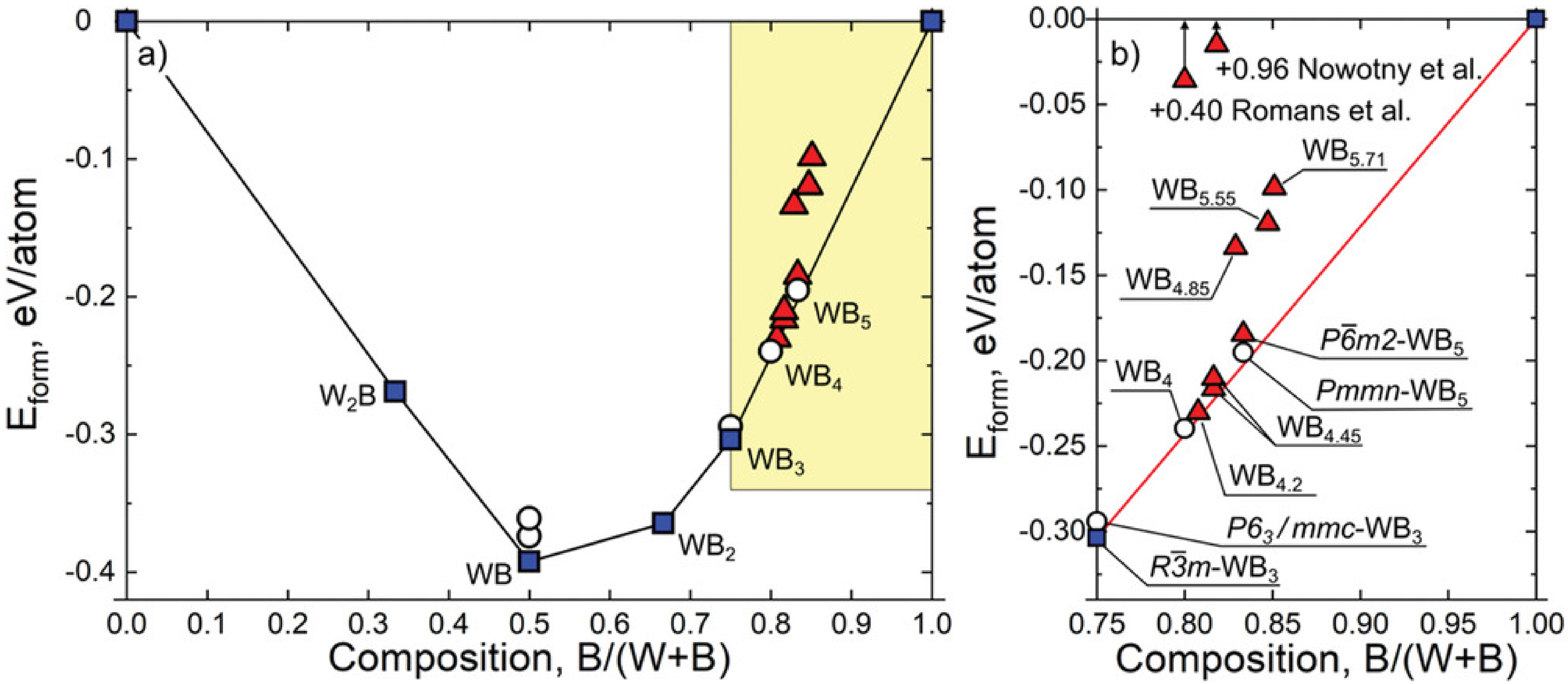


Crystal structure is disordered and composition varies from $WB_{4.18}$ to $WB_{4.86}$



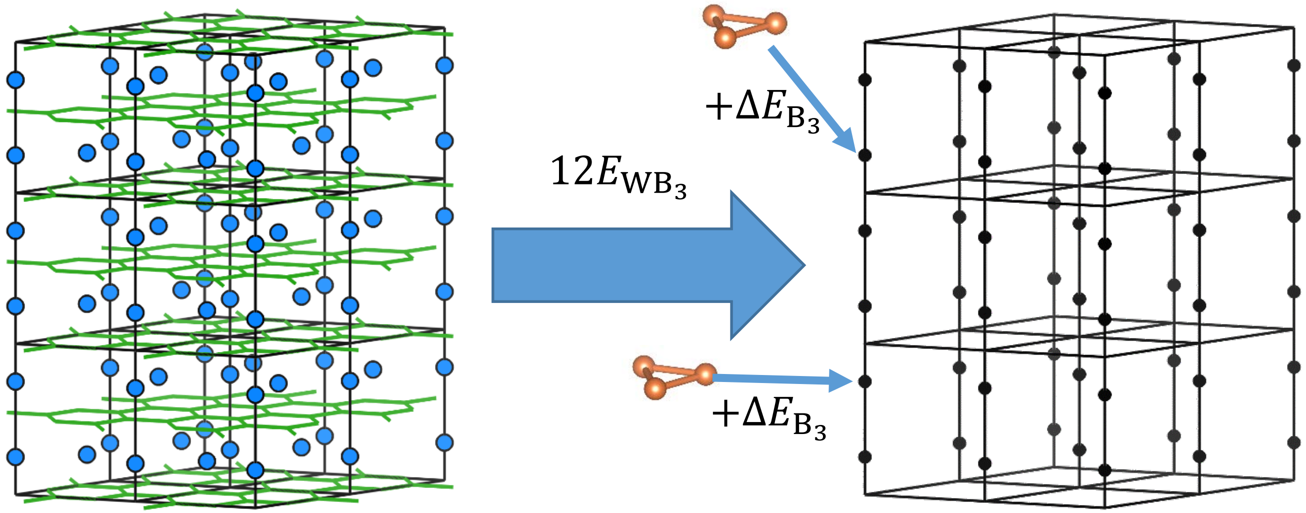
A.G. Kvashnin, et al., Adv. Sci., 2000775 (2020)

Stability of the Models



Synthesized higher tungsten boride has structural motifs that belong to predicted WB_5, but has disordered structure with the composition of $WB_{4.2}$

Lattice model



1. Total energy of the supercell made of N $P6_3/mmc$-WB_3 unit cells can be calculated as:

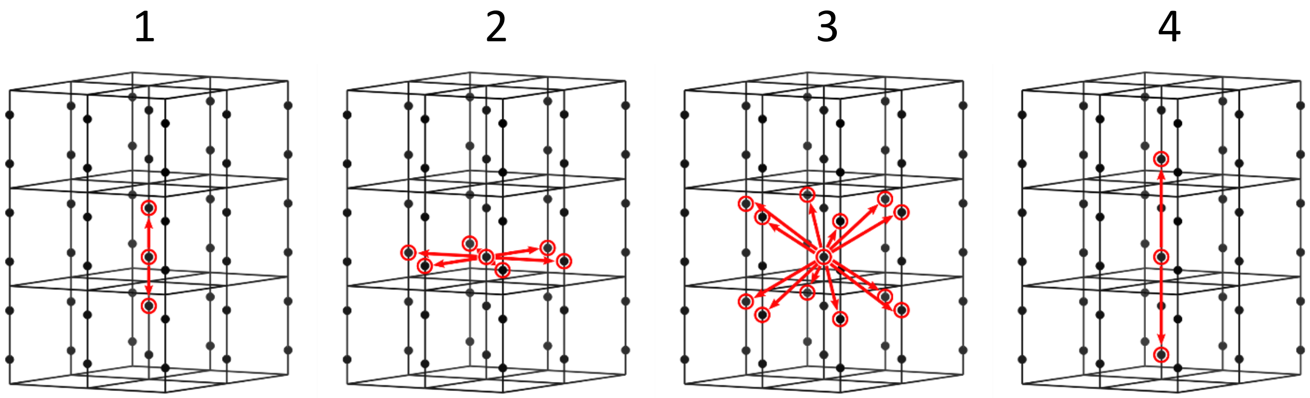
$$E_{N,n} = NE_{WB_3} + n\Delta E_{B_3} + \frac{1}{2}\sum_{i \neq j} K_{ij}\, s_i s_j$$

2. Fit of the parameters of interaction K_{ij}:

Neighbor order	Number of neighbors	Distance	K (eV)
1	2	c/2	1.378
2	6	a	0.094
3	12	$\sqrt{a^2 + c^2/4}$	0.023
4	2	c	0.084

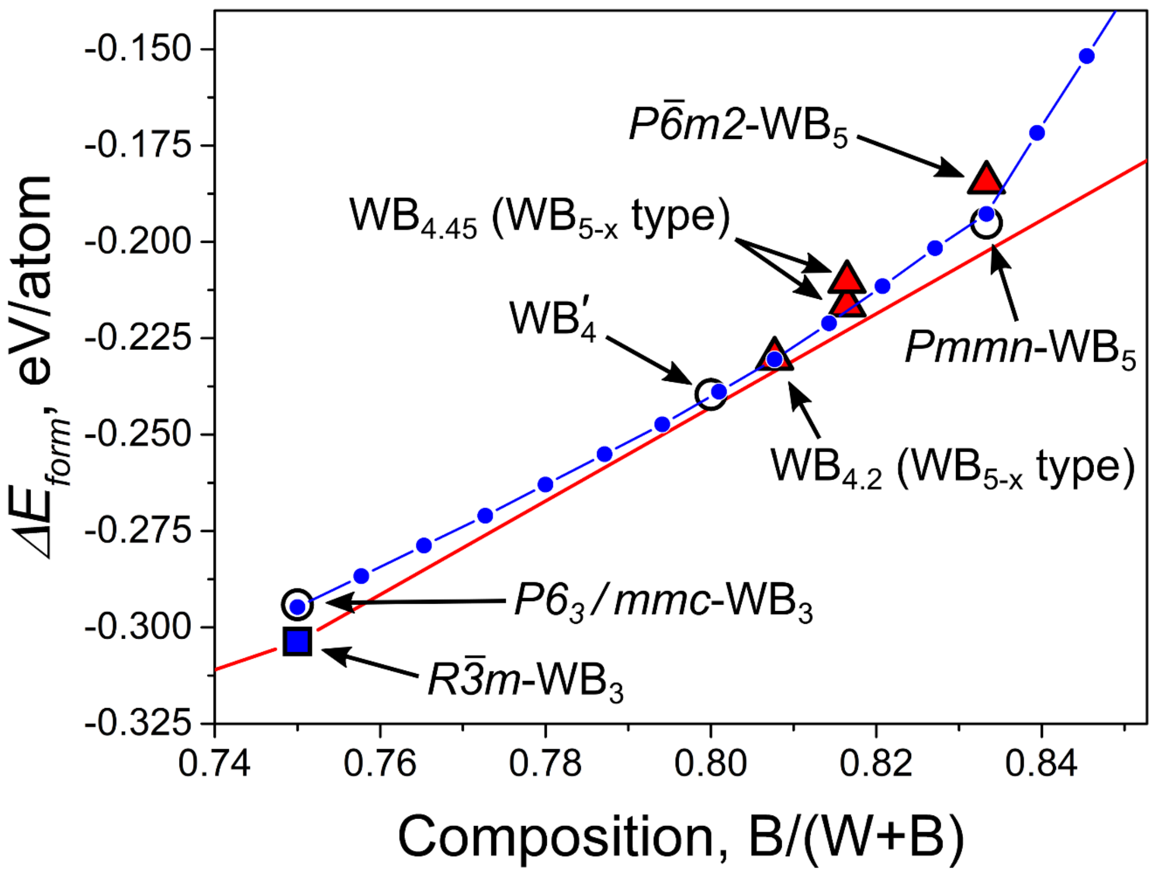
3. Search for the most stable composition, corresponding to the optimal arrangement of the B_3 units within WB_3-WB_9 range

