Workshop on Crystal Structure Prediction: Exploring the Mendeleev Table as a Palette to Design New Materials

Computational search for supermaterials with optimal properties

Alexander Kvashnin

Skoltech
Skolkovo Institute of Science and Technology

16.01.2019, Trieste

USPEX Computational Materials Discovery

Outline

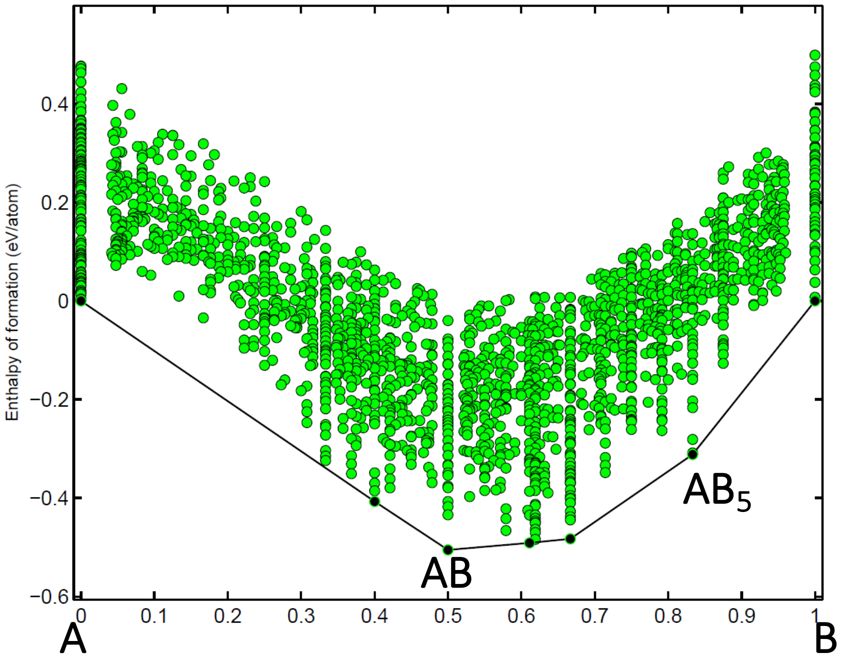
Superhard

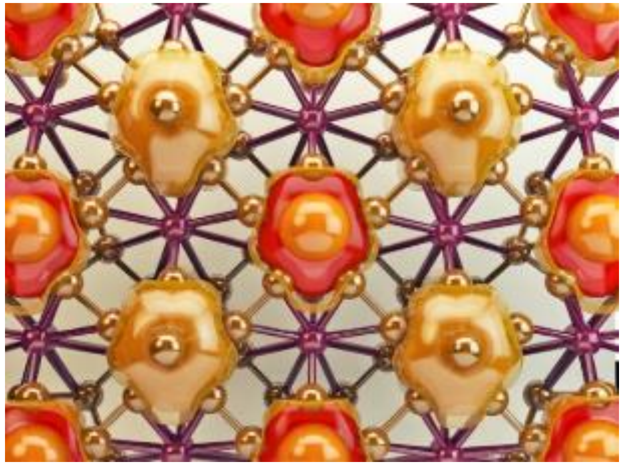
- Introduction + Motivation
- New tungsten boride theory + synthesis

Superconducting

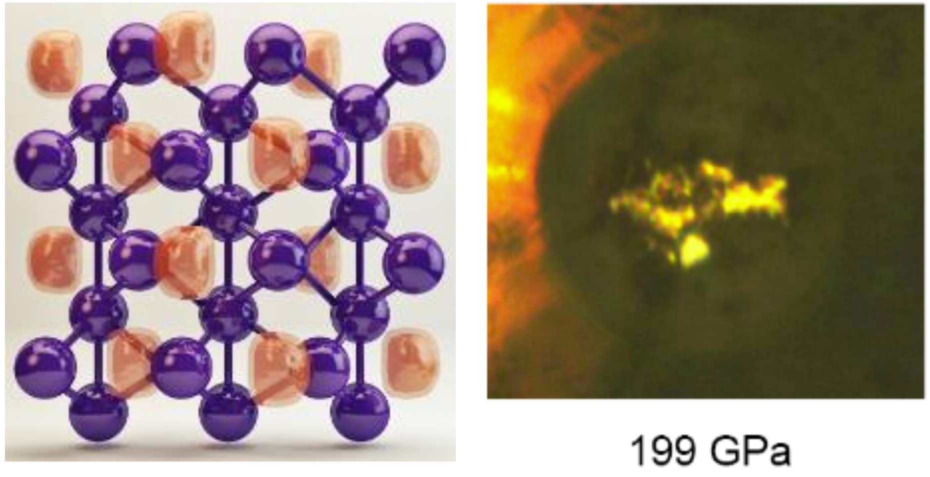
- Introduction + Motivation
- Metal hydrides
- U-H, theory + synthesis
- Ac-H
- Th-H, theory + synthesis

What is USPEX?

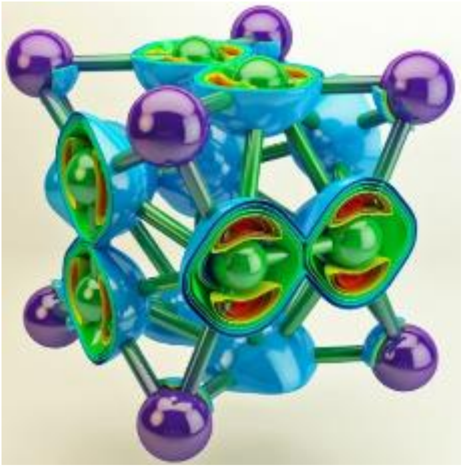




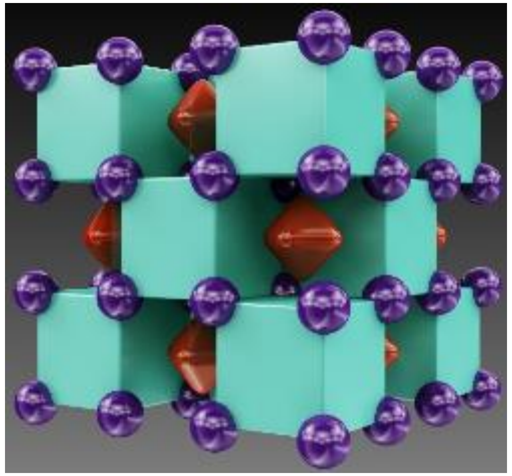
New superhard boron phase
(Oganov et al., *Nature*, 2009)



Transparent sodium allotrope
(Ma, Eremets, Oganov, *Nature*, 2009)



Unexpected sodium chlorides
(Zhang, Oganov, et al., Science, 2013)



New chemistry of helium
(Dong, Oganov, Goncharov,
Nat. Chem. 2017)

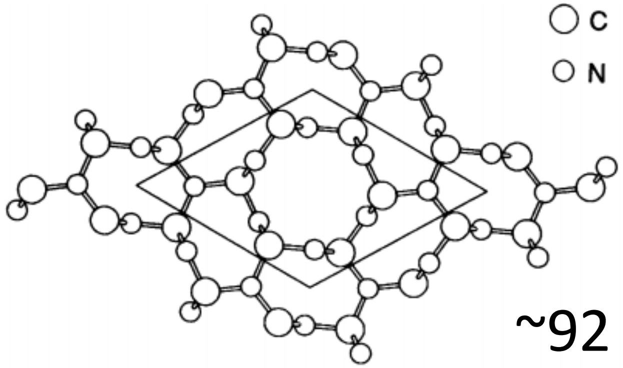
New XX Material

Superhard materials

Introduction

Diamond

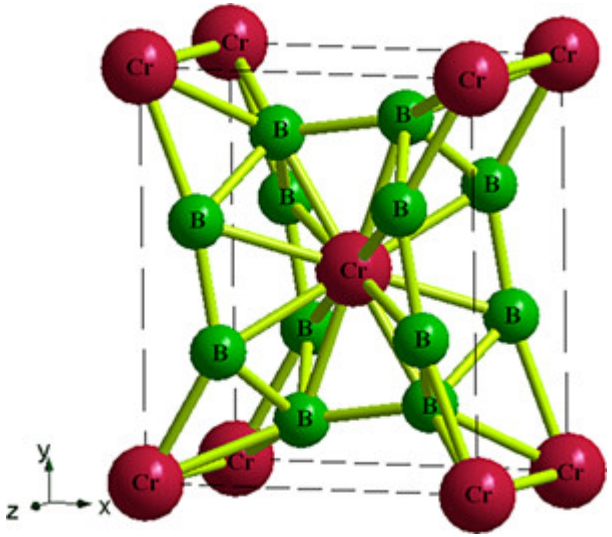
~98 GPa



~92 GPa

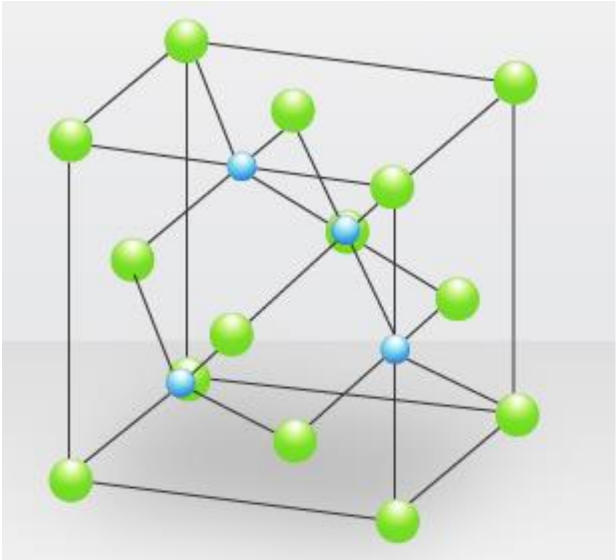
Science 245, 841 (1989)

Transition metal borides and carbides

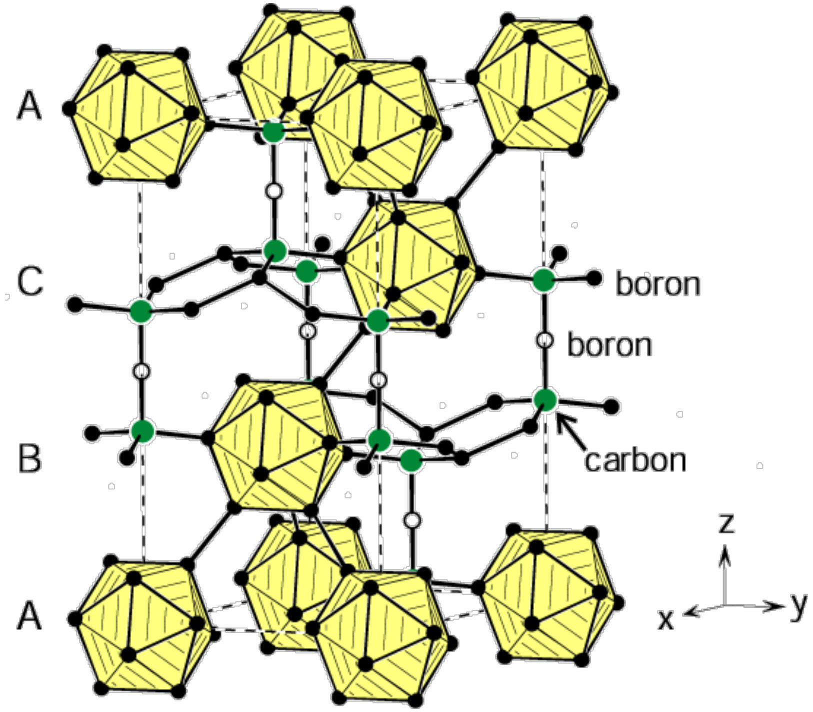


Phys. Chem. Chem. Phys., 2016,18, 2361

~50 GPa



c-BN ~60 GPa

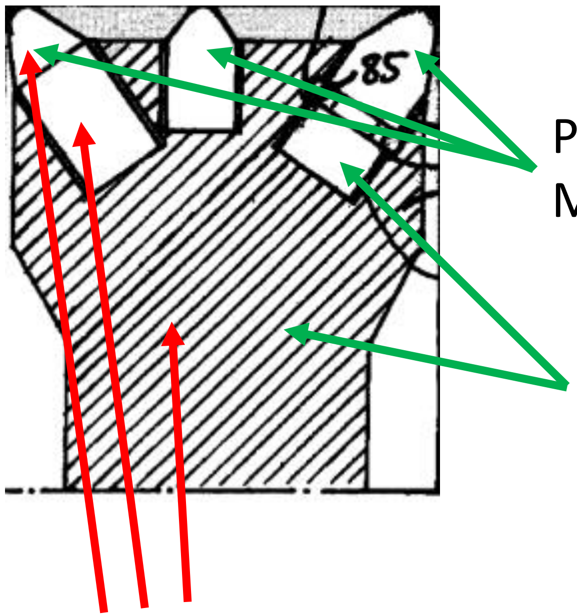


B_4C ~32 GPa

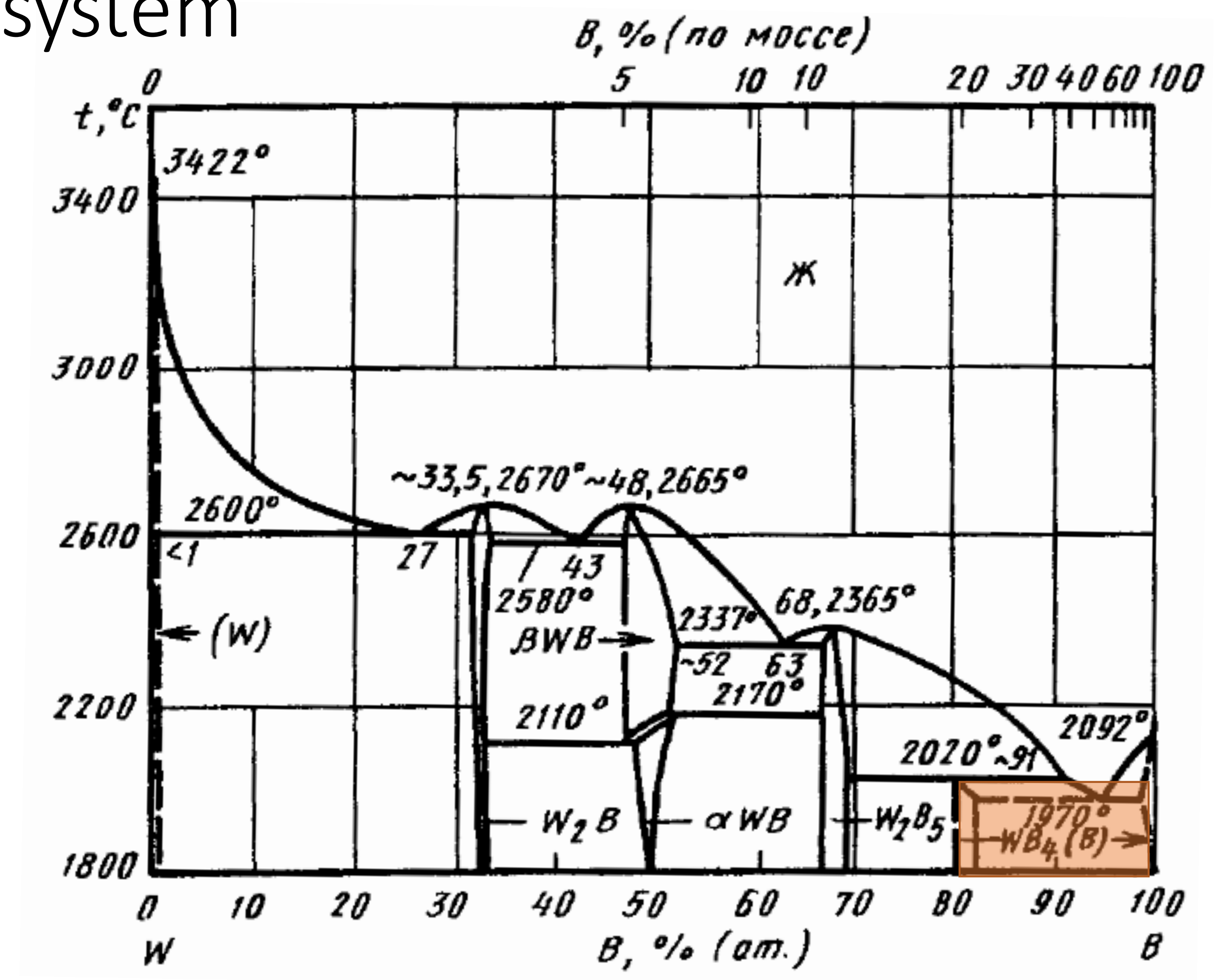
Why it is important?