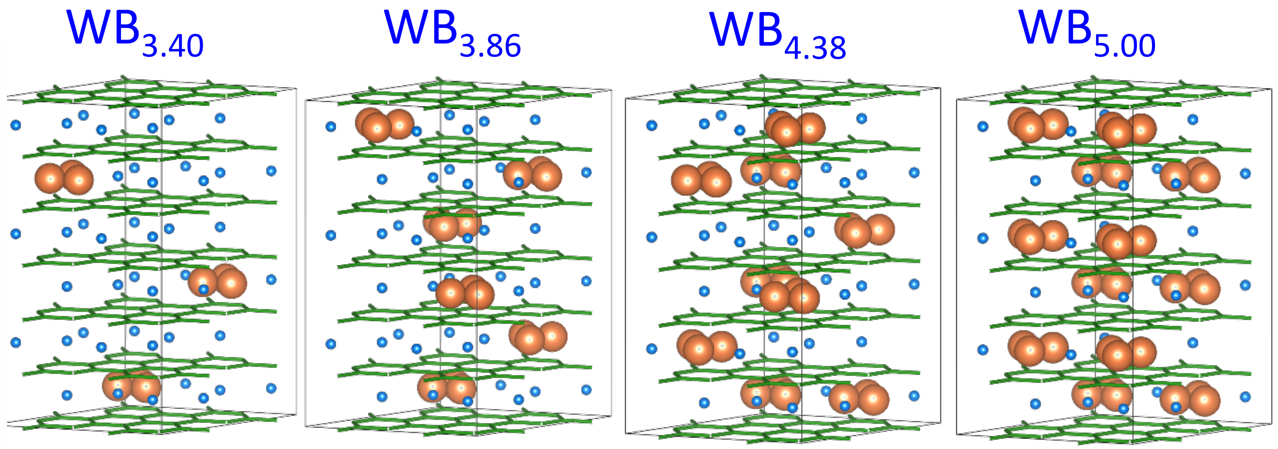
Interaction between neighbors:



A.G. Kvashnin, et al., Adv. Sci., 2000775 (2020)

Intermediate Compositions

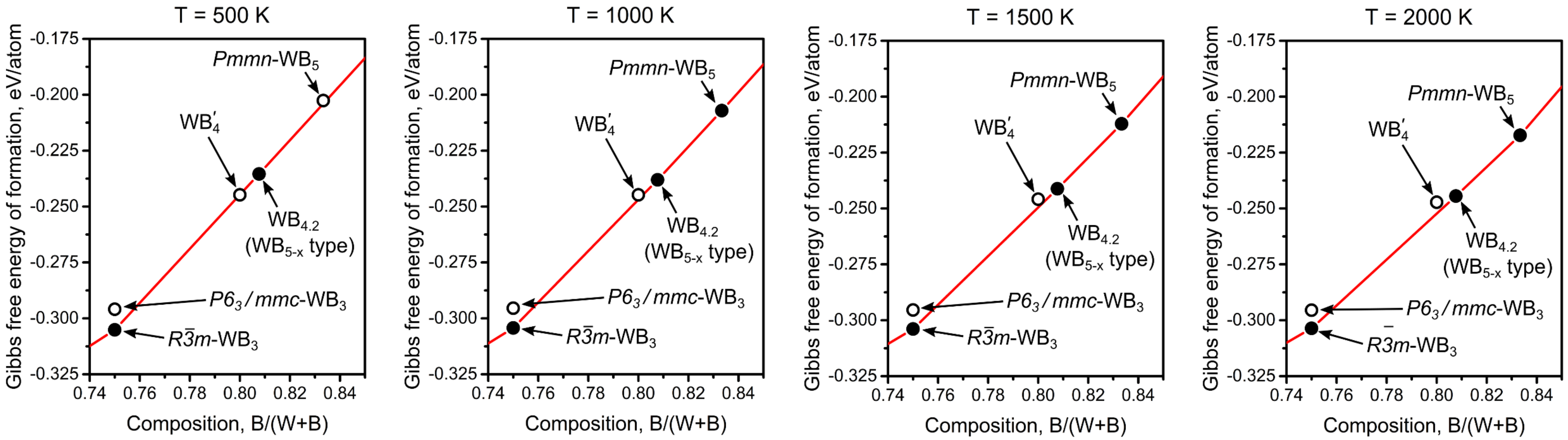




Developed lattice model proves the possibility of formation of disordered WB_{5-x} compounds during the synthesis

A.G. Kvashnin, et al., Adv. Sci., 2000775 (2020)

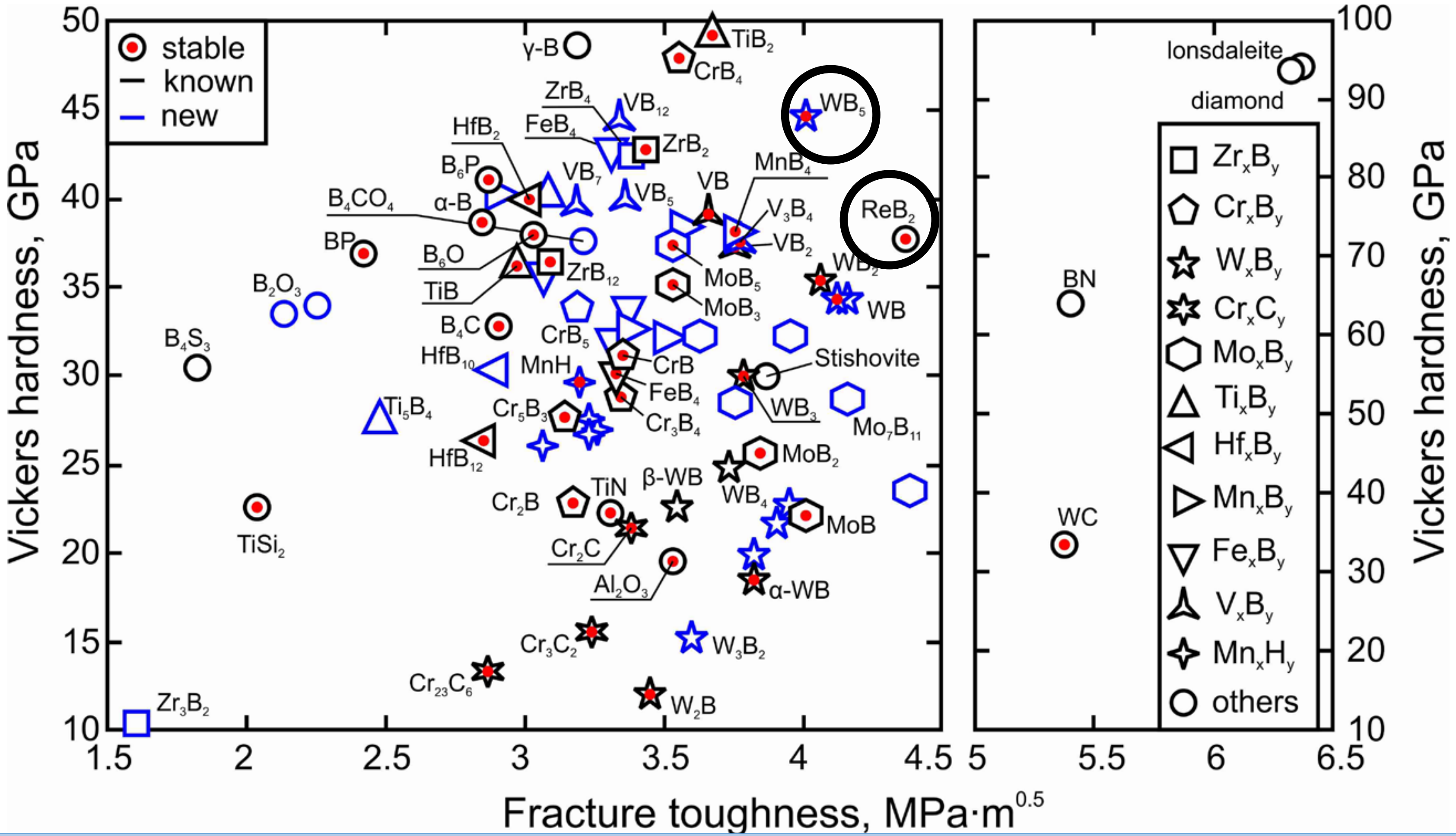
Stability of the Models



Increase of temperature leads to stabilization of disordered $WB_{4.2}$ compound and predicted WB_5. We showed that at high temperatures the probability of the formation of disordered structure with $WB_{4.2}$ composition is highest, which is confirmed by our experiments

A.G. Kvashnin, et al., Adv. Sci., 2000775 (2020)

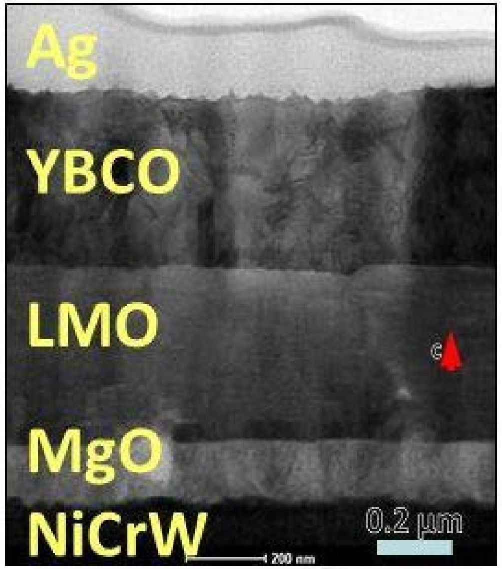
“treasure” map of superhard materials

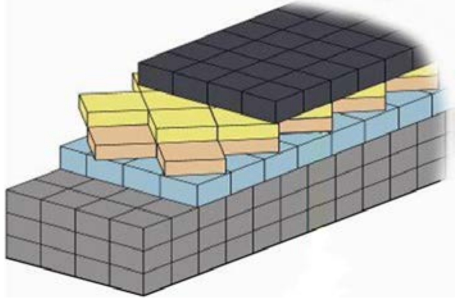


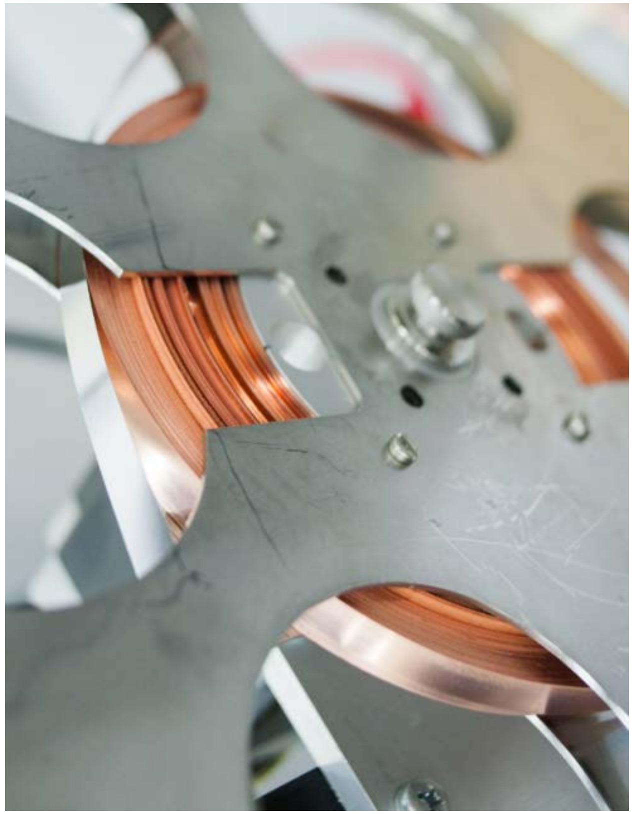
Predicted “treasure” map of distribution of hard and superhard materials allows one to determine the most perspective materials for synthesis and industrial applications

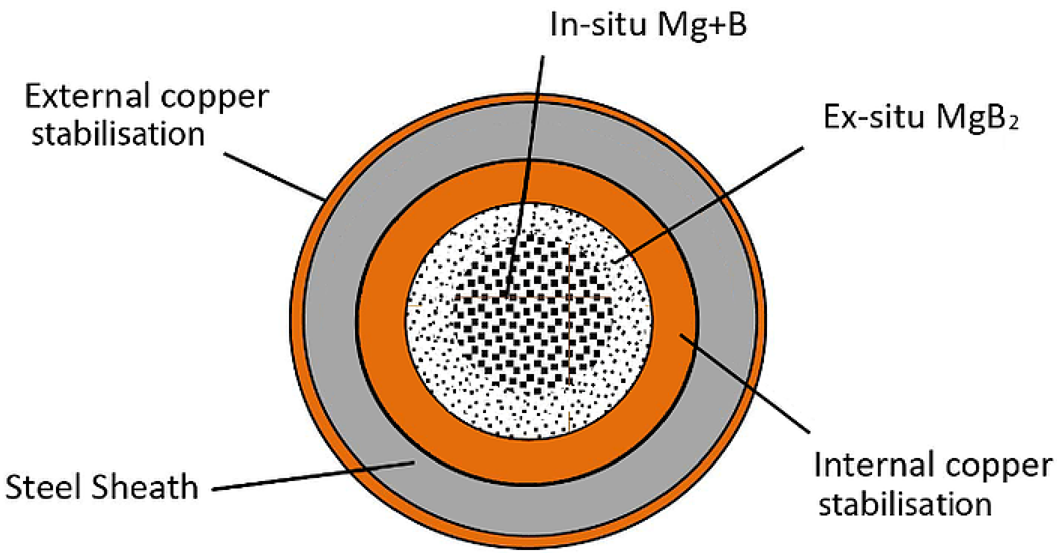
A.G. Kvashnin, et al., J. Appl. Phys., 126, 040901 (2019)

Superconducting materials





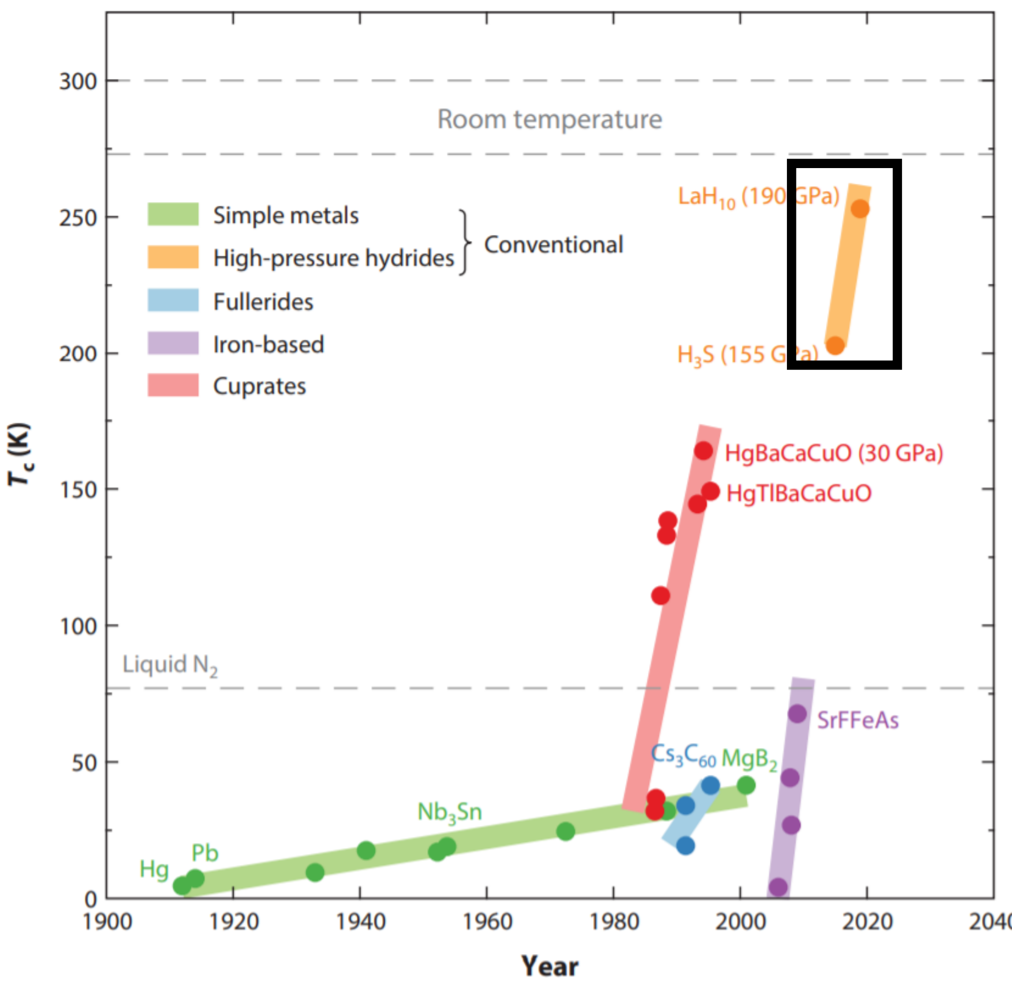




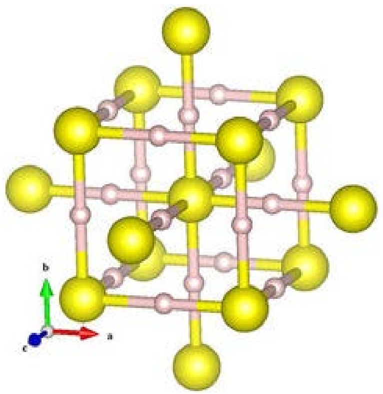
HTSC-2 ribbon based on the multilayered composite YBCO or BSCCO.
Tc = 90-110 K, j(crit) = 500 A/mm^2 at 77 K,
H(crit) = 20T at 4 K

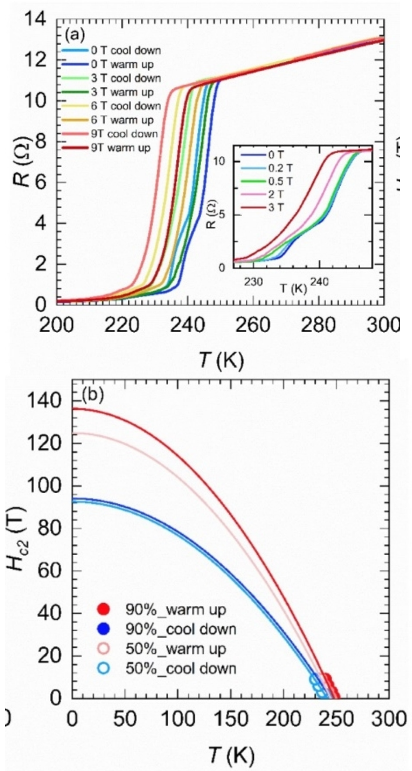
MgB_2-wire, *in situ* formed according to «powder in the tube» experimental scheme
Tc = 20-25 K (up to 39 K), j(crit) = 200 A/mm^2 at 4K, H(crit) = 10T at 4 K

Superconducting materials



Annu. Rev. Condens. Matter Phys. 11, 57–76 (2020)





OPEN

SUBJECT AREAS: THEORY AND COMPUTATION, CONDENSED-MATTER PHYSICS

Pressure-induced metallization of dense $(H_2S)_2H_2$ with high-T_c superconductivity

Defang Duan[1,2], Yunxian Liu[1], Fubo Tian[1], Da Li[1], Xiaoli Huang[1], Zhonglong Zhao[1], Hongyu Yu[1], Bingbing Liu[1], Wenjing Tian[2] & Tian Cui[1]

Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system

A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov & S. I. Shylin

Nature **525**, 73–76 (03 September 2015) | Download Citation

Potential high-T_c superconducting lanthanum and yttrium hydrides at high pressure

PNAS

Hanyu Liu[a], Ivan I. Naumov[a], Roald Hoffmann[b], N. W. Ashcroft[c], and Russell J. Hemley[d,e,1]

Evidence for Superconductivity above 260 K in Lanthanum Superhydride at Megabar Pressures

Maddury Somayazulu, Muhtar Ahart, Ajay K. Mishra, Zachary M. Geballe, Maria Baldini, Yue Meng, Viktor V. Struzhkin, and Russell J. Hemley

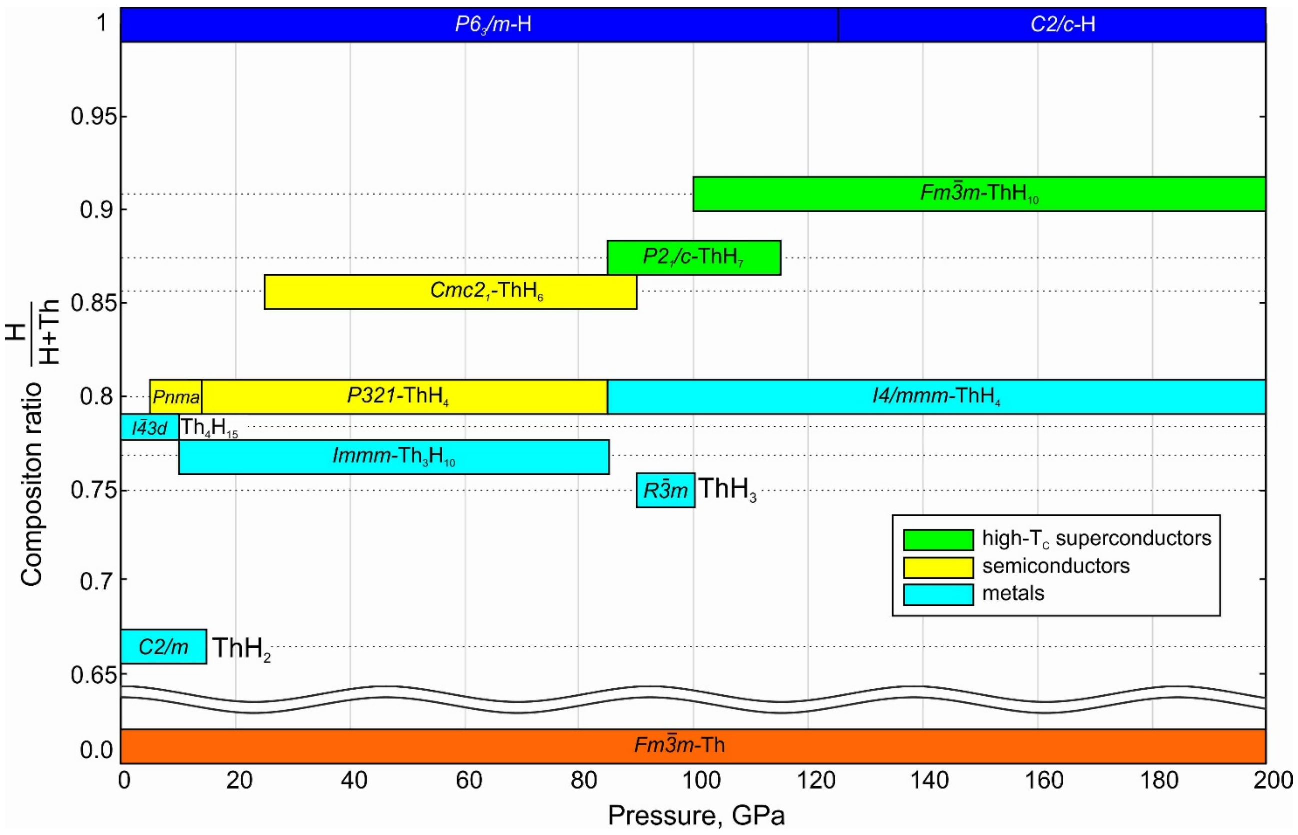
Phys. Rev. Lett. **122**, 027001 – Published 14 January 2019

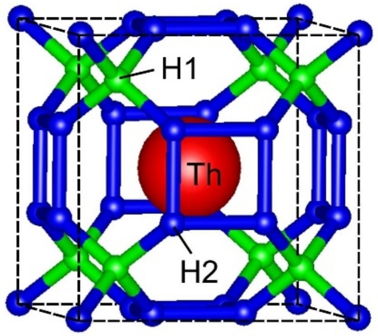
Superconductivity at 250 K in lanthanum hydride under high pressures

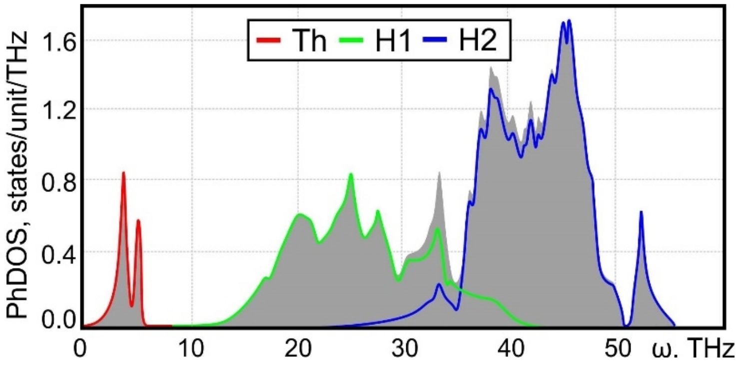
A. P. Drozdov, P. P. Kong, V. S. Minkov, S. P. Besedin, M. A. Kuzovnikov, S. Mozaffari, L. Balicas, F. F. Balakirev, D. E. Graf, V. B. Prakapenka, E. Greenberg, D. A. Knyazev, M. Tkacz & M. I. Eremets