- Ease in synthesis and production
- These materials have high melting temperature
- High hardness allows them to be used in many other different fields of technology

Possible applications:
- Manufacturing industry
- Mining industry

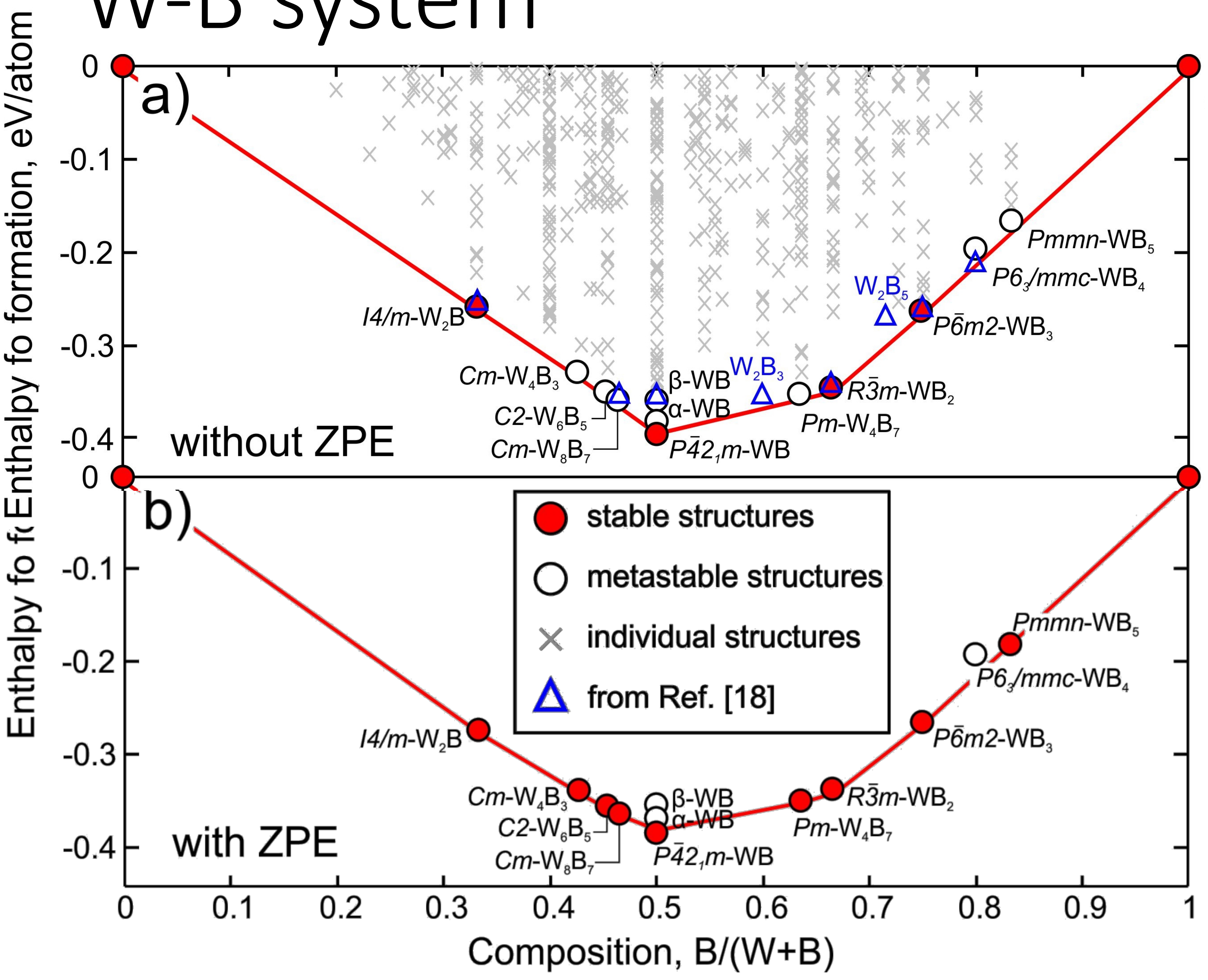


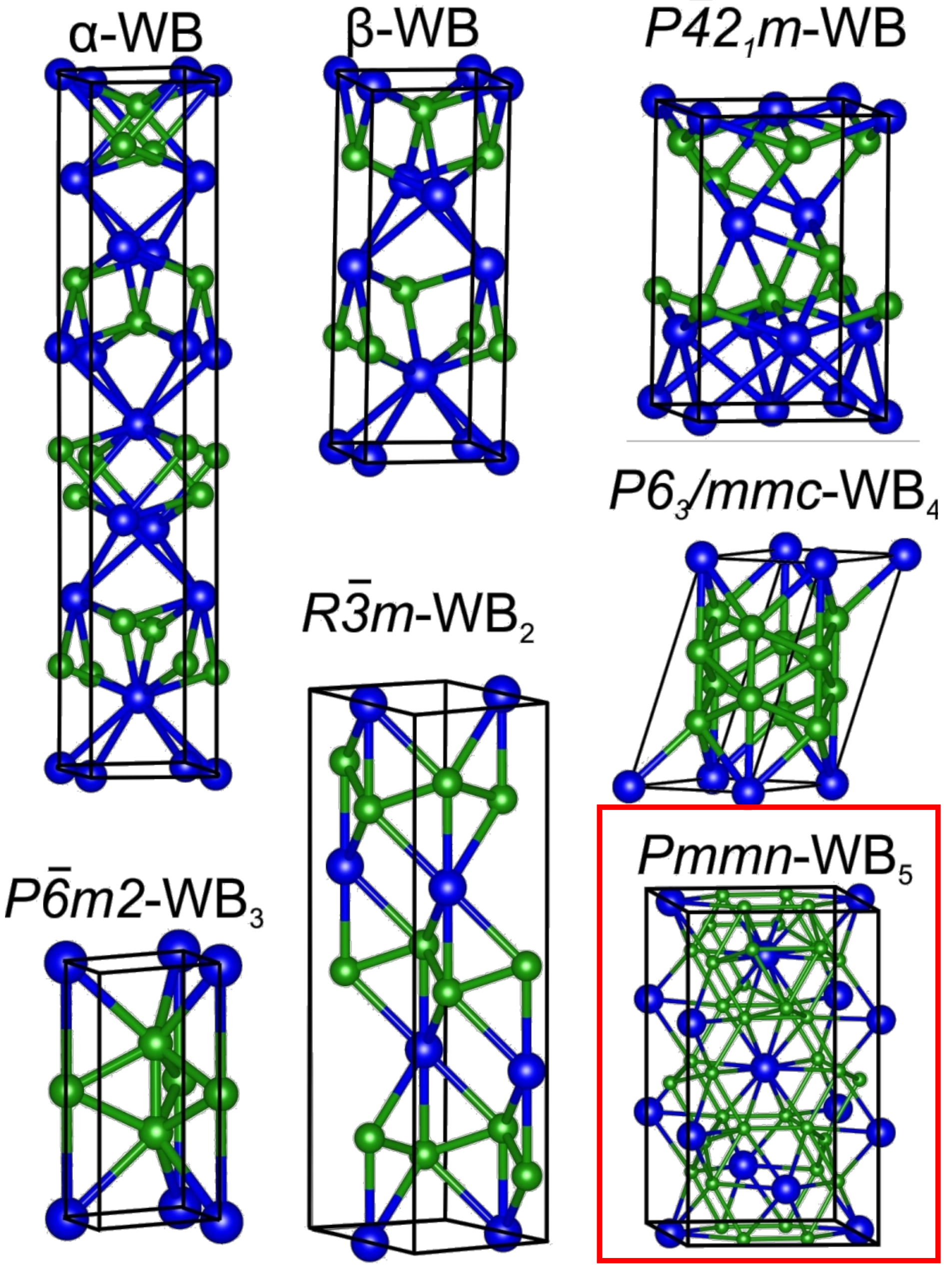
W-B system



B, % (по моссе)
0
5
10 10
20 30 40 60 100
t, °C
3422°
3400
3000
2600
2200
1800
Ж
~33,5, 2670° ~48, 2665°
2600°
<1
27
43
2580°
(W)
βWB
2337°
68, 2365°
~52 63
2170°
2110°
2092°
2020° ~91
1970°
W2B
αWB
W2B5
WB4 (B)
0 10 20 30 40 50 60 70 80 90 100
W
B, % (ат.)
B

W-B system

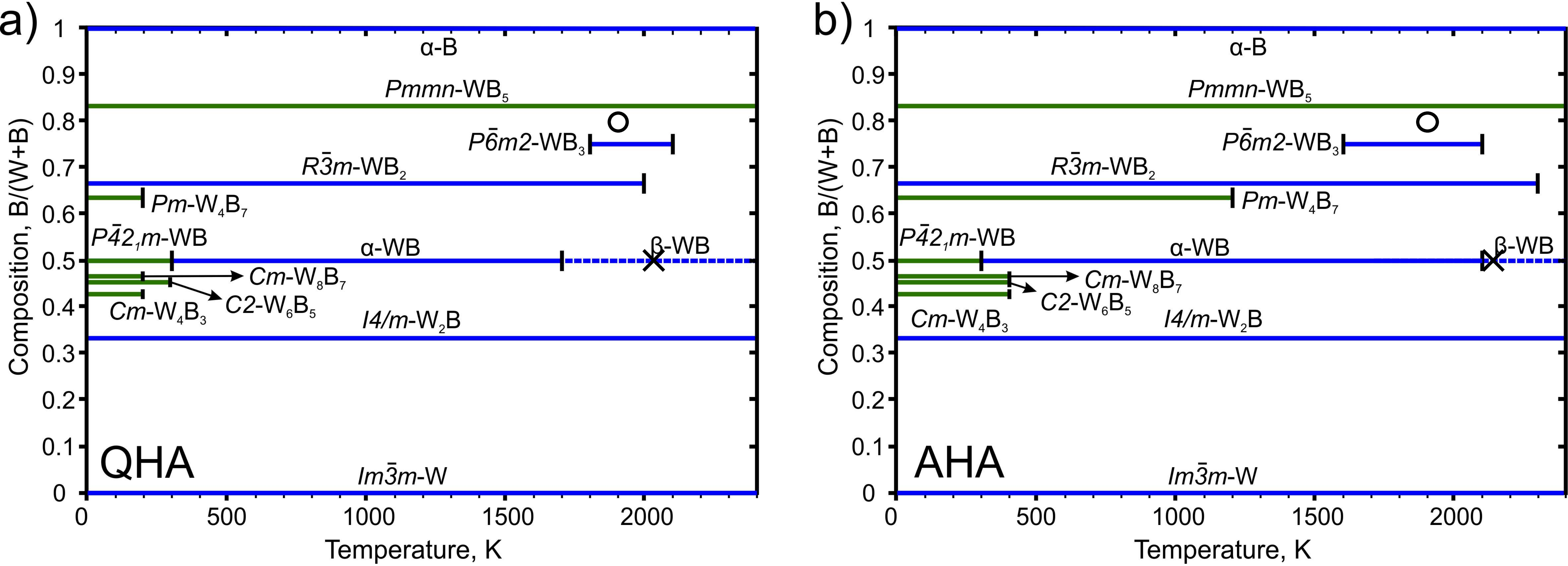




Vickers hardness of WB_5 is 45 GPa

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

Temperature stability

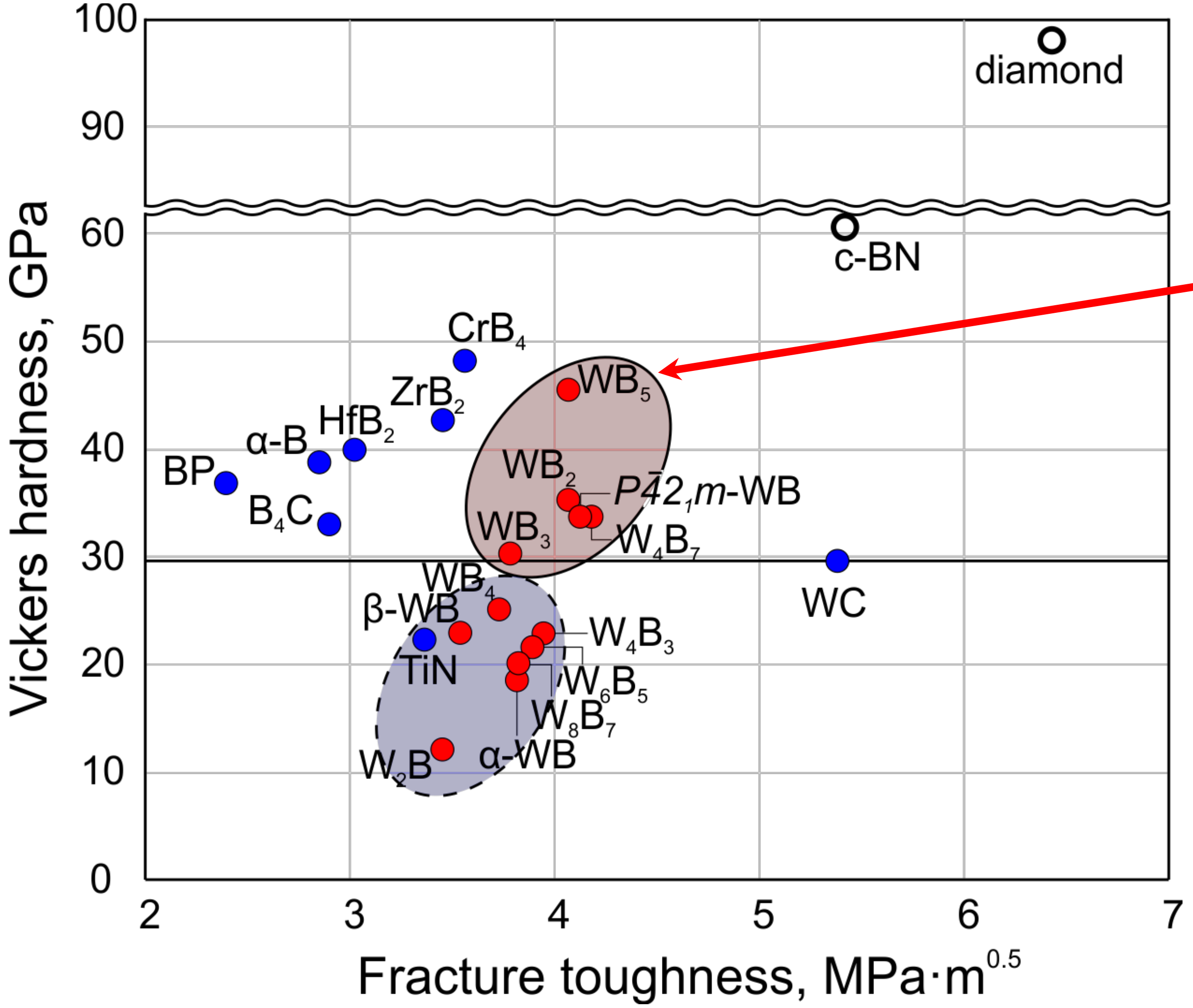


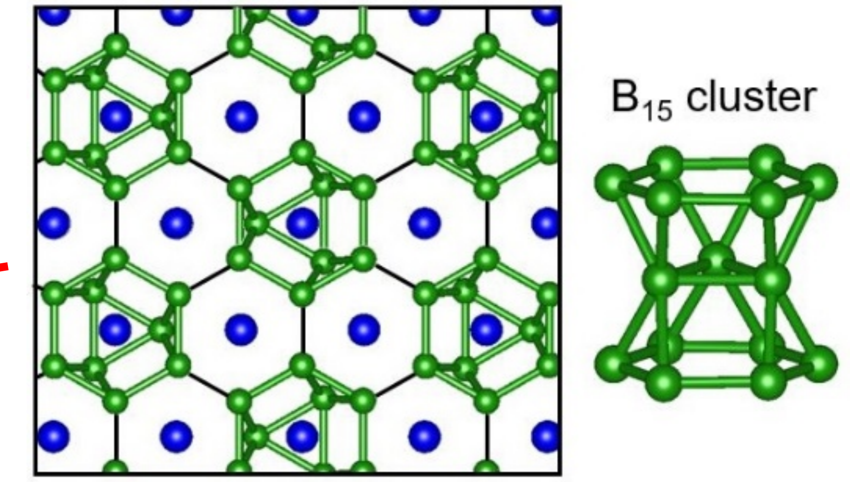
[x] J. Phase Equilibria 1995, 16 (2), 150–161

[o] Sov. Powder Metall. Met. Ceram. 1974, 13 (1), 1–3

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

Hardness vs Fracture toughness



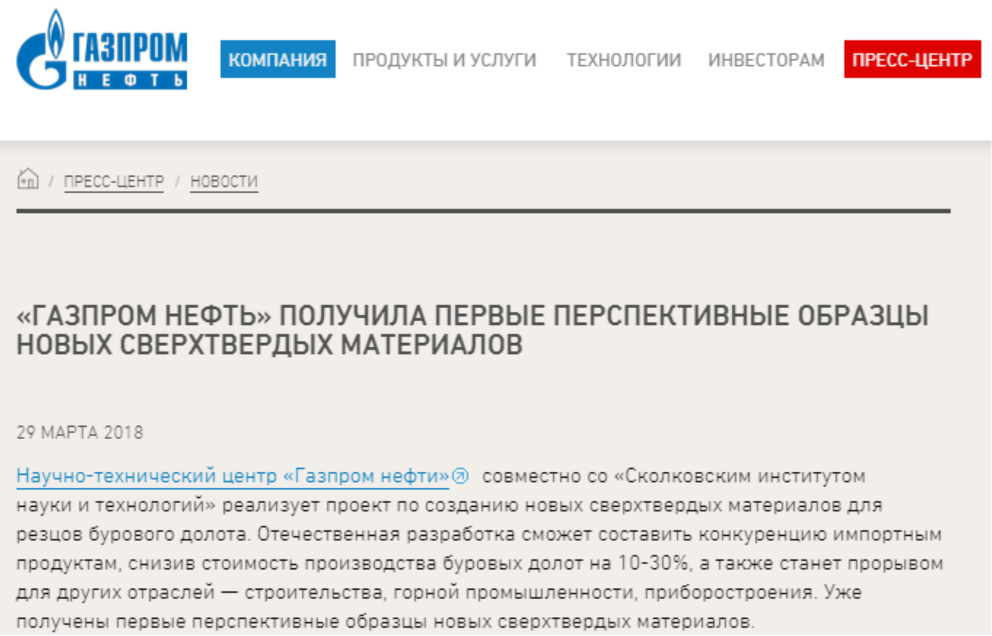


Ashby plot may show the material with optimal combination of Vickers hardness and fracture toughness.

WB_5 is new optimal material

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

Hardness vs Fracture toughness


ГАЗПРОМ НЕФТЬ
КОМПАНИЯ ПРОДУКТЫ И УСЛУГИ ТЕХНОЛОГИИ ИНВЕСТОРАМ ПРЕСС-ЦЕНТР

/ ПРЕСС-ЦЕНТР / НОВОСТИ

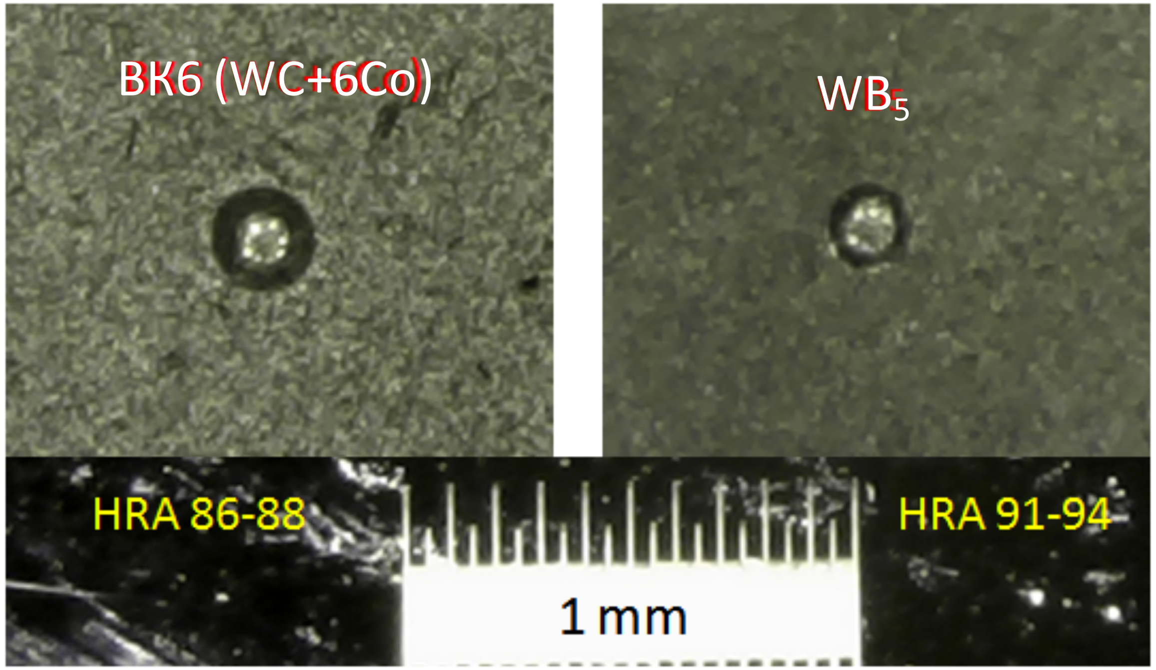
«ГАЗПРОМ НЕФТЬ» ПОЛУЧИЛА ПЕРВЫЕ ПЕРСПЕКТИВНЫЕ ОБРАЗЦЫ НОВЫХ СВЕРХТВЕРДЫХ МАТЕРИАЛОВ

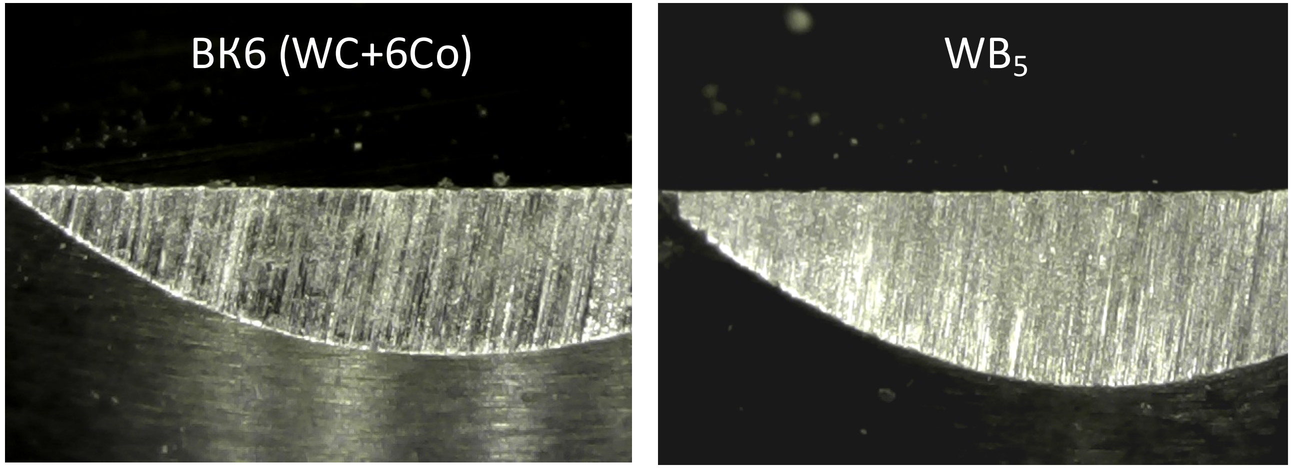
29 МАРТА 2018

Научно-технический центр «Газпром нефти» совместно со «Сколковским институтом науки и технологий» реализует проект по созданию новых сверхтвердых материалов для резцов бурового долота. Отечественная разработка сможет составить конкуренцию импортным продуктам, снизив стоимость производства буровых долот на 10-30%, а также станет прорывом для других отраслей — строительства, горной промышленности, приборостроения. Уже получены первые перспективные образцы новых сверхтвердых материалов.

Samples of new superhard material

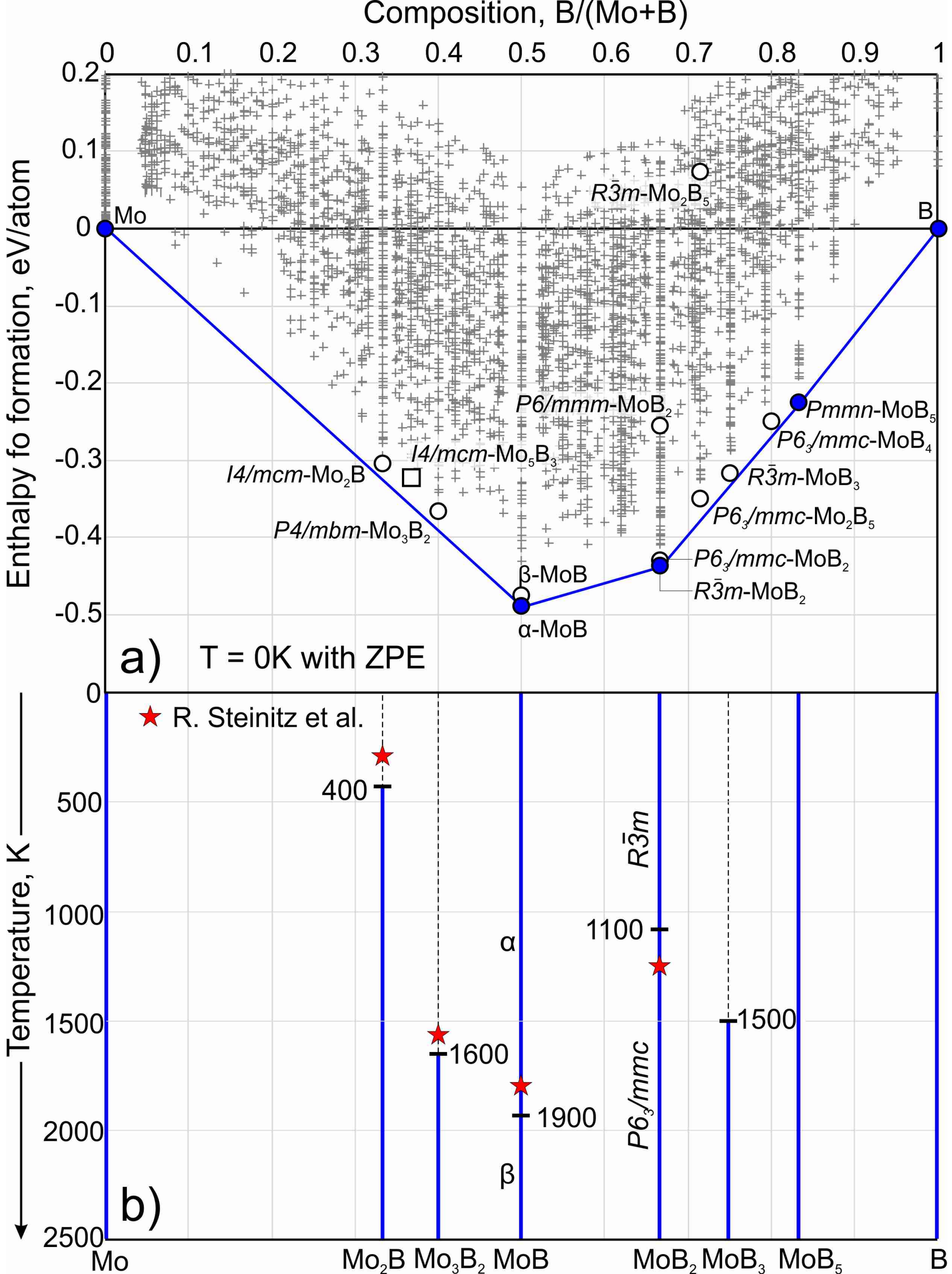
Measurements of hardness and fracture toughness



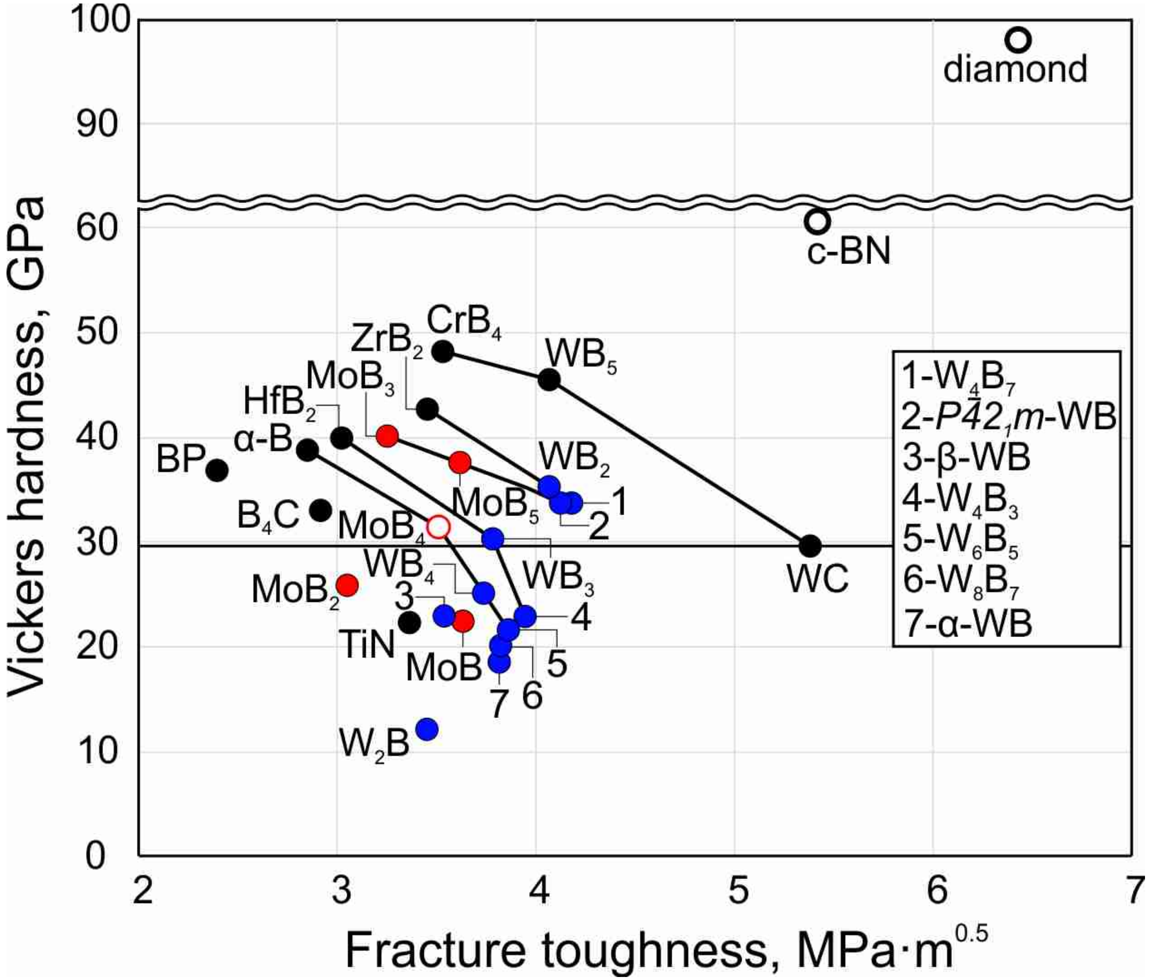


A.G. Kvashnin, et al., Mat. & Design, In prep.