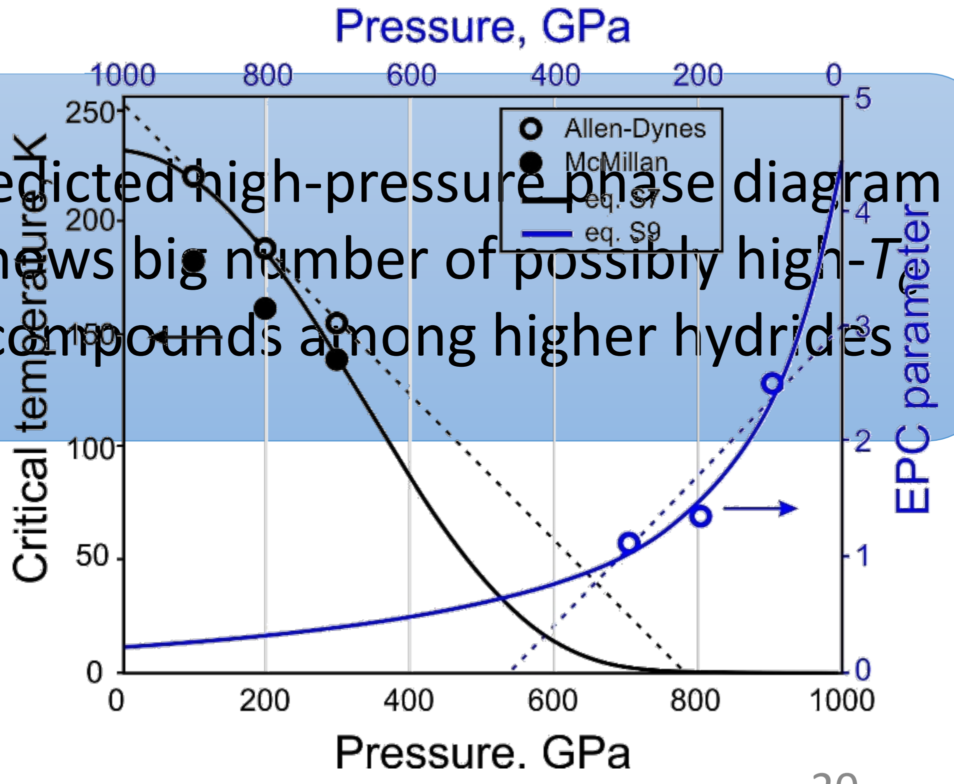
Nature **569**, 528–531 (2019) | Download Citation

Search for stable thorium hydrides









Predicted high-pressure phase diagram shows big number of possibly high-T_C compounds among higher hydrides

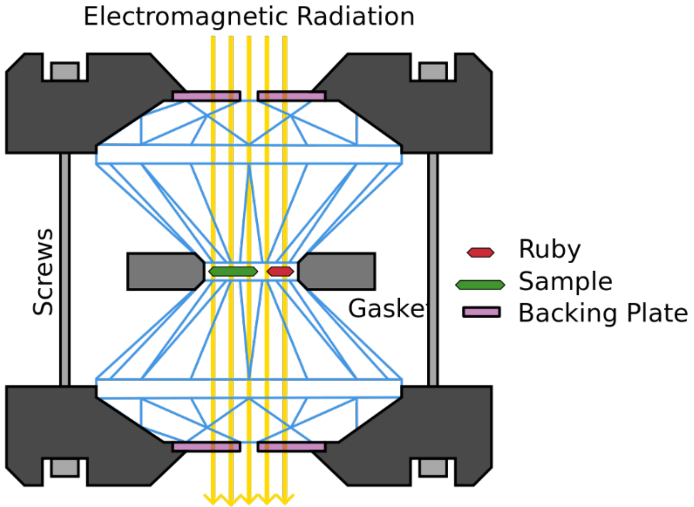
New higher hydride – ThH_{10} was predicted having the lowest stability pressure among other higher metal hydrides with very high T_C ~ 220 K

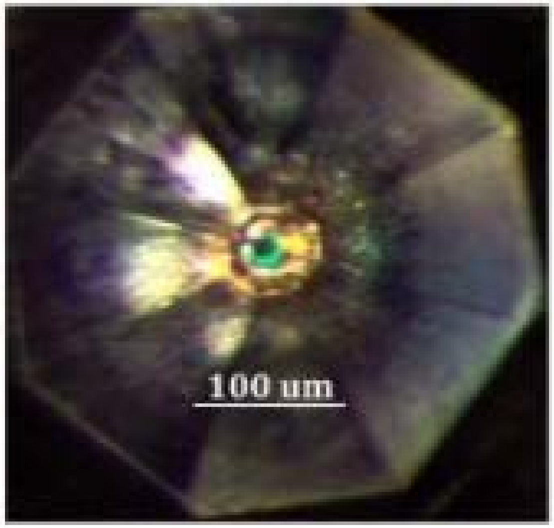
A.G. Kvashnin et al. ACS App. Mat. Interfaces, 10, 43809 (2018)

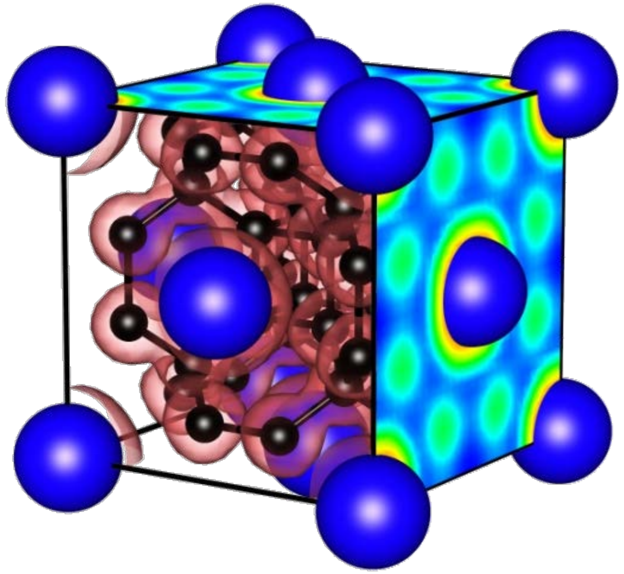
Synthesis of ThH_{10}

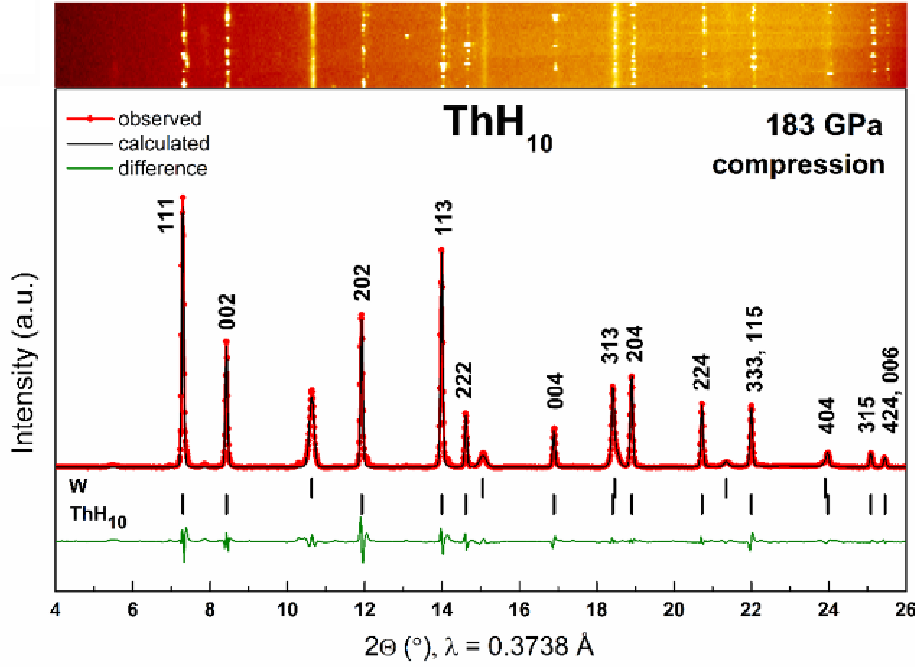
183 GPa, 1800 K

ESRF
The European Synchrotron





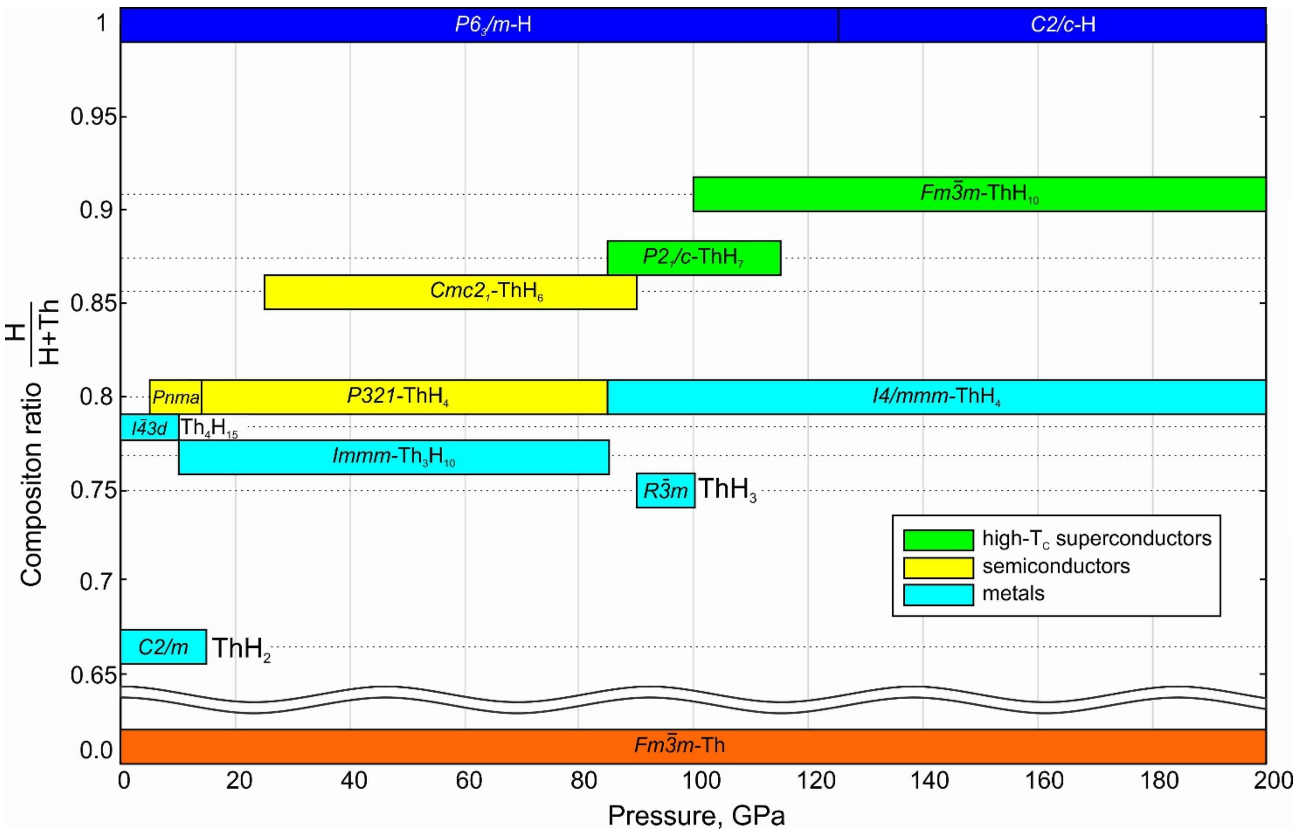


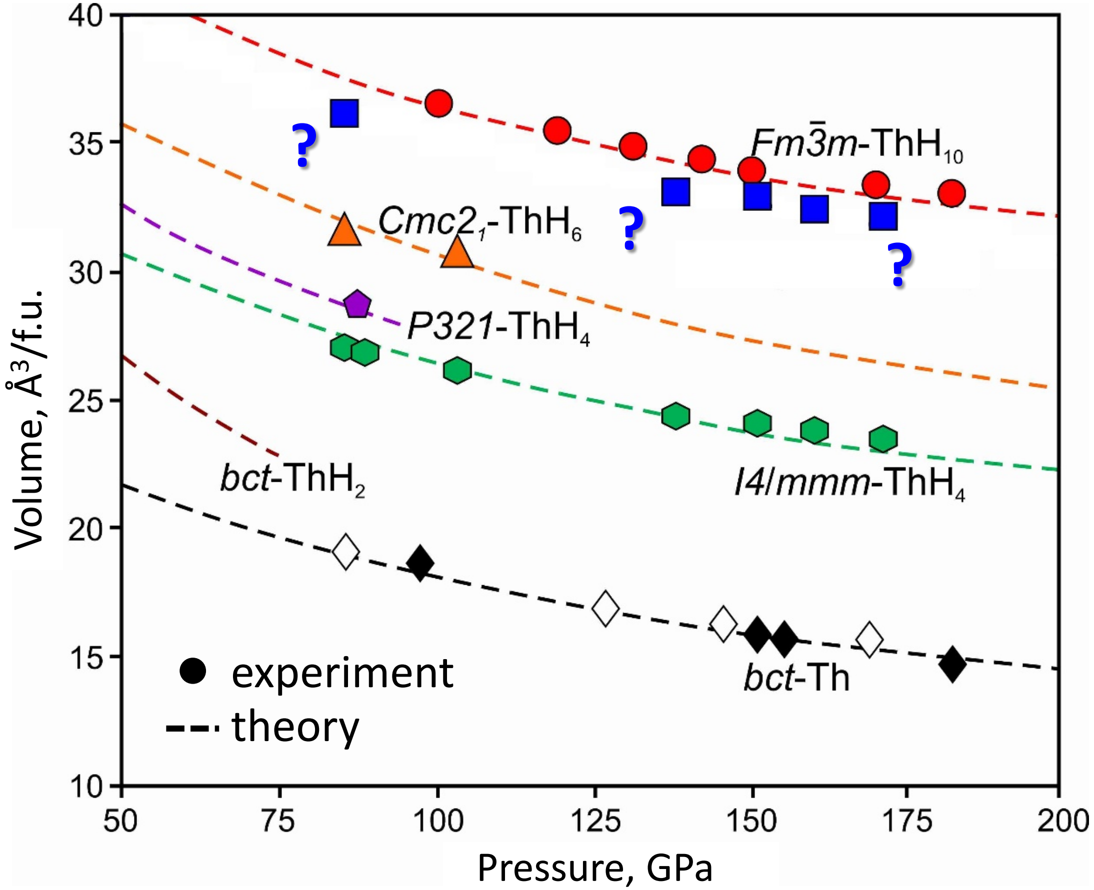


Results of computational search allowed us to perform targeted synthesis of high-T_C ThH_{10}