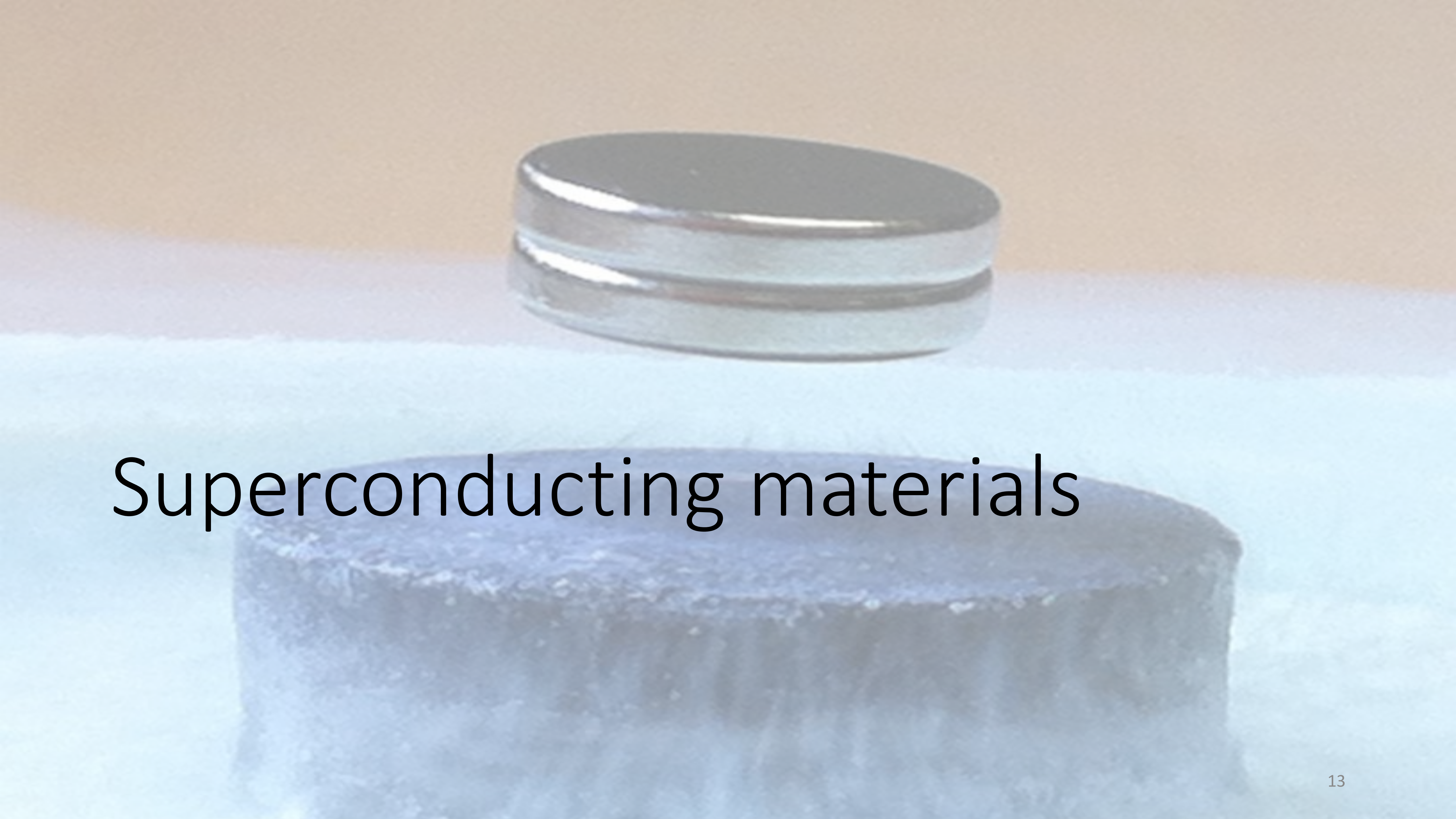
Mo-B system



- New MoB_5 is stable in the entire temperature range
- MoB_4 is metastable.
- MoB_5 has lower hardness compared to WB_5

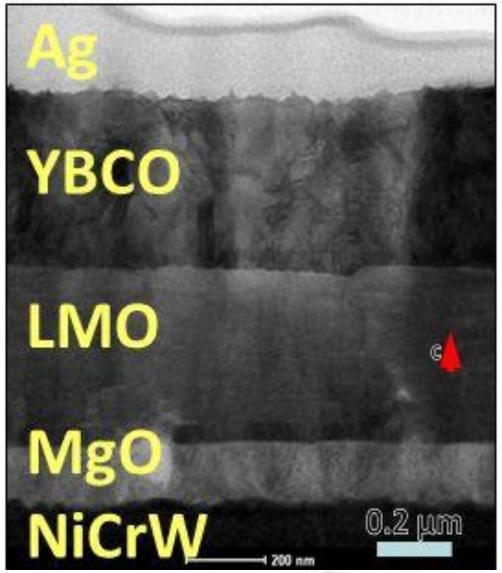


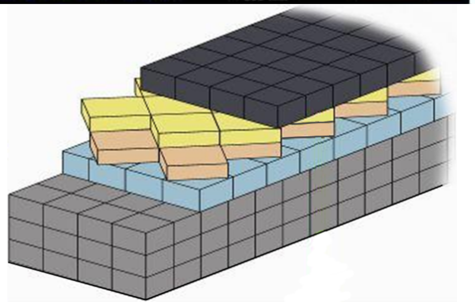
A.G. Kvashnin, et al., Submitted 2018

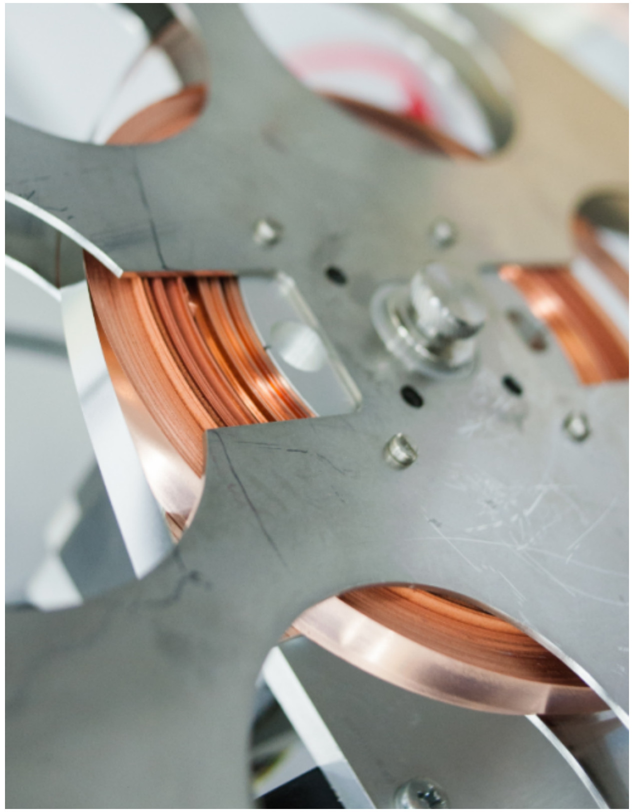


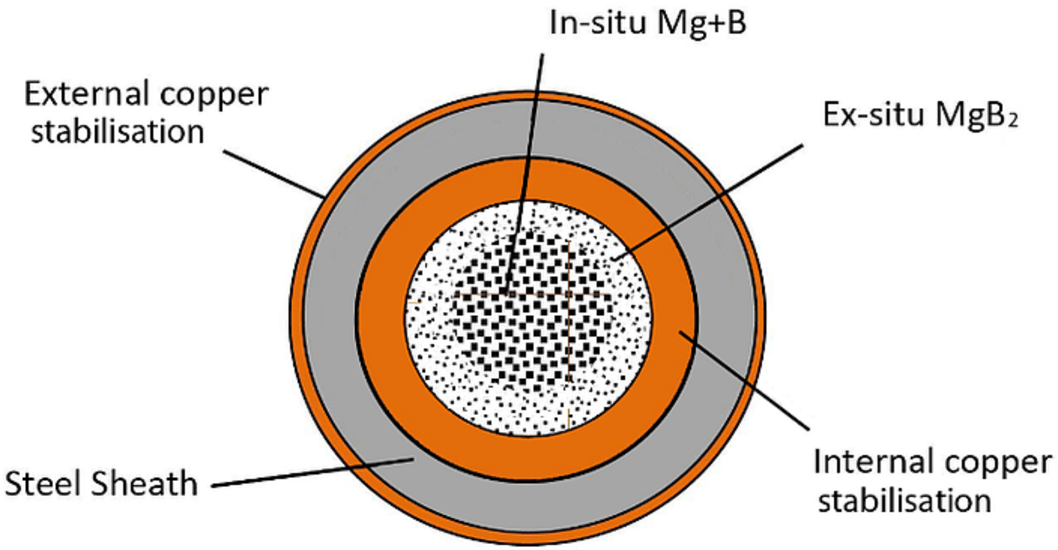
Superconducting materials

Introduction + Motivation





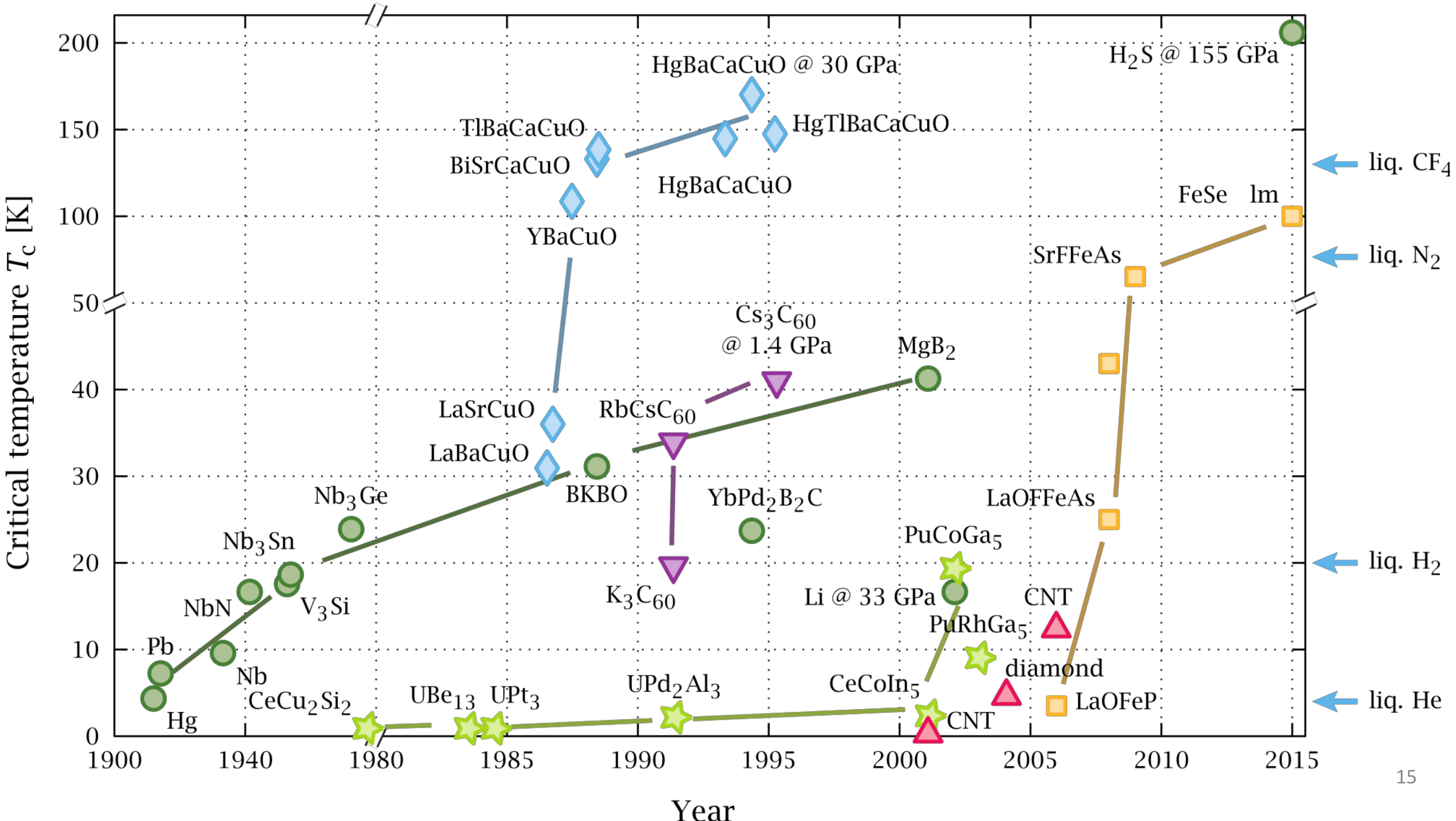




HTSC-2 ribbon based on the multilayered composite YBCO or BSCCO.
Tc = 90-110 K, j(crit) = 500 A/mm^2 at 77 K,
H(crit) = 20T at 4 K

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

Introduction + Motivation



OPEN

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

SUBJECT AREAS:

THEORY AND COMPUTATION

CONDENSED MATTER PHYSICS

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]

[1]State Key Laboratory of Superhard Materials, College of physics, Jilin University, Changchun, 130012, P. R. China, [2]State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun, 130012, P. R. China.

Received 7 July 2014

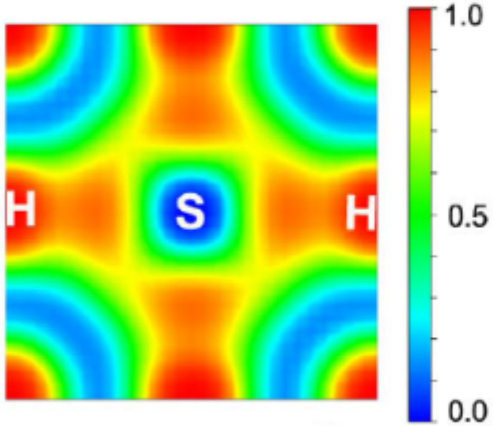
Accepted 29 September 2014

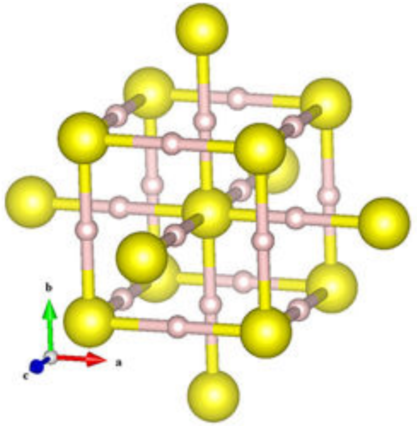
Published 10 November 2014

Correspondence and requests for materials should be addressed to T.C. (cuitian@jlu.edu.cn)

The high pressure structures, metallization, and superconductivity of recently synthesized H_2-containing compounds $(H_2S)_2H_2$ are elucidated by *ab initio* calculations. The ordered crystal structure with *P*1 symmetry is determined, supported by the good agreement between theoretical and experimental X-ray diffraction data, equation of states, and Raman spectra. The *Cccm* structure is favorable with partial hydrogen bond symmetrization above 37 GPa. Upon further compression, H_2 molecules disappear and two intriguing metallic structures with *R*3m and *Im*-3*m* symmetries are reconstructive above 111 and 180 GPa, respectively. The predicted metallization pressure is 111 GPa, which is approximately one-third of the currently suggested metallization pressure of bulk molecular hydrogen. Application of the Allen-Dynes-modified McMillan equation for the *Im*-3*m* structure yields high T_c values of 191 K to 204 K at 200 GPa, which is among the highest values reported for H_2-rich van der Waals compounds and MH_3 type hydride thus far.

SCIENTIFIC REPORTS | 4 : 6968 | DOI: 10.1038/srep06968 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 (2015) | doi:10.1038/nature14964

Received 25 June 2015 | Accepted 22 July 2015 | Published online 17 August 2015

A superconductor is a material that can conduct electricity without resistance below a superconducting transition temperature, T_c. The highest T_c that has been achieved to date is in the copper oxide system[1]: 133 kelvin at ambient pressure[2] and 164 kelvin at high pressures[3]. As the nature of superconductivity in these materials is still not fully understood (they are not conventional superconductors), the prospects for achieving still higher transition temperatures by this route are not clear. In contrast, the Bardeen–Cooper–Schrieffer theory of conventional superconductivity gives a guide for achieving high T_c with no theoretical upper bound—all that is needed is a favourable combination of high-frequency phonons, strong electron–phonon coupling, and a high density of states[4]. These conditions can in principle be fulfilled for metallic hydrogen and covalent compounds dominated by hydrogen[5, 6], as hydrogen atoms provide the necessary high-frequency phonon modes as well as the strong electron–phonon coupling. Numerous calculations support this idea and have predicted transition temperatures in the range 50–235 kelvin for many hydrides[7], but only a moderate T_c of 17 kelvin has been observed experimentally[8]. Here we investigate sulfur hydride[9], where a T_c of 80 kelvin has been predicted[10]. We find that this system transforms to a metal at a pressure of approximately 90 gigapascals. On cooling, we see signatures of superconductivity: a sharp drop of the resistivity to zero and a decrease of the transition temperature with magnetic field, with magnetic susceptibility measurements confirming a T_c of 203 kelvin. Moreover, a pronounced isotope shift of T_c in sulfur deuteride is suggestive of an electron–phonon mechanism of superconductivity that is consistent with the Bardeen–Cooper–Schrieffer scenario. We argue that the phase responsible for high-T_c superconductivity in this system is likely to be H_3S, formed from H_2S by decomposition under pressure. These findings raise hope for the prospects for achieving room-temperature superconductivity in other hydrogen-based materials.

The highest Tc=135 K (Putilin, Antipov, 1993) was beaten: theoretical group (T.Cui, 2014) predicted new material H_3S with Tc~200 K. This was confirmed by the experiment (group of M. Eremets, 2015).

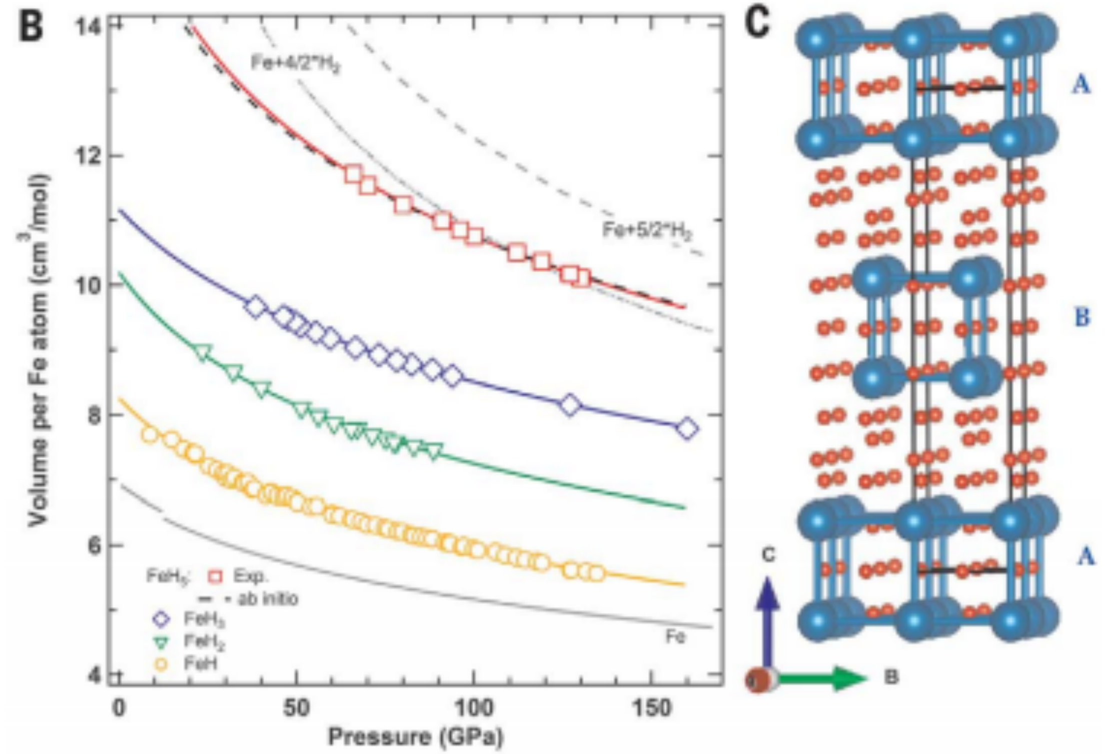
HIGH-PRESSURE PHYSICS

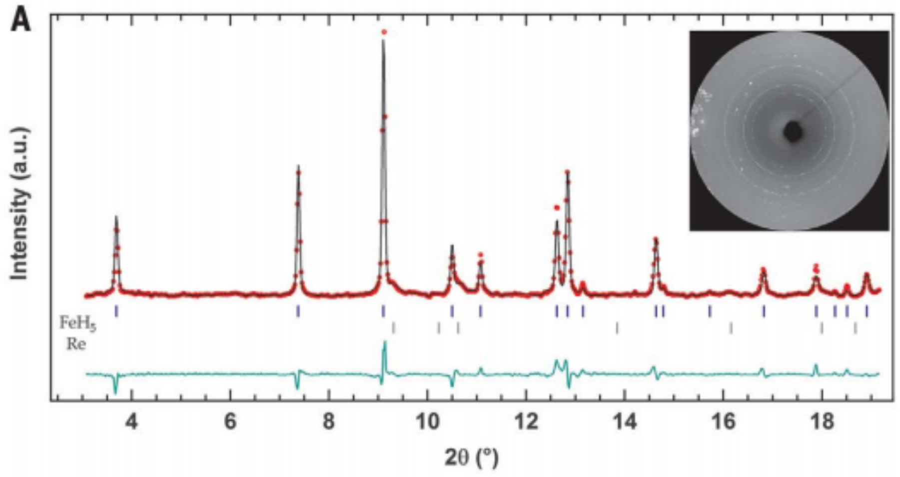
Synthesis of FeH_5: A layered structure with atomic hydrogen slabs

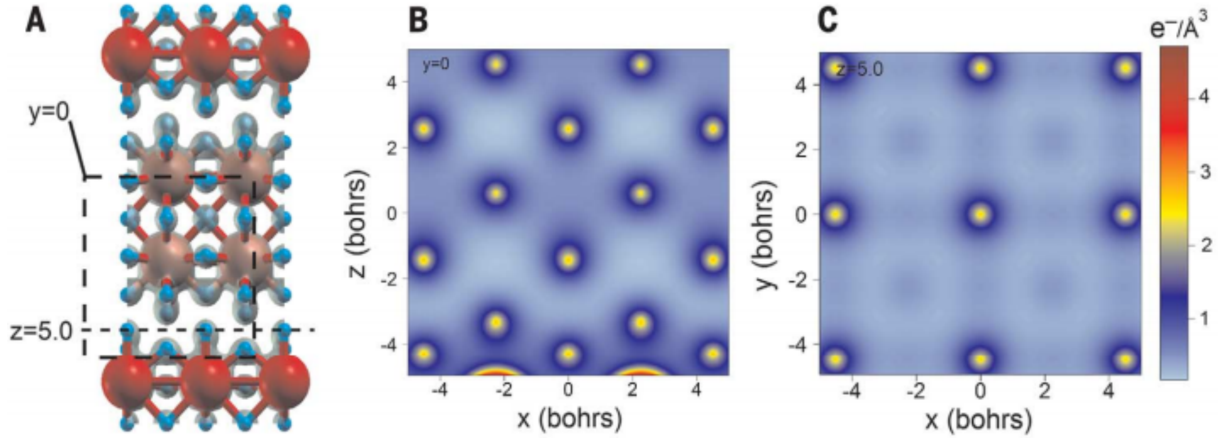
C. M. Pépin,[1,2]* G. Geneste,[1] A. Dewaele,[1] M. Mezouar,[3] P. Loubeyre[1]*

High pressure promotes the formation of polyhydrides with unusually high hydrogen-to-metal ratios. These polyhydrides have complex hydrogenic sublattices. We synthesized iron pentahydride (FeH_5) by a direct reaction between iron and H_2 above 130 gigapascals in a laser-heated diamond anvil cell. FeH_5 exhibits a structure built of atomic hydrogen only. It consists of intercalated layers of quasicubic FeH_3 units and four-plane slabs of thin atomic hydrogen. The distribution of the valence electron density indicates a bonding between hydrogen and iron atoms but none between hydrogen atoms, presenting a two-dimensional metallic character. The discovery of FeH_5 suggests a low-pressure path to make materials that approach bulk dense atomic hydrogen.

Pépin *et al.*, *Science* **357**, 382–385 (2017)



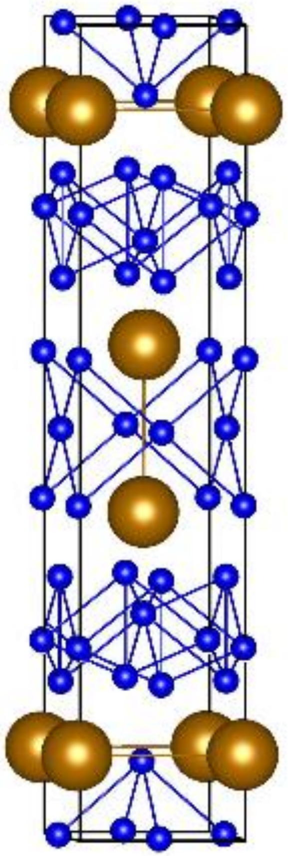




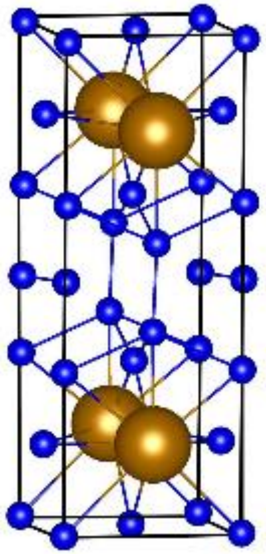
New FeH_5 phase was synthesized at 135 GPa

Superconductivity has not been studied

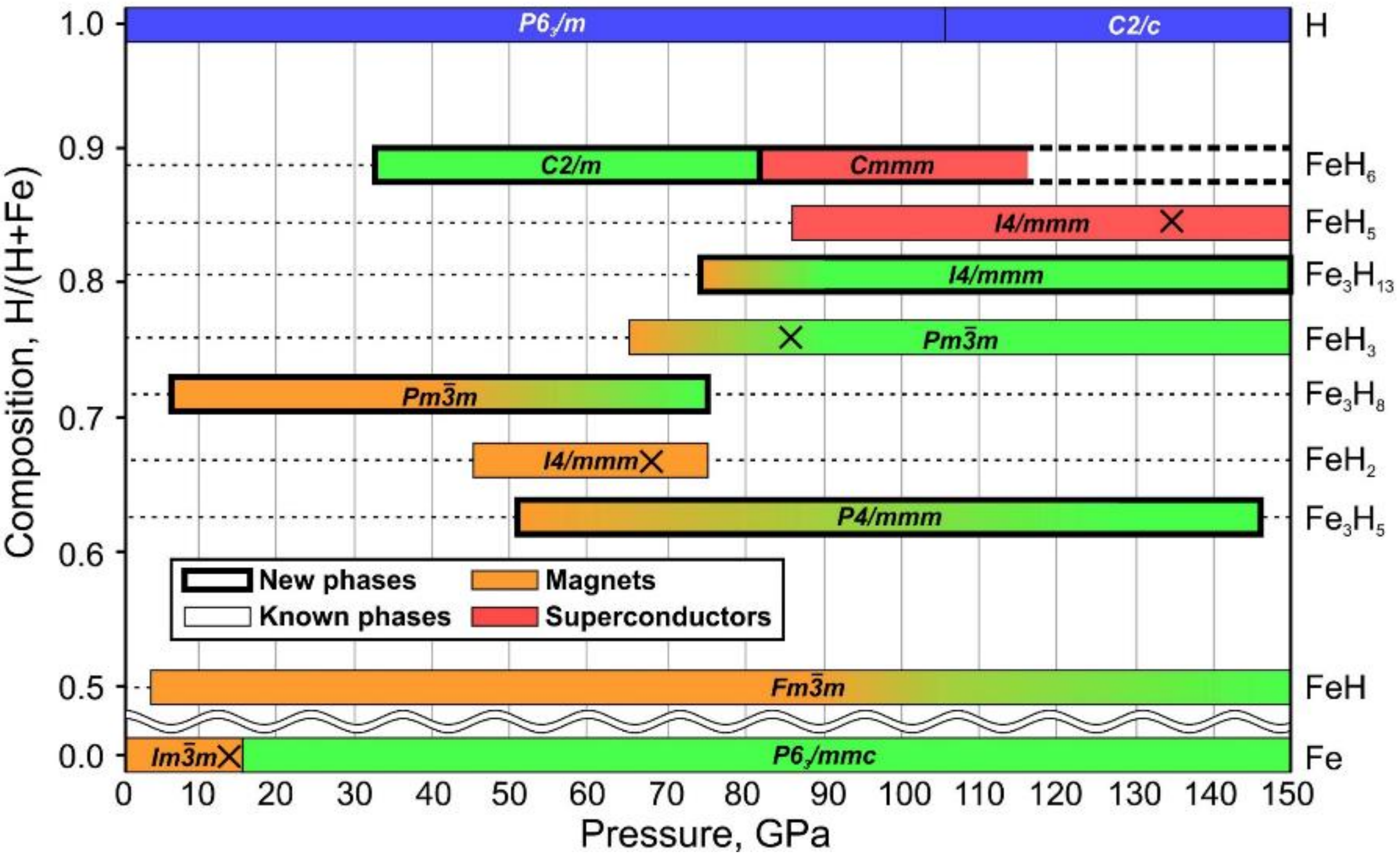
Prediction of new Fe-H phases



FeH_5



FeH_6



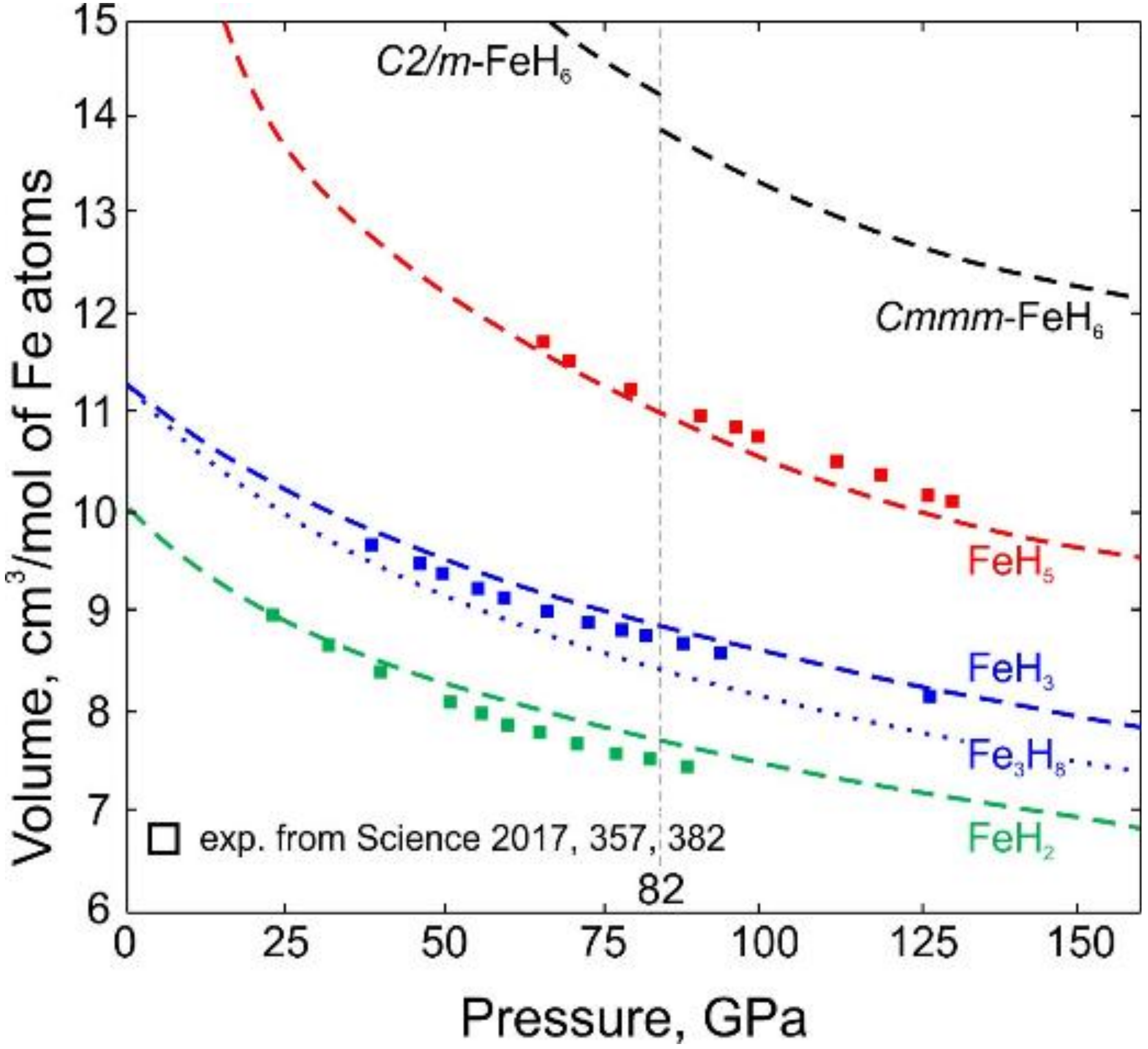
J. Appl. Phys. **1982**, *53* (3), 2064–2065

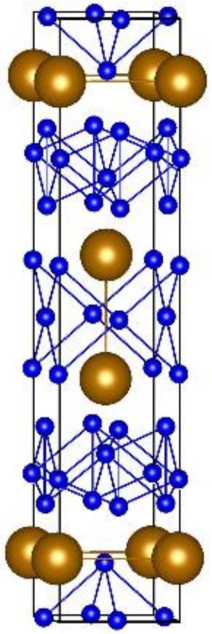
Phys. Rev. Lett. **2014**, *113* (26), 265504