D.V. Semenok, A.G. Kvashnin et al., Mat. Today, 33, 36-44 (2020)

Equations of states

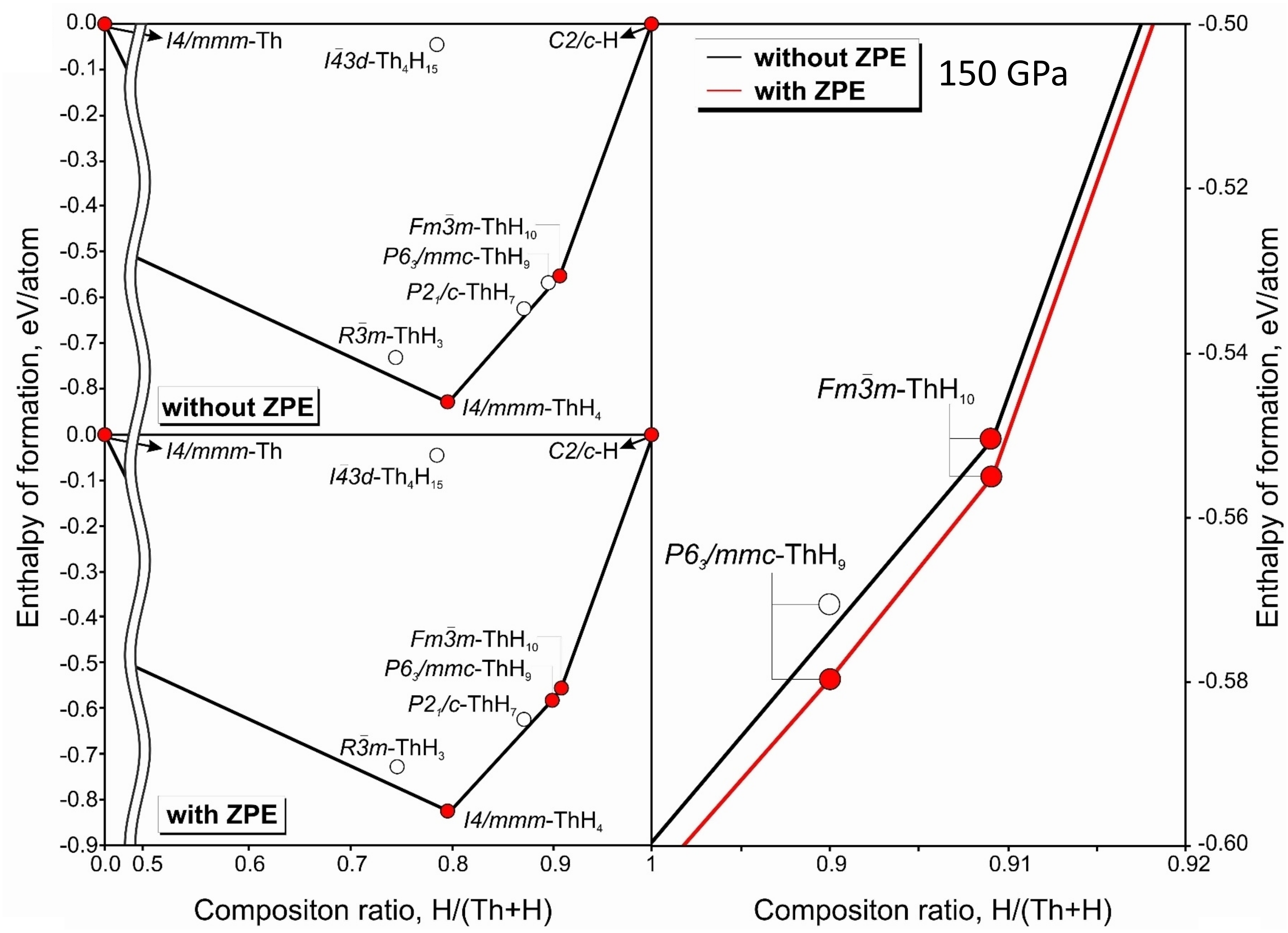


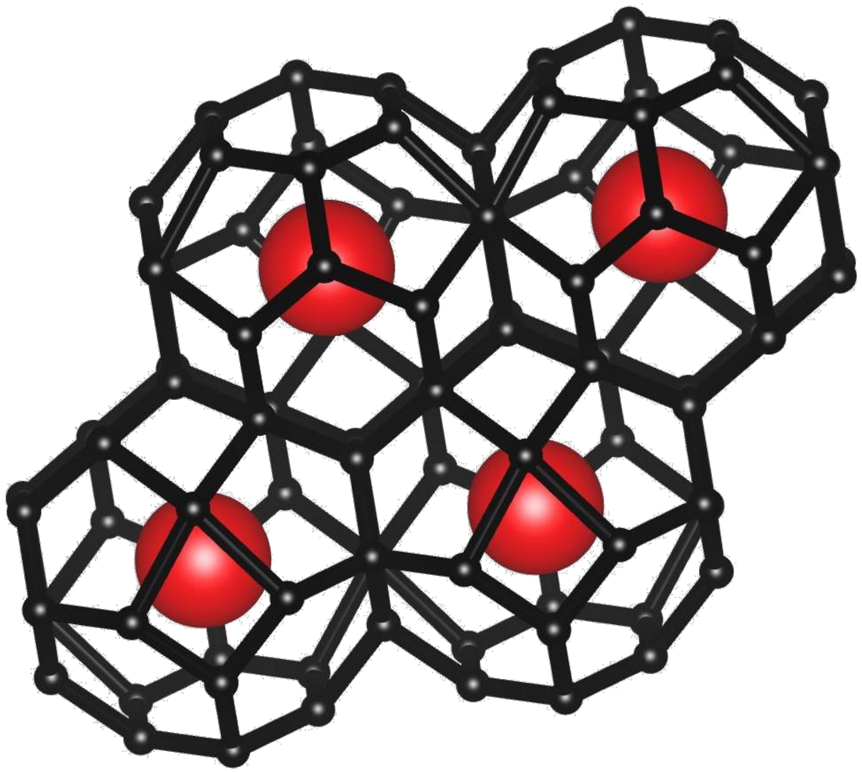


All predicted thorium hydrides were synthesized

D.V. Semenok, A.G. Kvashnin et al., Mat. Today, 33, 36-44 (2020)