Science **2017**, *357* (6349), 382–385

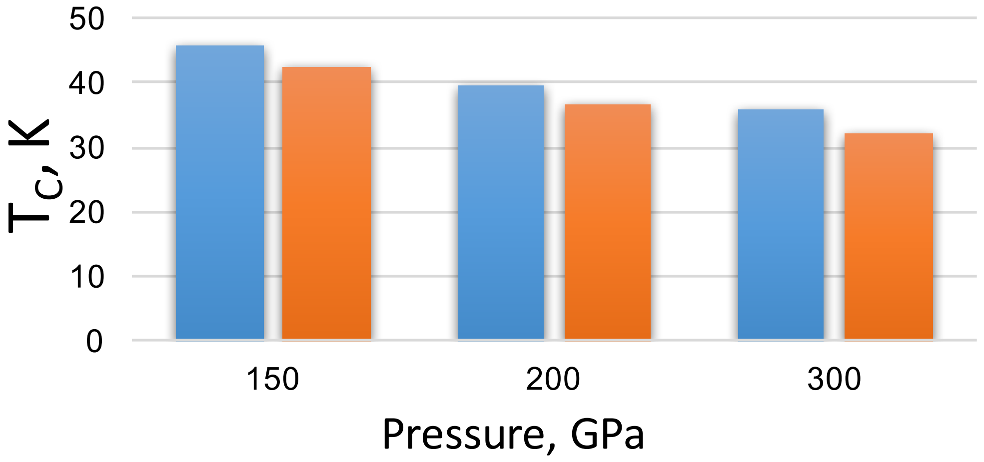
A.G. Kvashnin, I.A. Kruglov, D.V. Semenok, A.R. Oganov, J. Phys. Chem. C, 2018, 122 (8), pp 4731–4736

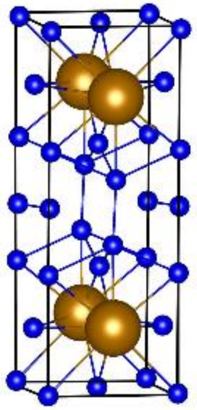
Properties of FeH_5 and FeH_6



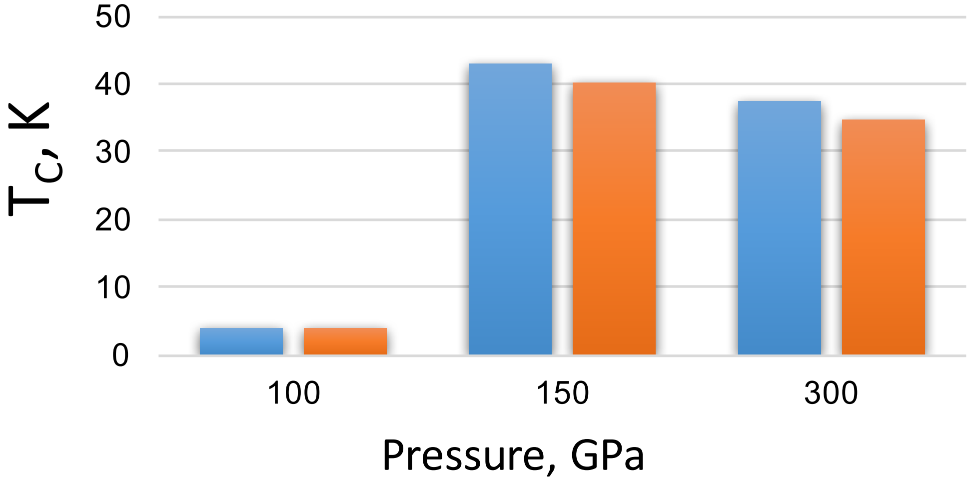


FeH_5





FeH_6



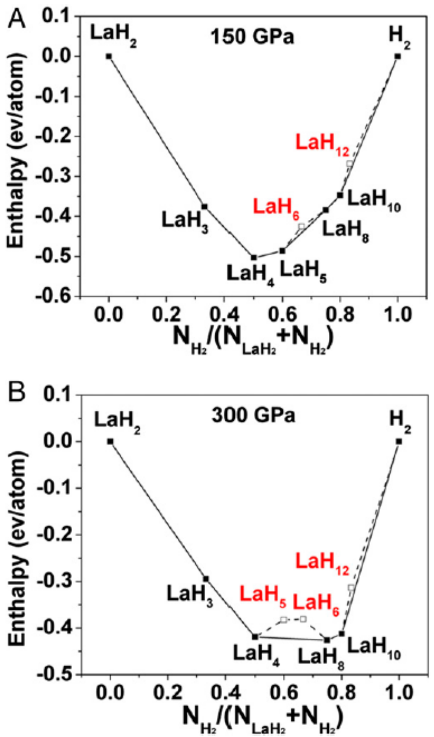
A.G. Kvashnin, I.A. Kruglov, D.V. Semenok, A.R. Oganov, J. Phys. Chem. C, 2018, 122 (8), pp 4731–4736

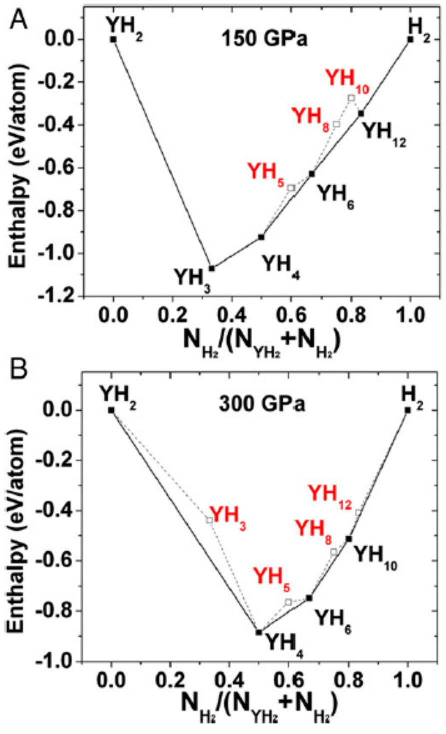
Potential high-T_c superconducting lanthanum and yttrium hydrides at high pressure

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

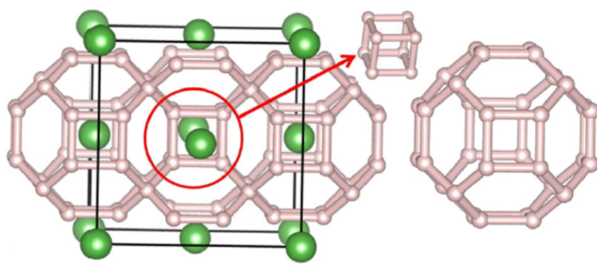
[a]Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015; [b]Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853; [c]Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853; [d]Department of Civil and Environmental Engineering, The George Washington University, Washington, DC 20052; and [e]School of Applied and Engineering Physics, Cornell University, Ithaca, NY 14853

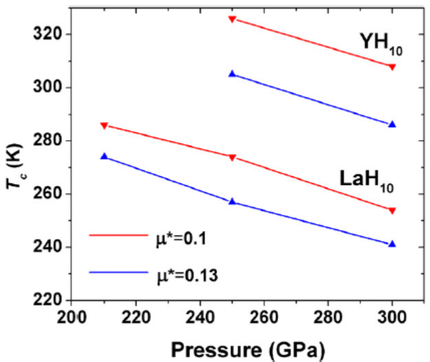
Contributed by Russell J. Hemley, May 5, 2017 (sent for review March 20, 2017; reviewed by Panchapakesan Ganesh, Jeffrey M. McMahon, and Dimitrios Papaconstantopoulos)





The maximal T_C ~ 250-300 K at ~250 GPa





Cornell University Library

Superconductivity at 215 K in lanthanum hydride at high pressures

A. P. Drozdov, V. S. Minkov, S. P. Besedin, P. P. Kong, M. A. Kuzovnikov, D. A. Knyazev, M. I. Eremets

(Submitted on 21 Aug 2018)

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

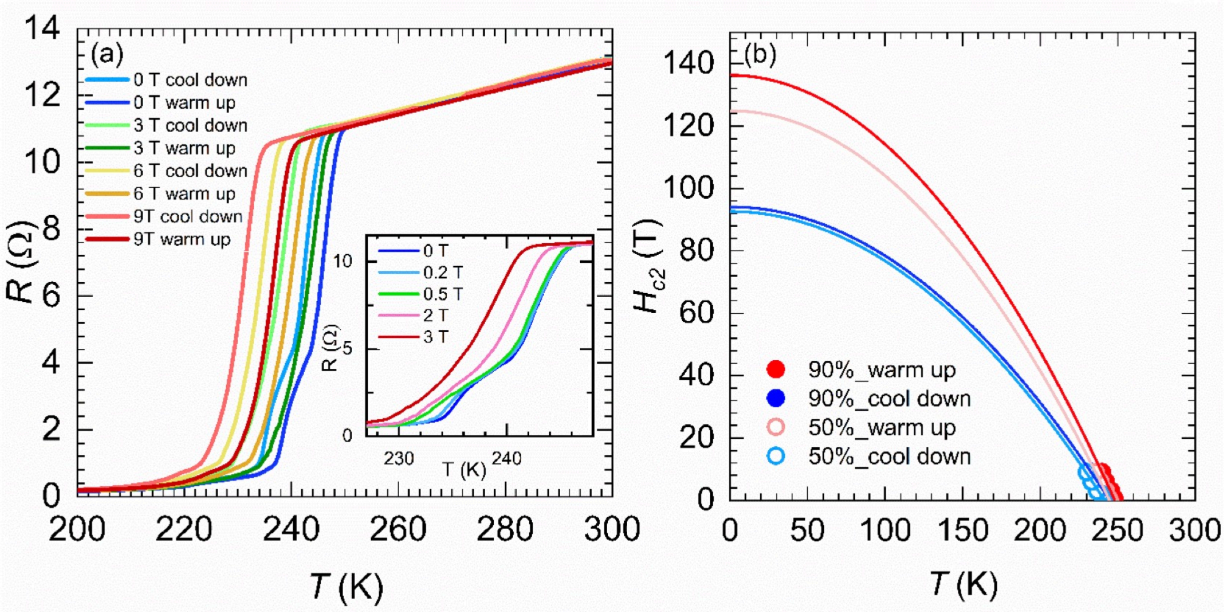
Maddury Somayazulu, Muhtar Ahart, Ajay K. Mishra, Zachary M. Geballe, Maria Baldini, Yue Meng, Viktor V. Struzhkin, and Russell J. Hemley

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

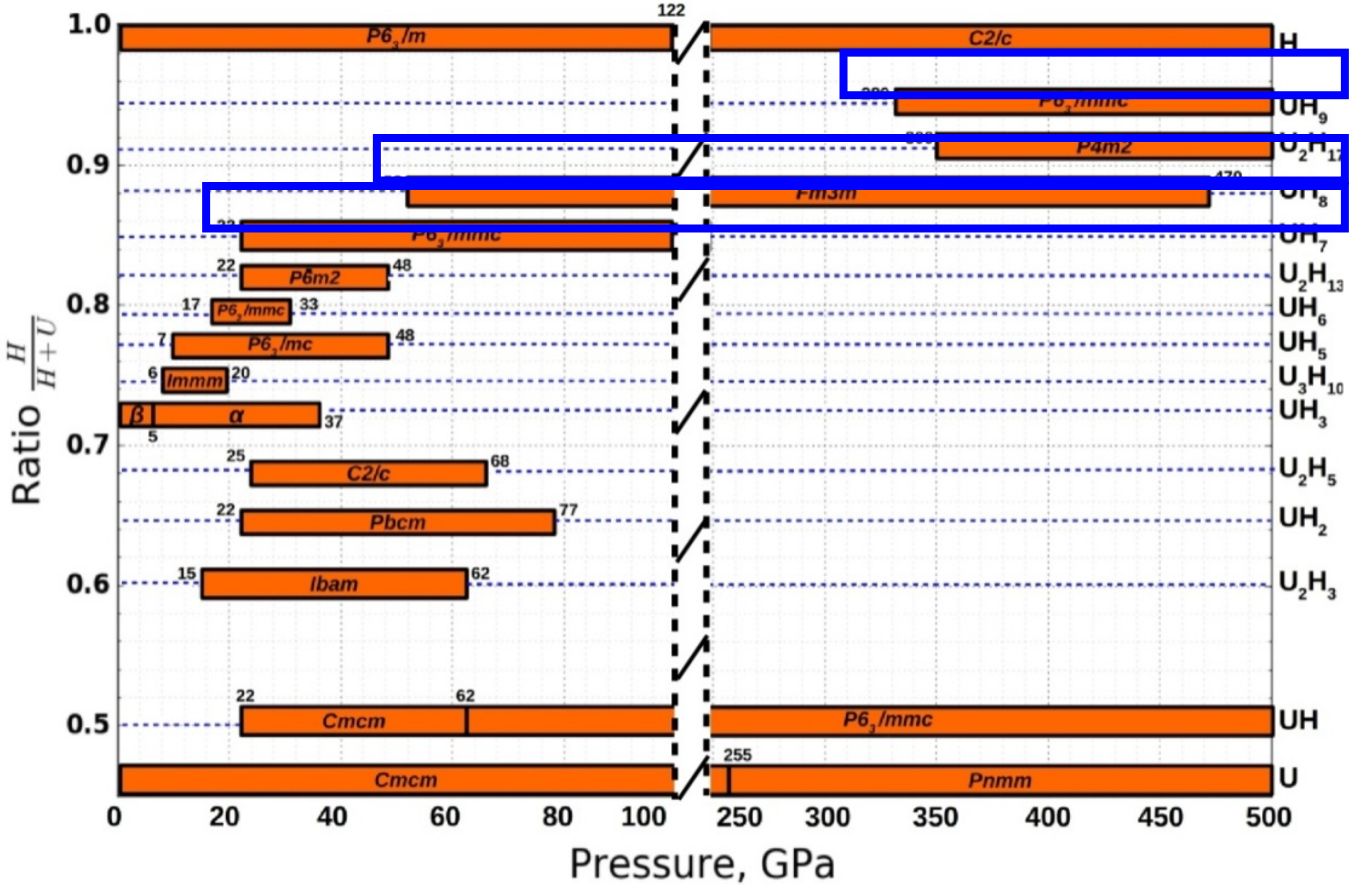
Superconductivity at 250 K in lanthanum hydride under high pressures

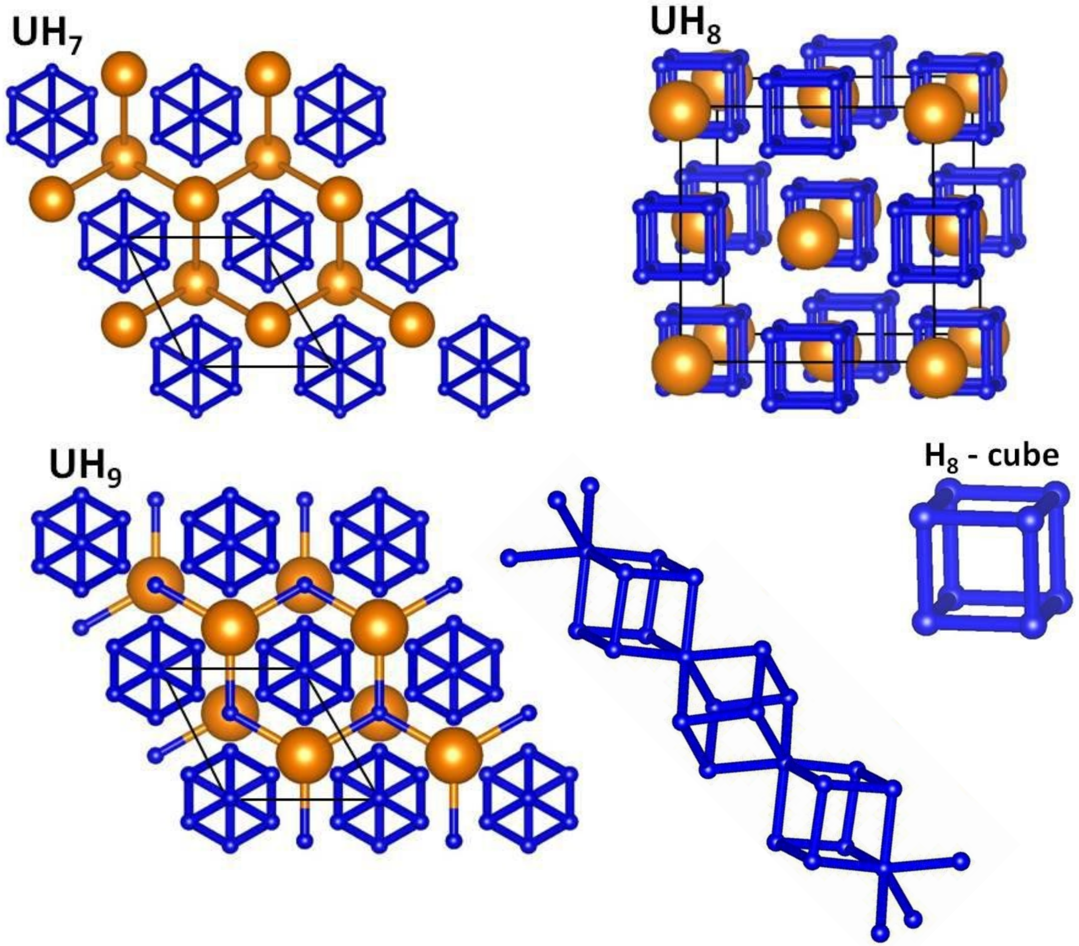
A. P. Drozdov, P. P. Kong, V. S. Minkov, S. P. Besedin, M. A. Kuzovnikov, S. Mozaffari, L. Balicas, F. Balakirev, D. Graf, V. B. Prakapenka, E. Greenberg, D. A. Knyazev, M. Tkacz, M. I. Eremets

(Submitted on 4 Dec 2018)



U-H system



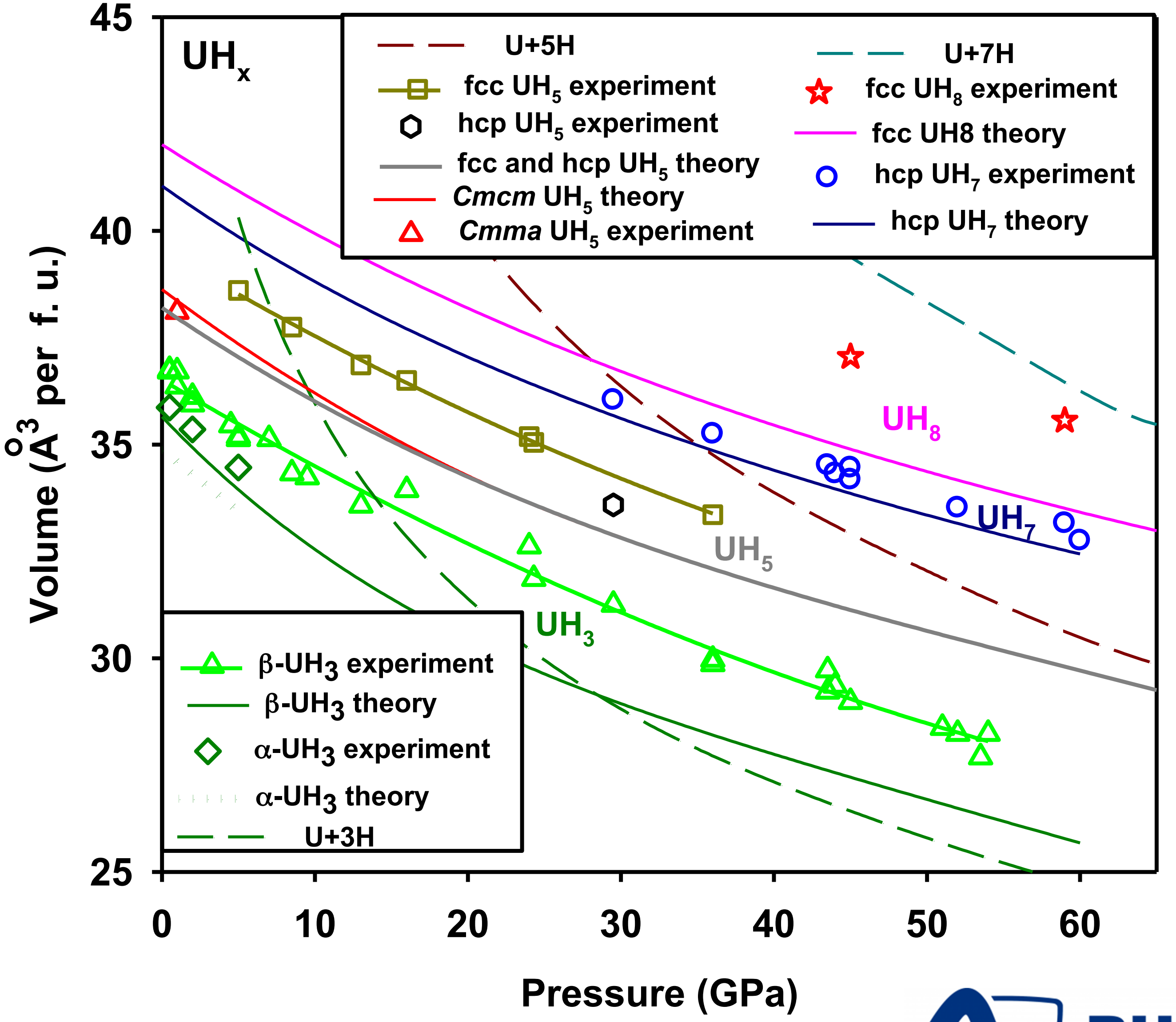


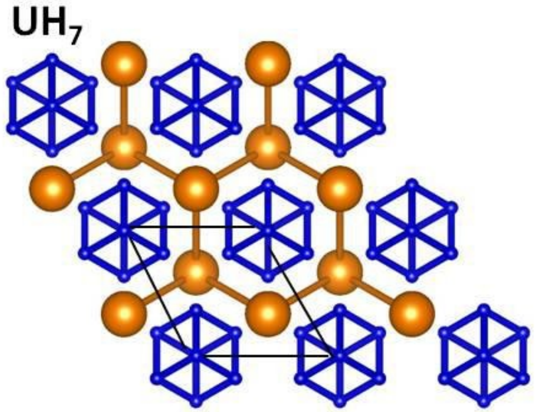
ВНИИА

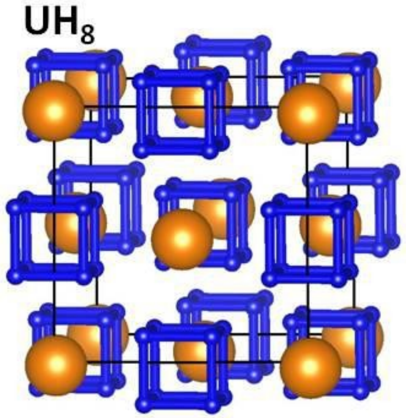
Carnegie Science | Geophysical Laboratory

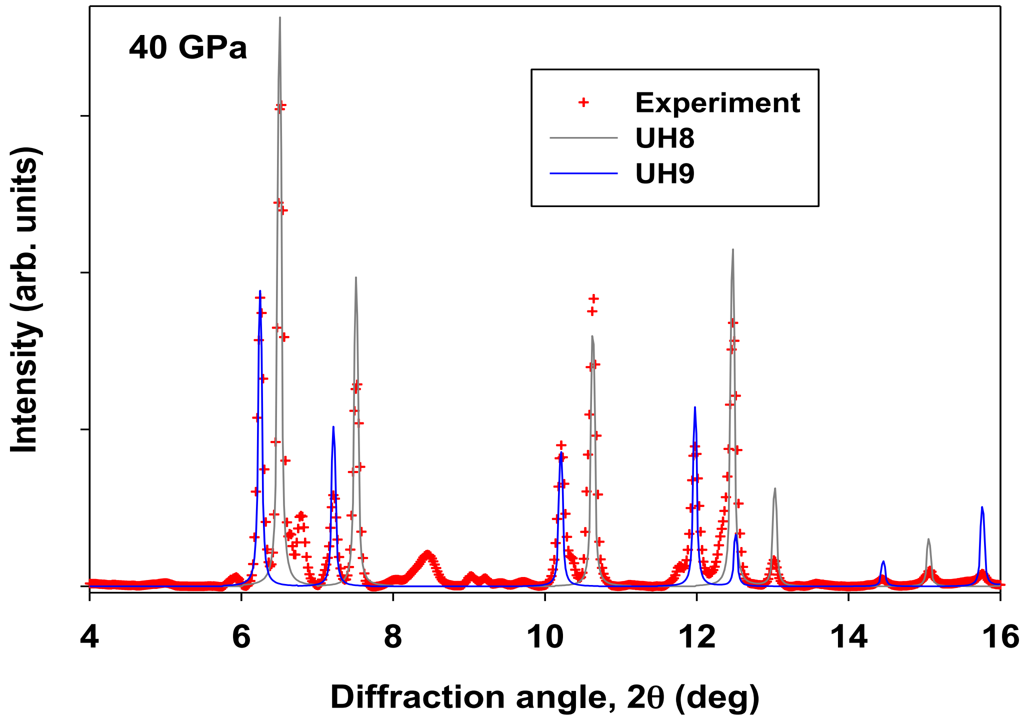
I.A. Kruglov, A.G. Kvashnin … A.R. Oganov et al. Sci. Adv. 2018

U-H system









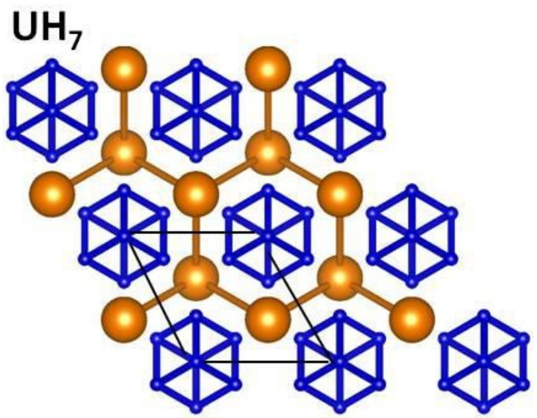
ВНИИА

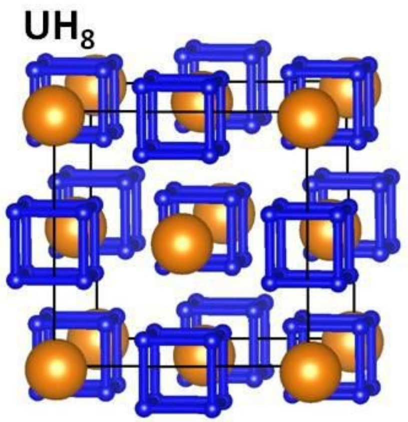
Carnegie Science | Geophysical Laboratory

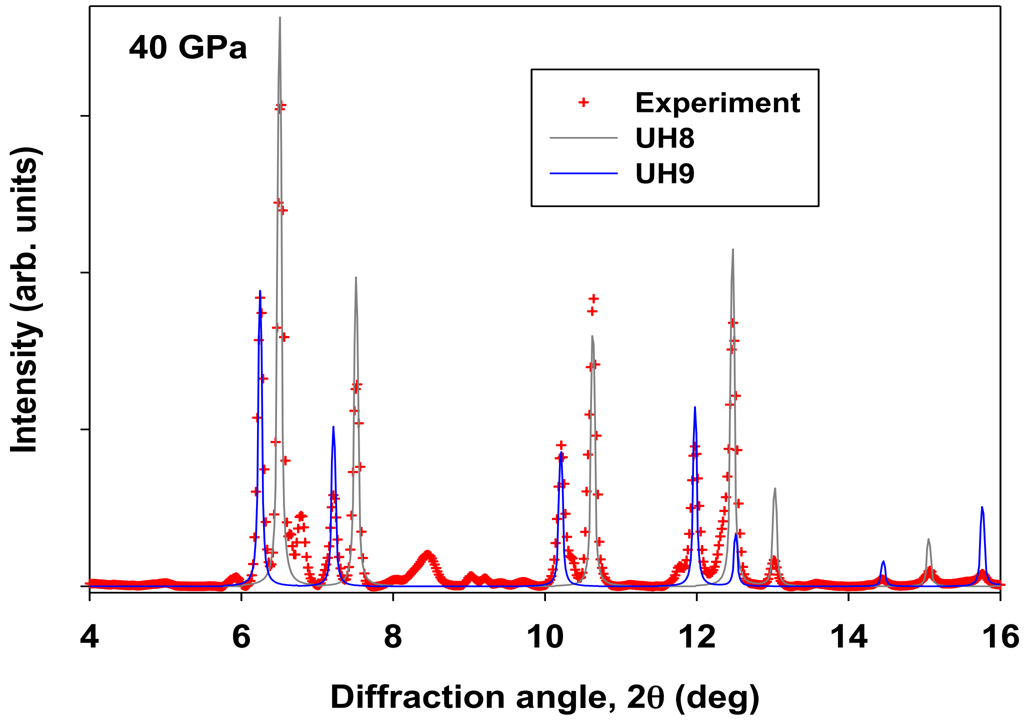
I.A. Kruglov, A.G. Kvashnin … A.R. Oganov et al. Sci. Adv. 2018

U-H system

Phase	Space group	P, GPa	ω_{log}, K	λ	T_c, K
UH_7	$P6_3/mmc$	20	873.8	0.83	54.1 43.7
		0	764.9	0.95	65.8 56.7
UH_8	$Fm\bar{3}m$	50	873.7	0.73	33.3 23.4
		0	450.3	1.13	55.2 46.2
UH_9	$P6_3/mmc$	300	933.4	0.67	31.2 19.9