METASTABLE ThH_9

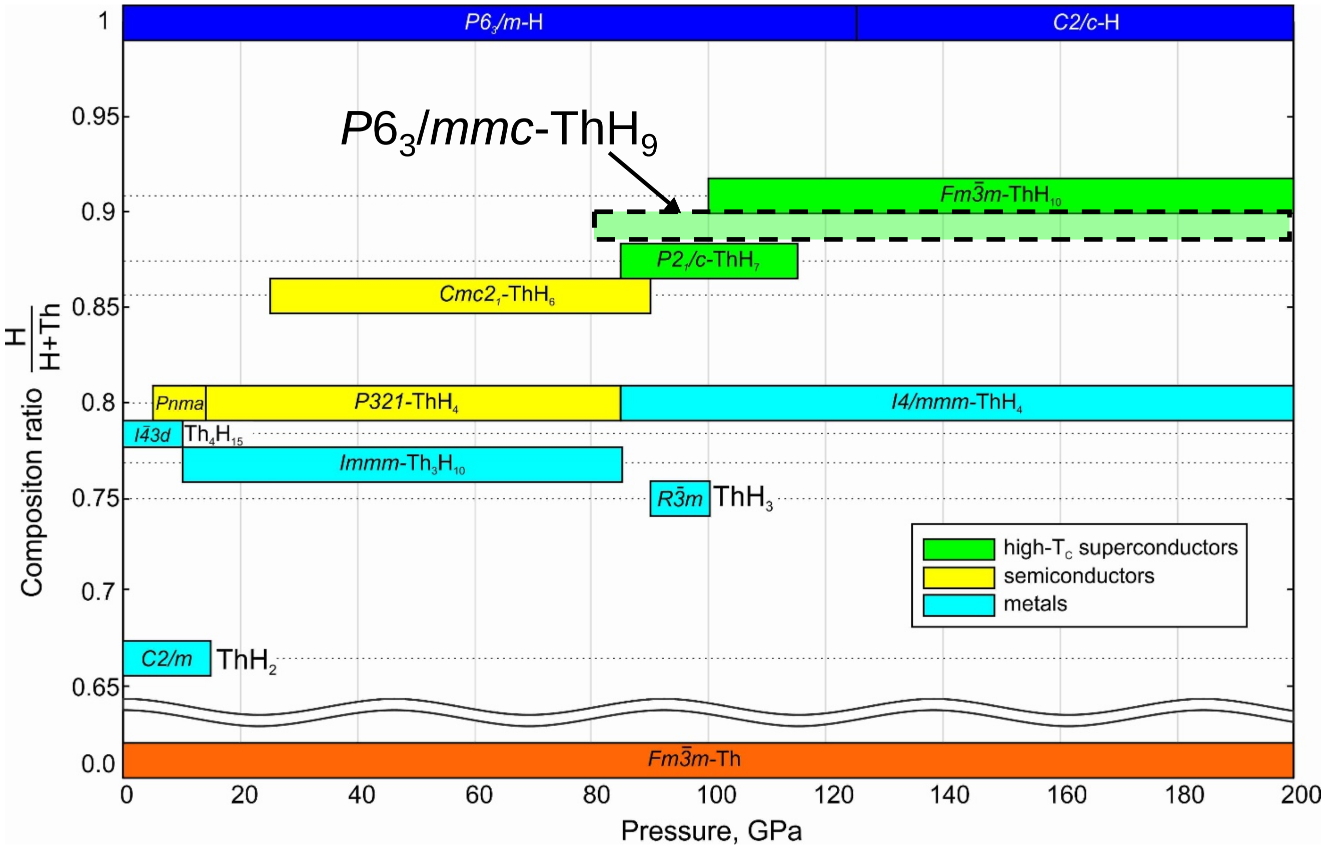


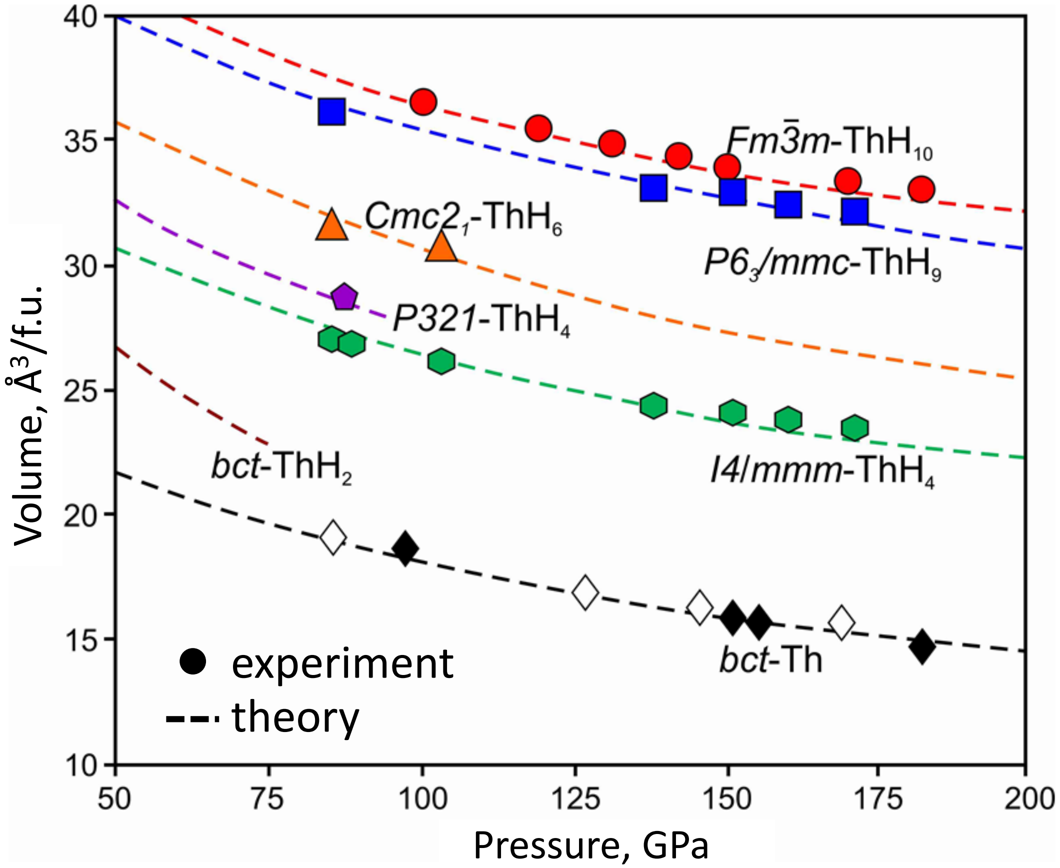


ZPE contribution leads to stabilization of ThH_9

D.V. Semenok, A.G. Kvashnin et al., Mat. Today, 33, 36-44 (2020)

Equations of states

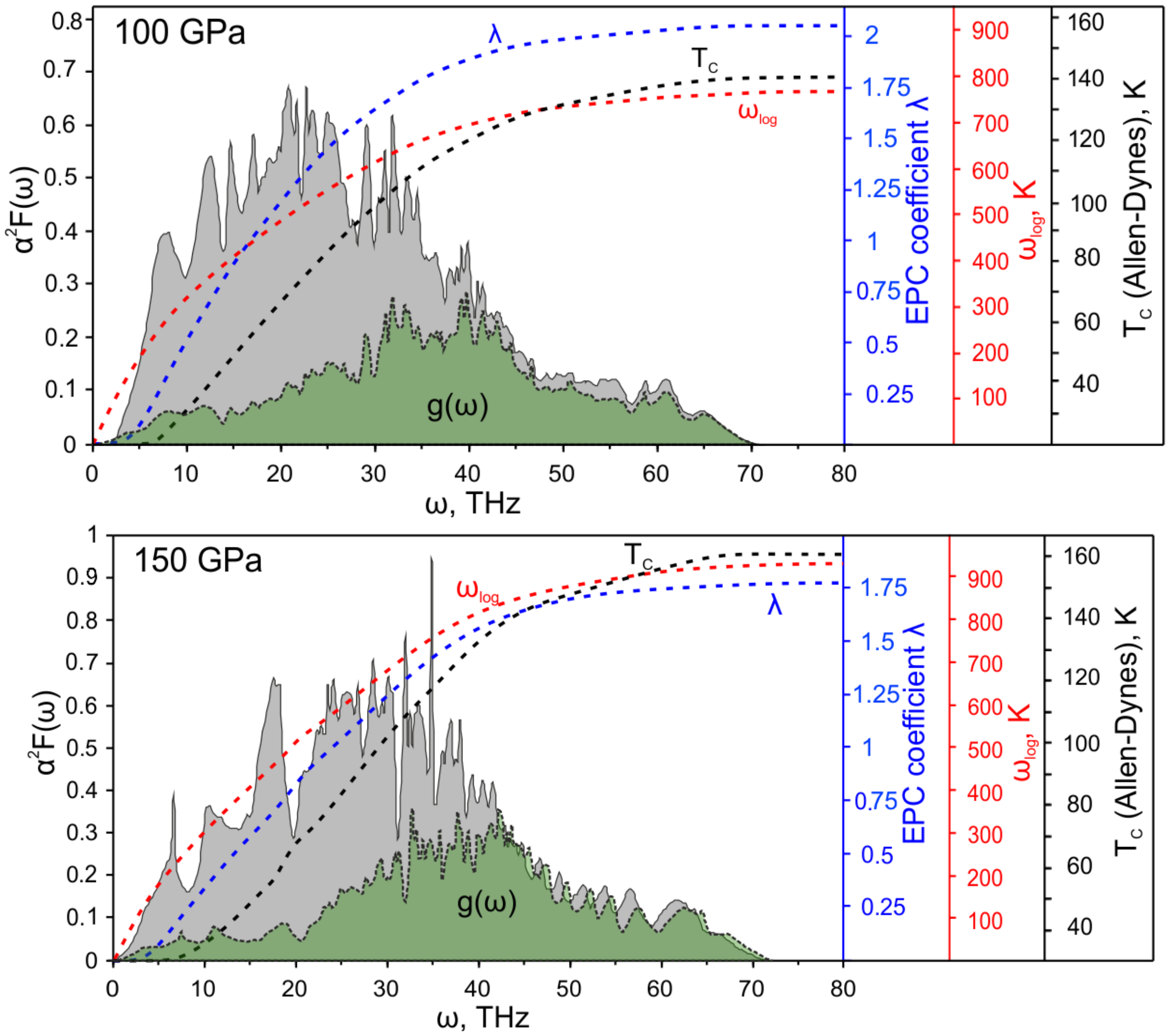




Based on experiments we show that ZPE contribution is crucial for description of the stability of higher metal hydrides under pressure

D.V. Semenok, A.G. Kvashnin et al., Mat. Today, 33, 36-44 (2020)

Superconductivity of ThH_9

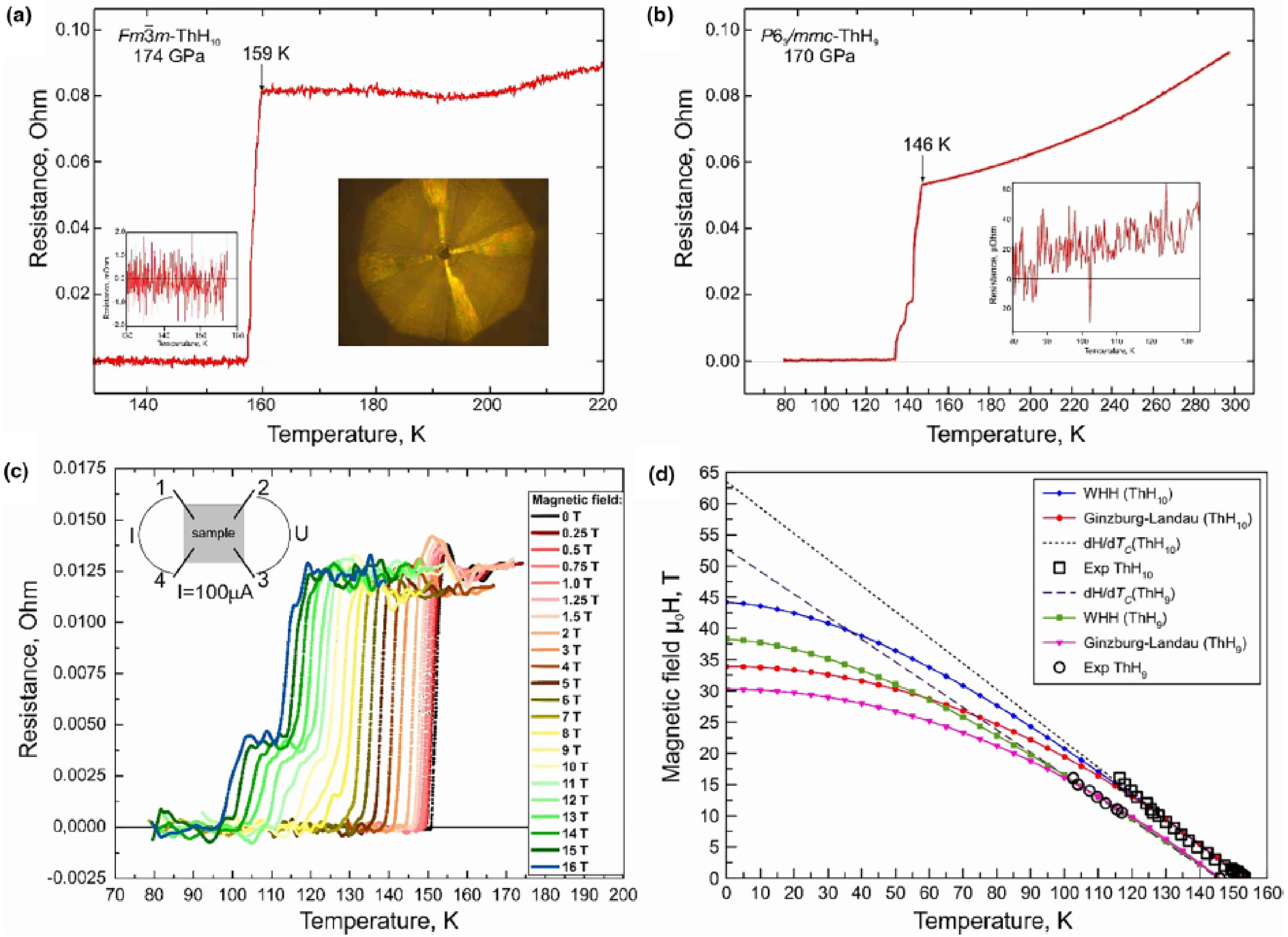


Parameter	$P6_3/mmc$-**ThH₉**	
	100 GPa	**150 GPa**
λ	2.15	1.73
ω_{log}, K	728	957
β	0.47–0.48	0.47–0.48
T_C (A–D), K	118–138	123–145
T_C ($P6_3/mmc$-ThD_9), K	85–99	89–104
$\Delta(0)$, meV	31.2–35.2	29.6–33.9
$\mu_0 H_C(0)$, T	37–41	33–37
$\Delta C/T_C$, mJ/mol·K^2	25.8	19.3–19.9
γ, mJ/mol·K^2	8.69	7.52
$R_\Delta = 2\Delta(0)/k_B T_C$	5.11–5.24	4.74–4.89

ThH_9 – new high-T_C superconductor
λ = 2.15, T_C = 138 K (100 GPa)
λ = 1.73, T_C = 145 K (150 GPa)

D.V. Semenok, A.G. Kvashnin et al., Mat. Today, 33, 36-44 (2020)

Experiments on ThH_9 and ThH_{10}



Performed experiments confirmed the superconducting properties of new ThH_{10} and ThH_9.

ThH_{10}: T_C = 159 K at 174 GPa
ThH_9: T_C = 146 K at 170 GPa

ФЕДЕРАЛЬНОЕ ГОСУДАРСТВЕННОЕ БЮДЖЕТНОЕ УЧРЕЖДЕНИЕ НАУКИ
Физический институт имени П.Н.Лебедева Российской академии наук
Ф И А Н

ИК РАН

D.V. Semenok, A.G. Kvashnin et al., Mat. Today, 33, 36-44 (2020)

Synthesis+T_C

Theory T_C

Synthesis

H_3S (203 K @ 150 GPa)
Nature 525, 73 (2014)

H_3P (100 K @ 200 GPa)
arXiv:1508.06224

YH_{10} (326 K @ 250 GPa)
PNAS 114, 6990 (2017)

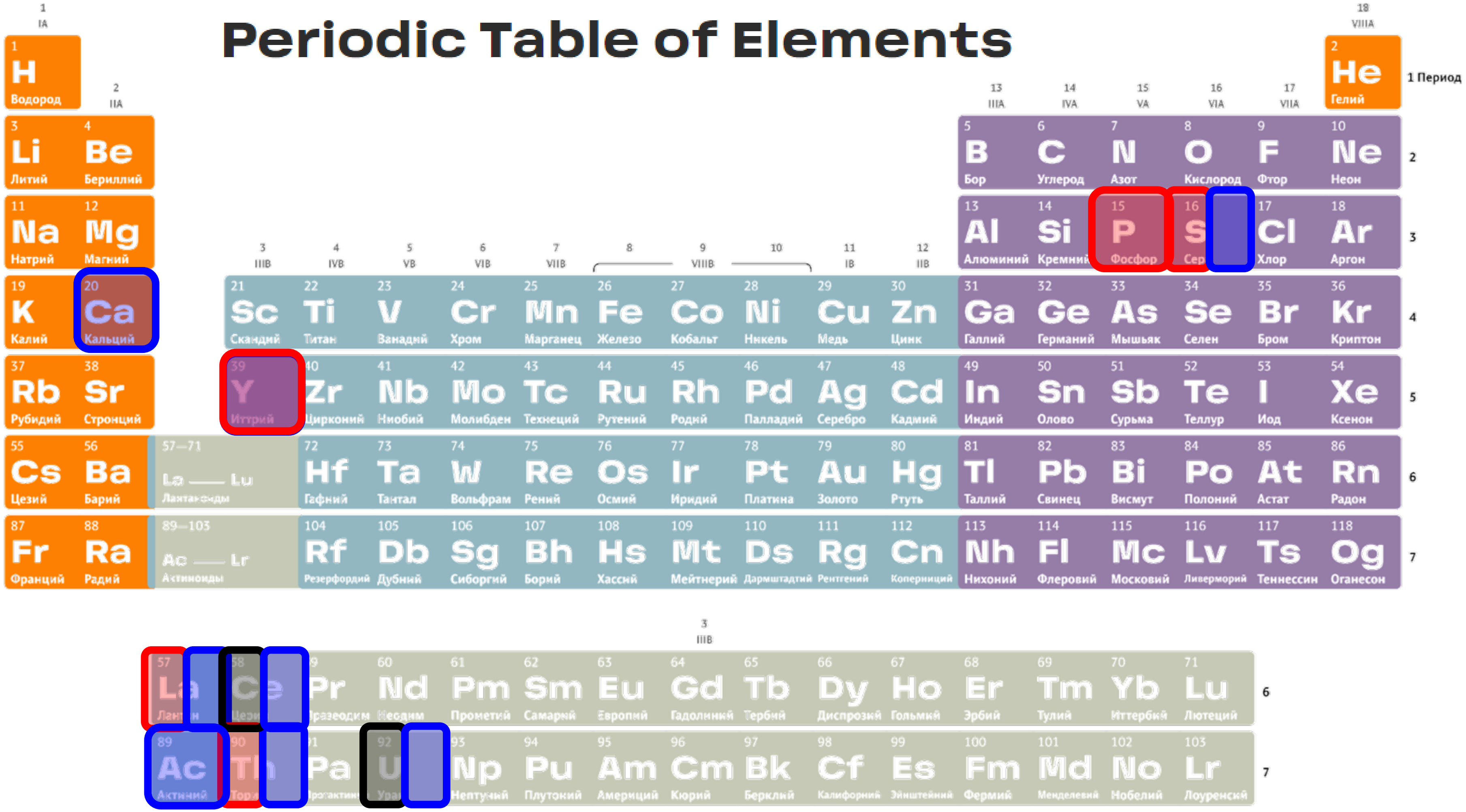
LaH_{10} (260 K @ 190 GPa)
PNAS 114, 6990 (2017)

CaH_6 (235 K @ 150 GPa)
PNAS 109, 6463 (2012)

YH_9 (243 K @ 201 GPa)
arXiv:1909.10482

ThH_{10} (159 K @ 174 GPa)
Mat. Today 33, 36-44 (2020)

CeH_9 (117 K @ 200 GPa)
Nat. Comm. 10, 4453 (2019)
Nat. Comm. 10, 3461 (2019)

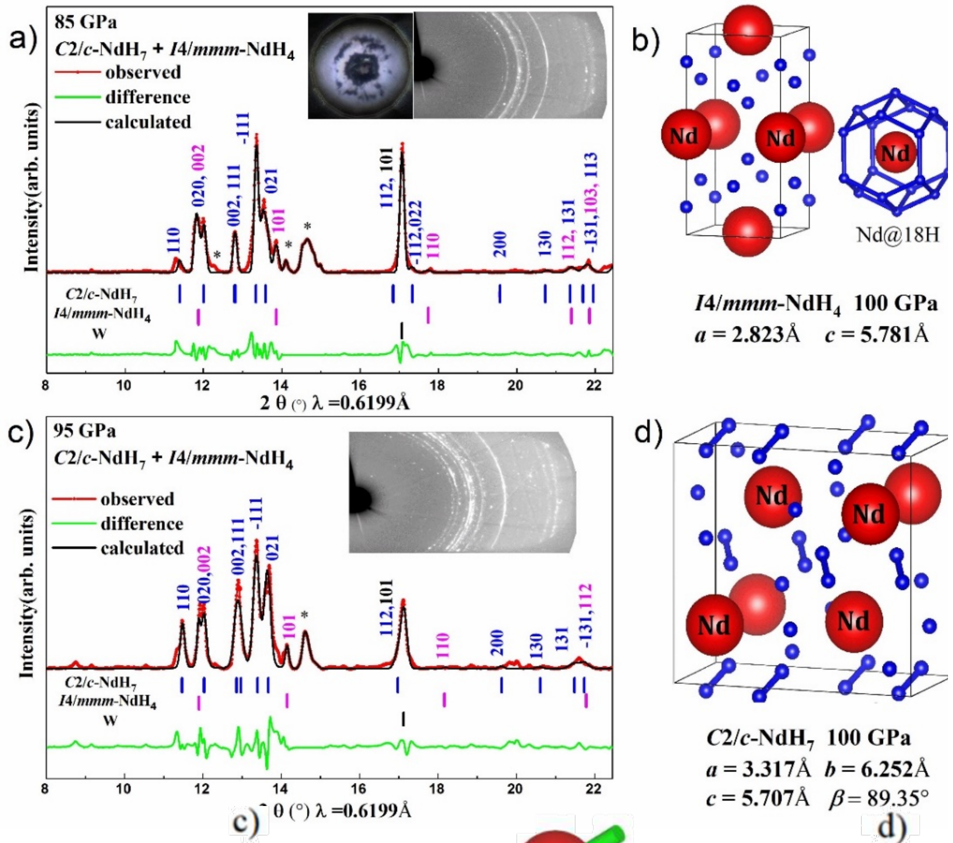


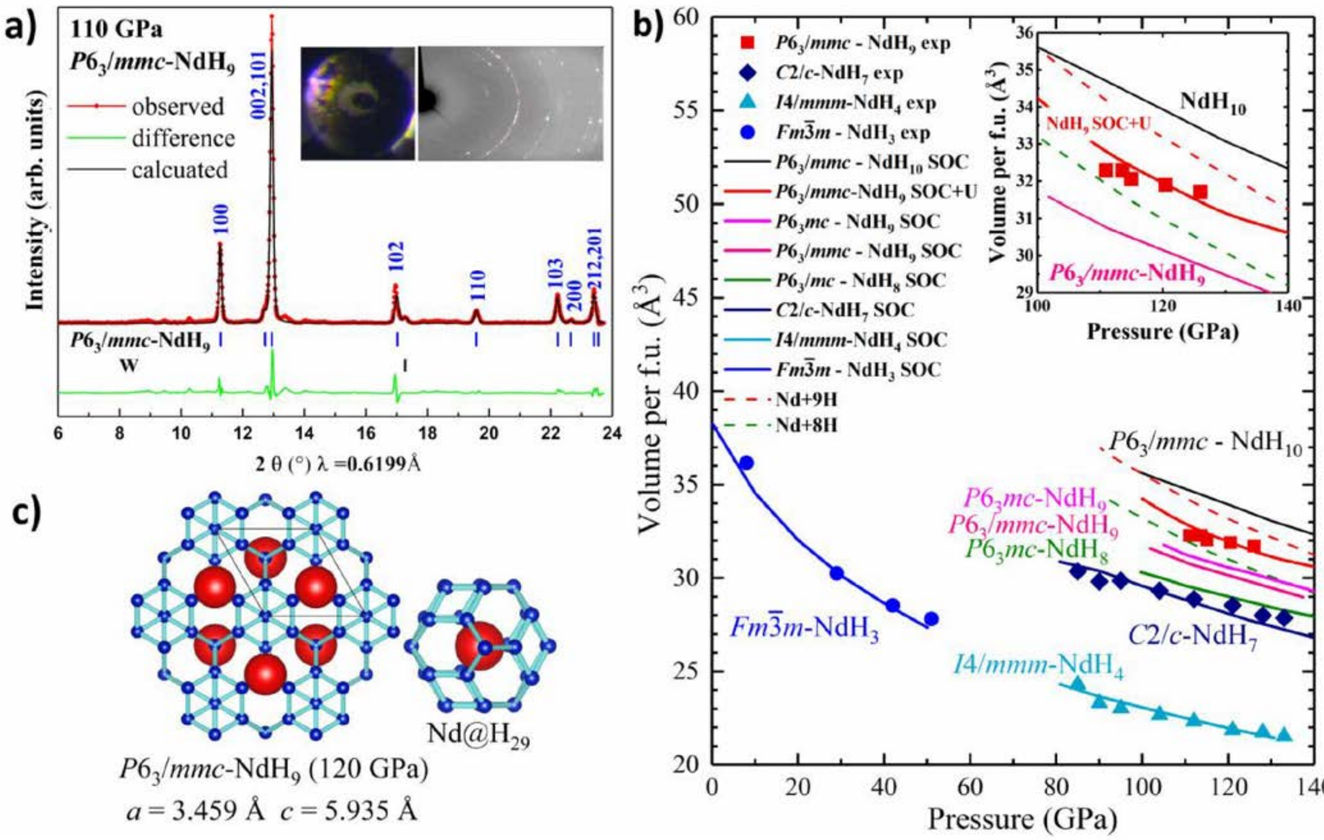
UH_7 (55 K @ 20 GPa)
Sci. Adv. 4, 10, eaat9776 (2018)
Phys. Rev. B 102, 014107 (2020)

AcH_{16} (200 K @ 150 GPa)
J. Phys. Chem. Lett., 8, 1920 (2018)

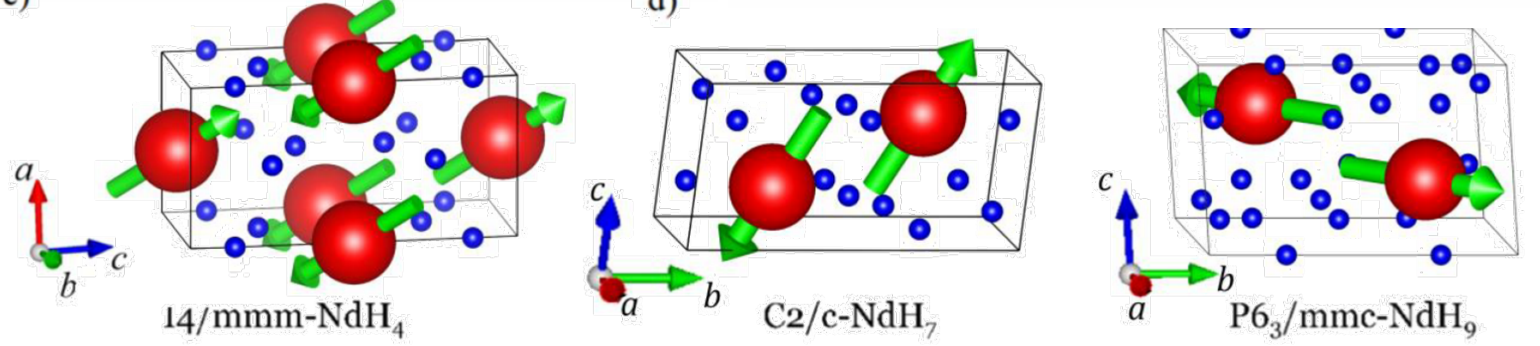
It is necessary to provide additional theoretical studies of SC-hydrides

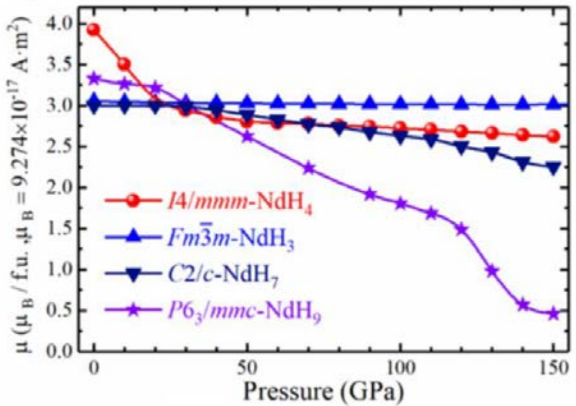
Magnetic hydrides NdH_9 and NdH_7





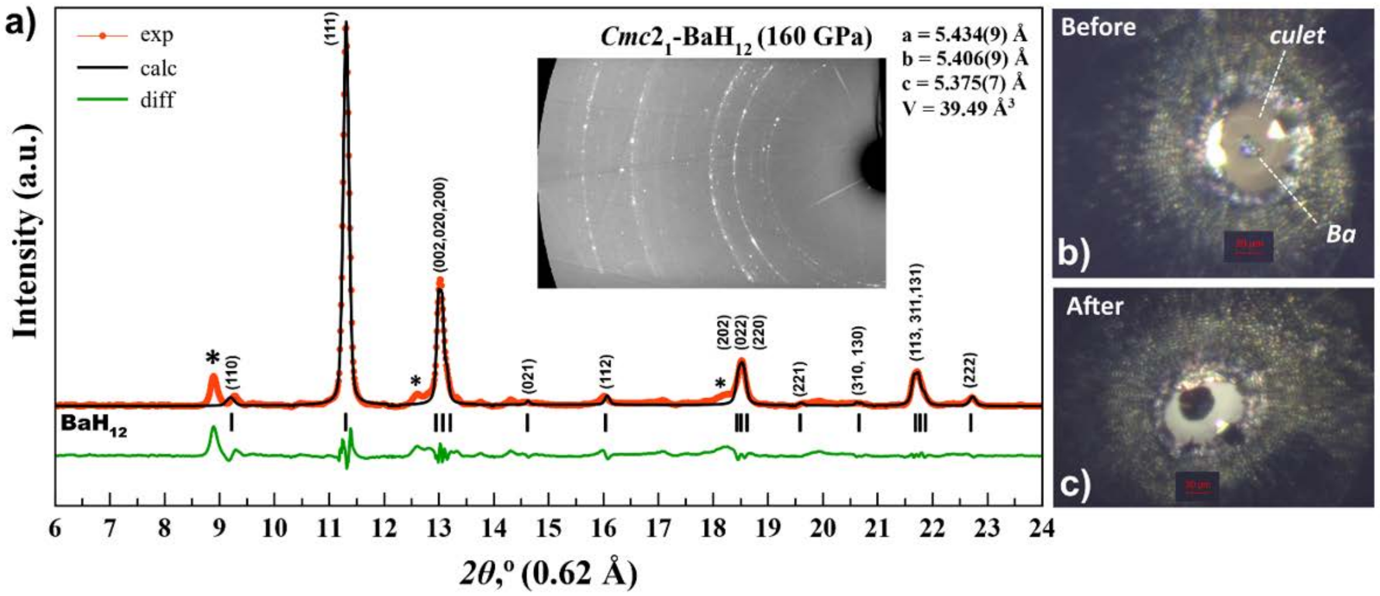
AFM

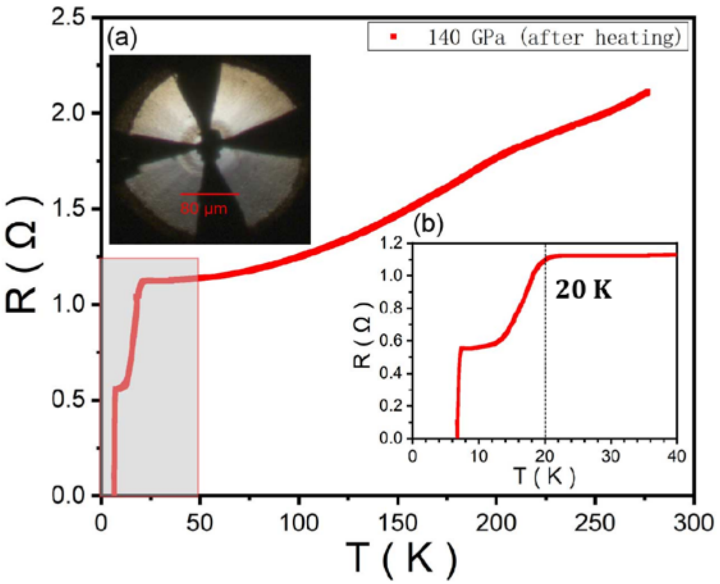


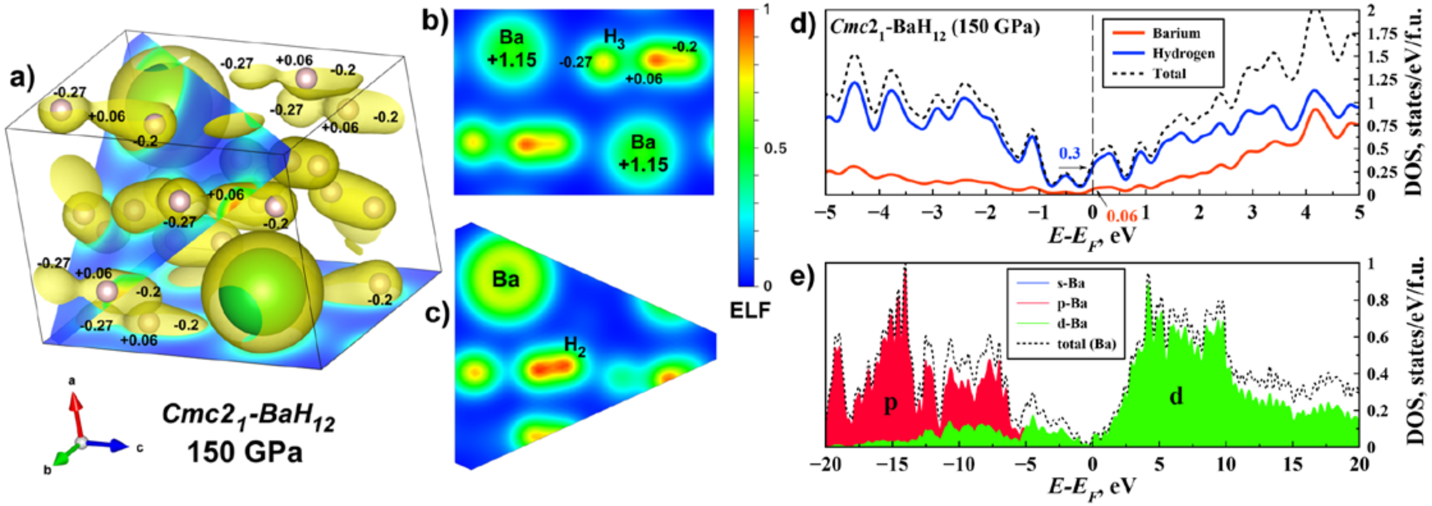


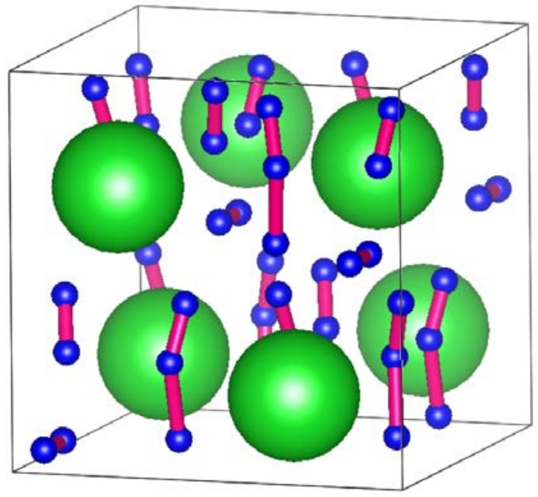
D. Zhou, D.V. Semenok, ..., A.G. Kvashnin et al., JACS, 142, 2803 (2020)

Molecular metal: pseudocubic BaH_{12}









BaH_{12} (H_2, H_3^- groups)

W. Chen, D.V. Semenok, A.G. Kvashnin et al., Nat. Comm. (2020)

What is next?

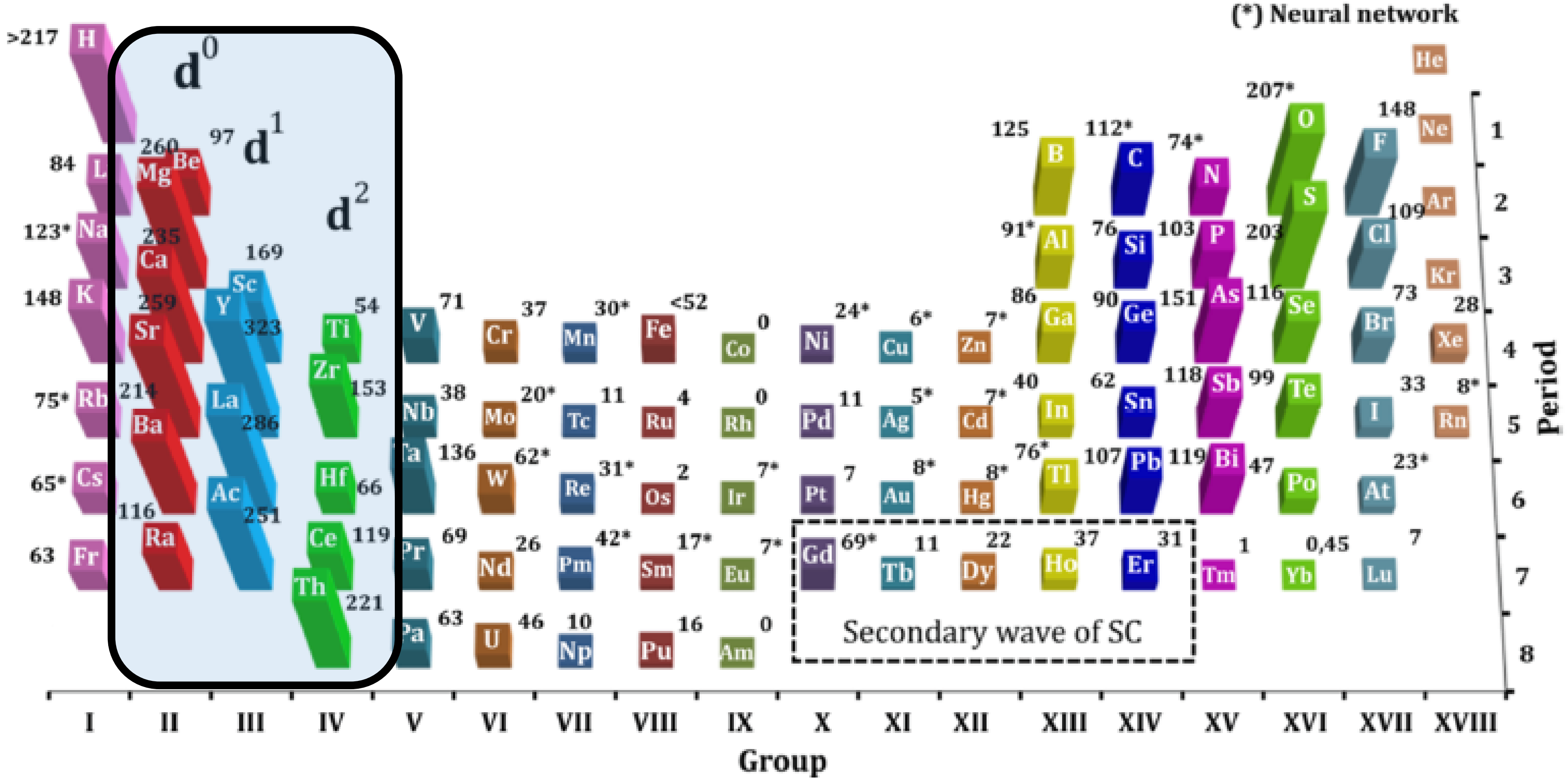
Do we need to test hydride systems one by one?

NOT NECESSARY

OR maybe we can predict T_c for all possible hydrides of all elements from Periodic Table?

YES

Distribution of **binary** high-T_c hydrides



DFT calculations, statistical analysis and neural network show that record high-TC hydrides are located in the d^0, d^1 and d^2 regions of elements Sc-Y-La-Ac (d^1-belt), Mg-Ca-Sr-Ba-Ra (d^0-belt), and Th (s^2d^2)

D.V. Semenok, …, A.G. Kvashnin et al., Curr. Opin. Solid State Mater. Sci. 100808 (2020)

What is next?

Search for more complex compounds

Ternary hydrides (Dmitrii Semenok, November 13, 12:30)

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