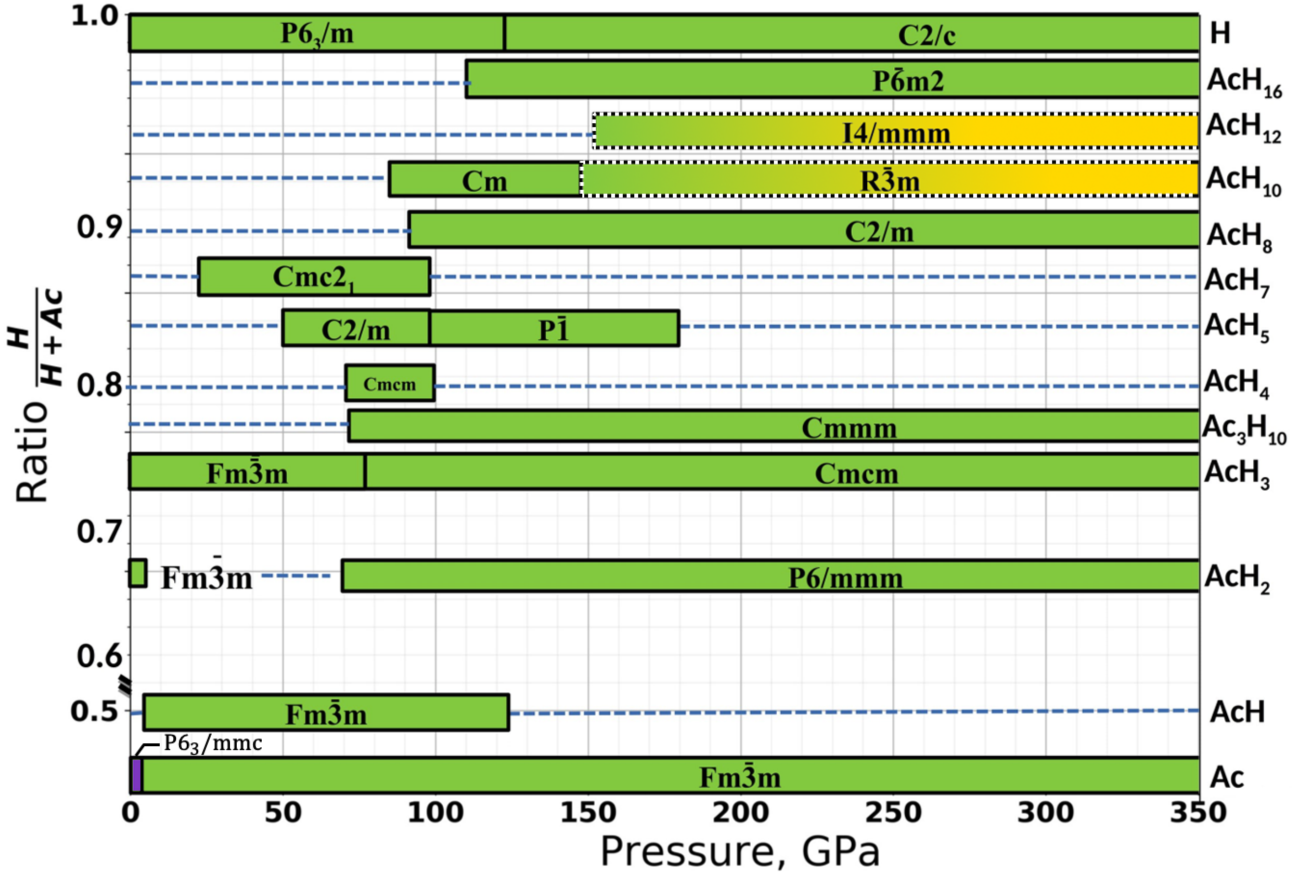


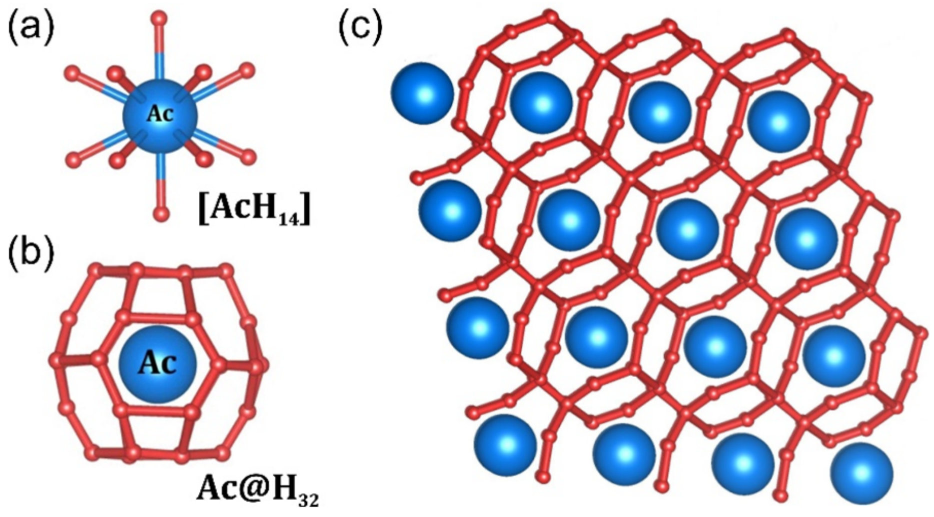


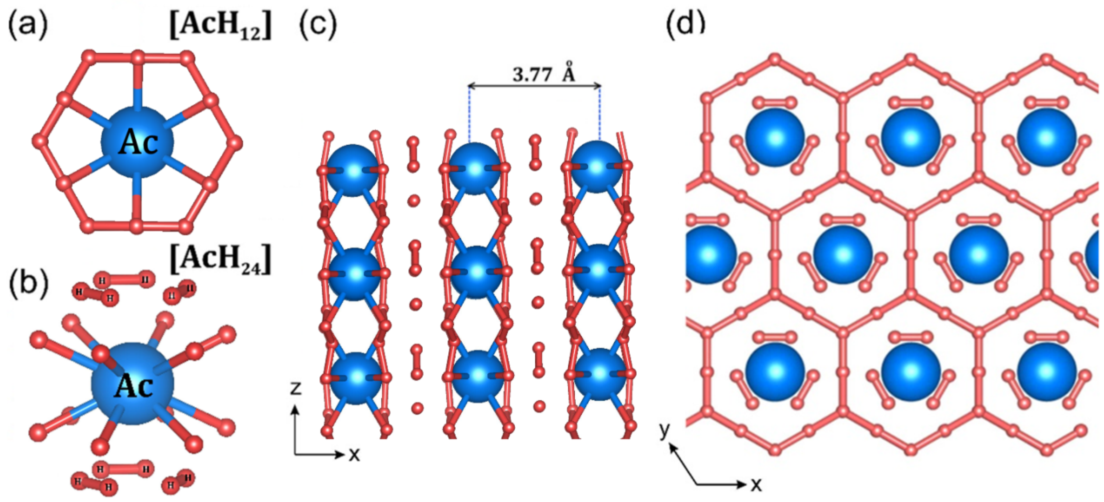
ВНИИА Carnegie Science | Geophysical Laboratory

I.A. Kruglov, A.G. Kvashnin … A.R. Oganov et al. Sci. Adv. 2018

Ac-H system

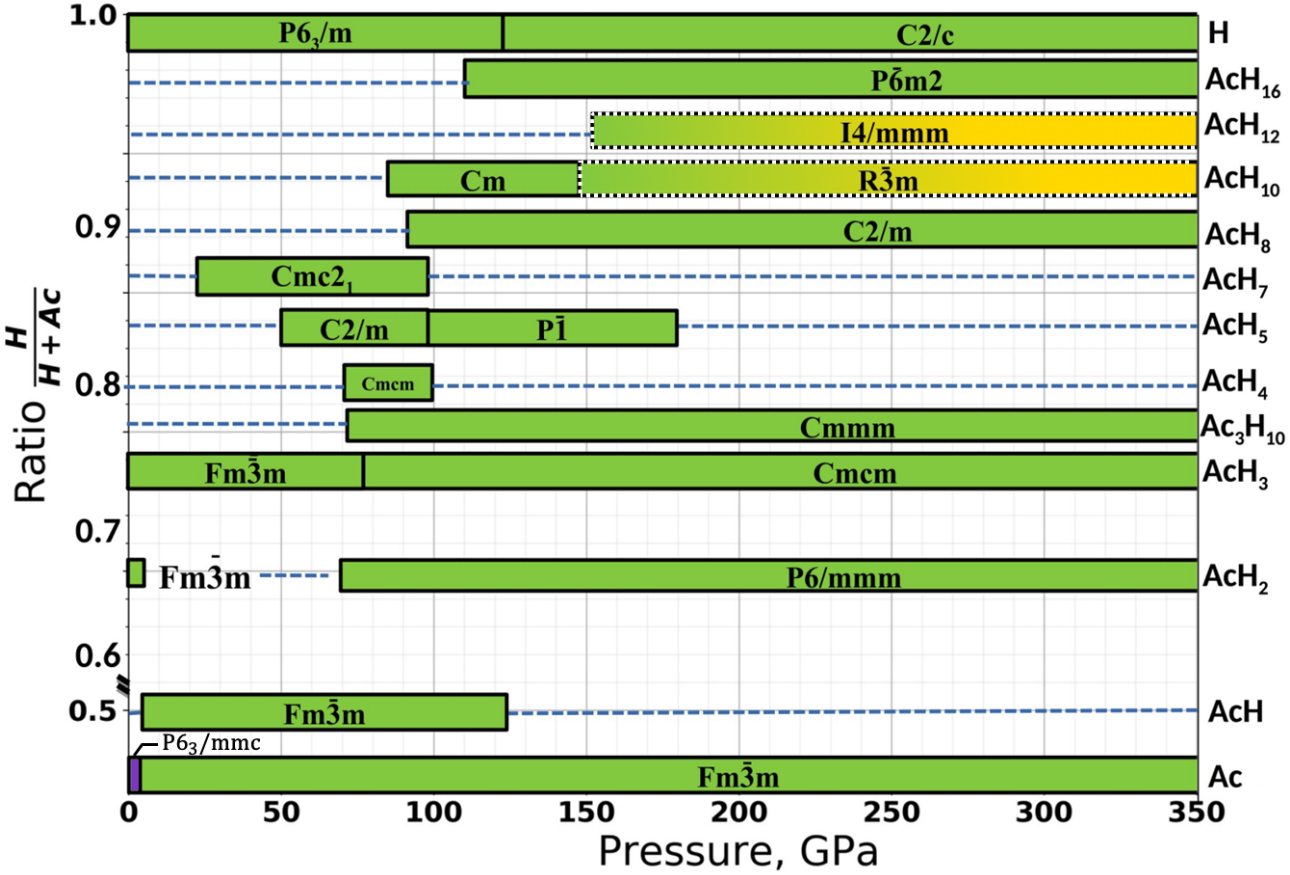


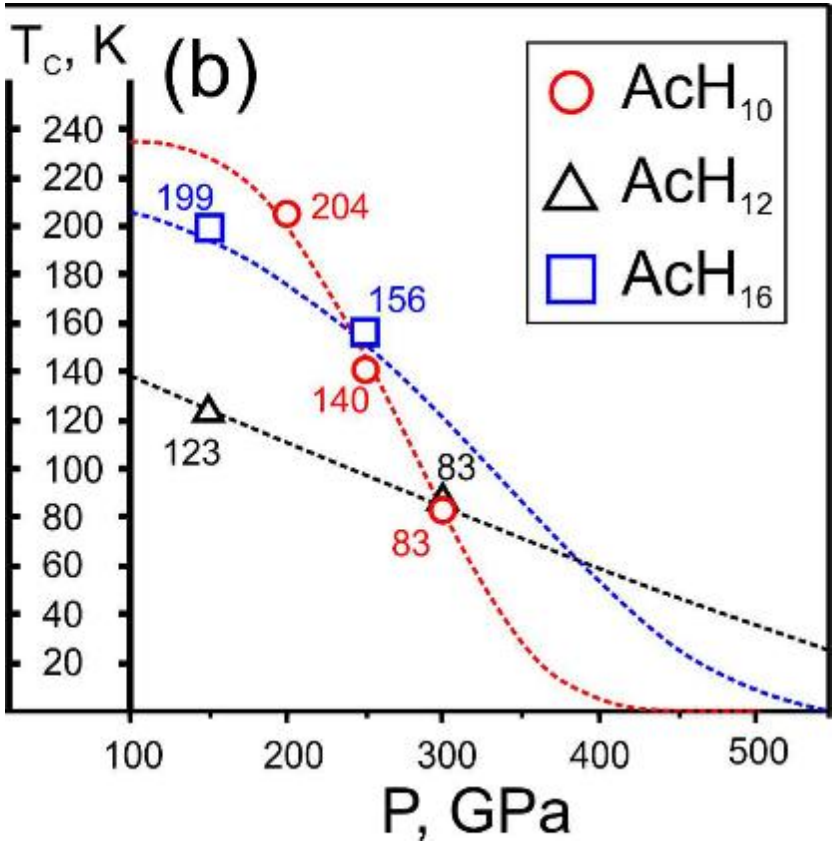




D.V. Semenok, A.G. Kvashnin, I.A. Kruglov, A.R. Oganov, J. Phys. Chem. Lett. 2018, 8, pp. 1920-1926

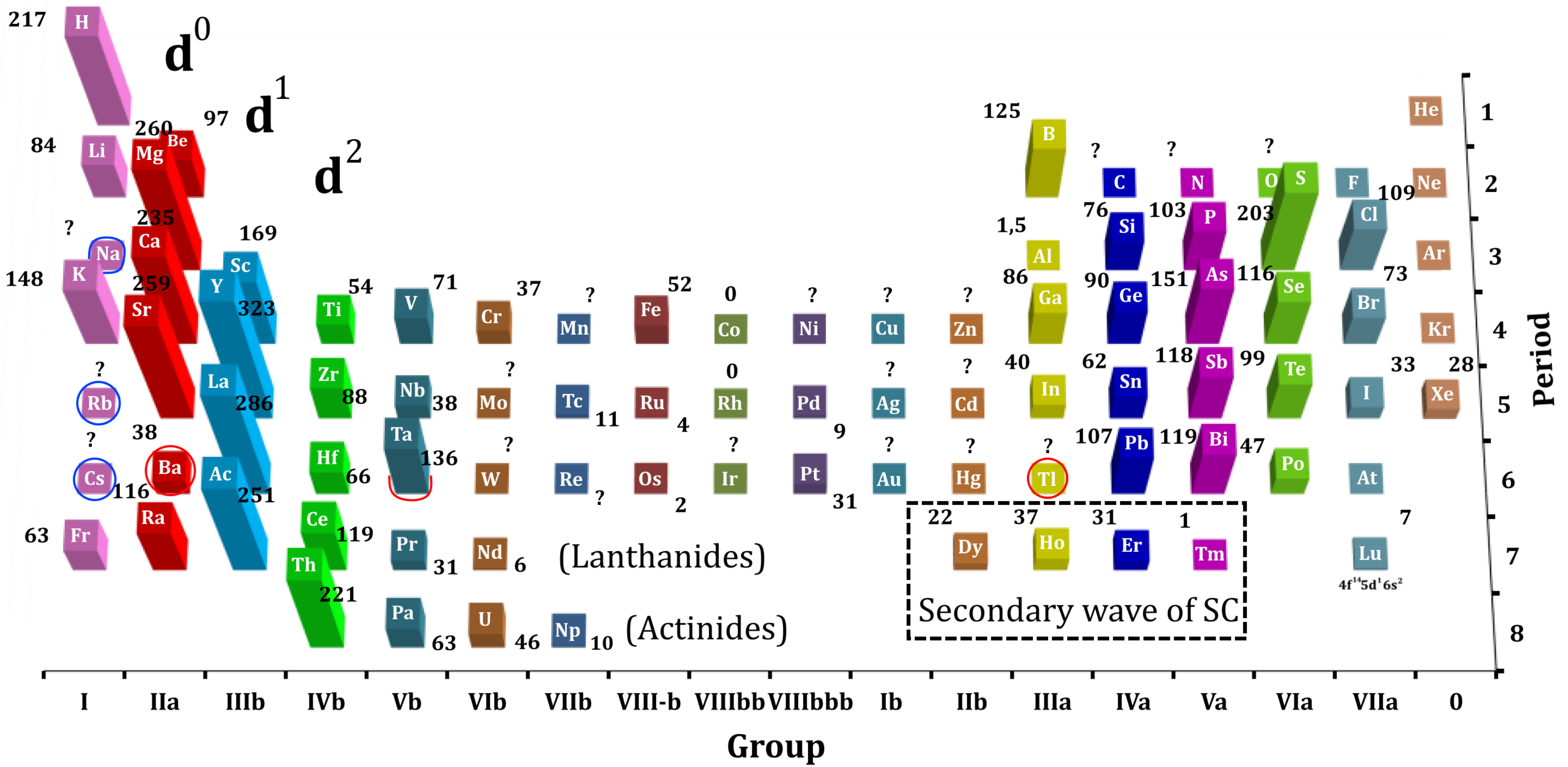
Ac-H system



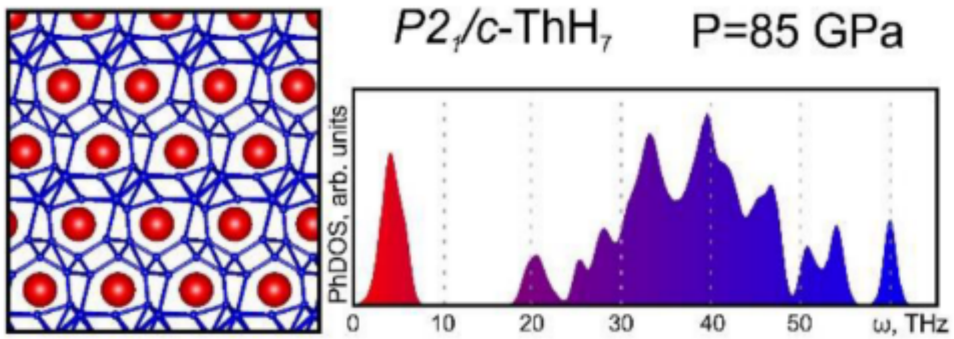


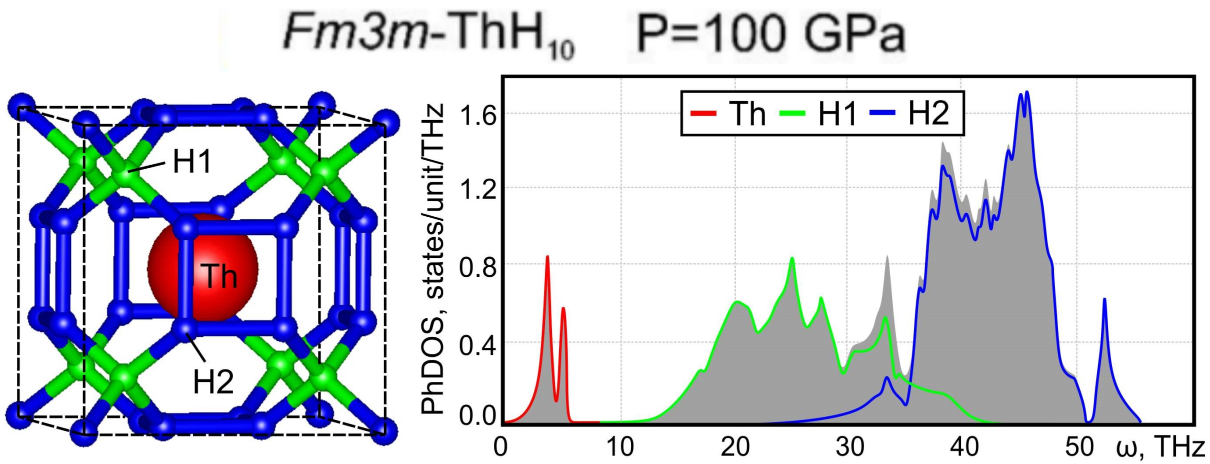
D.V. Semenok, A.G. Kvashnin, I.A. Kruglov, A.R. Oganov, J. Phys. Chem. Lett. 2018, 8, pp. 1920-1926

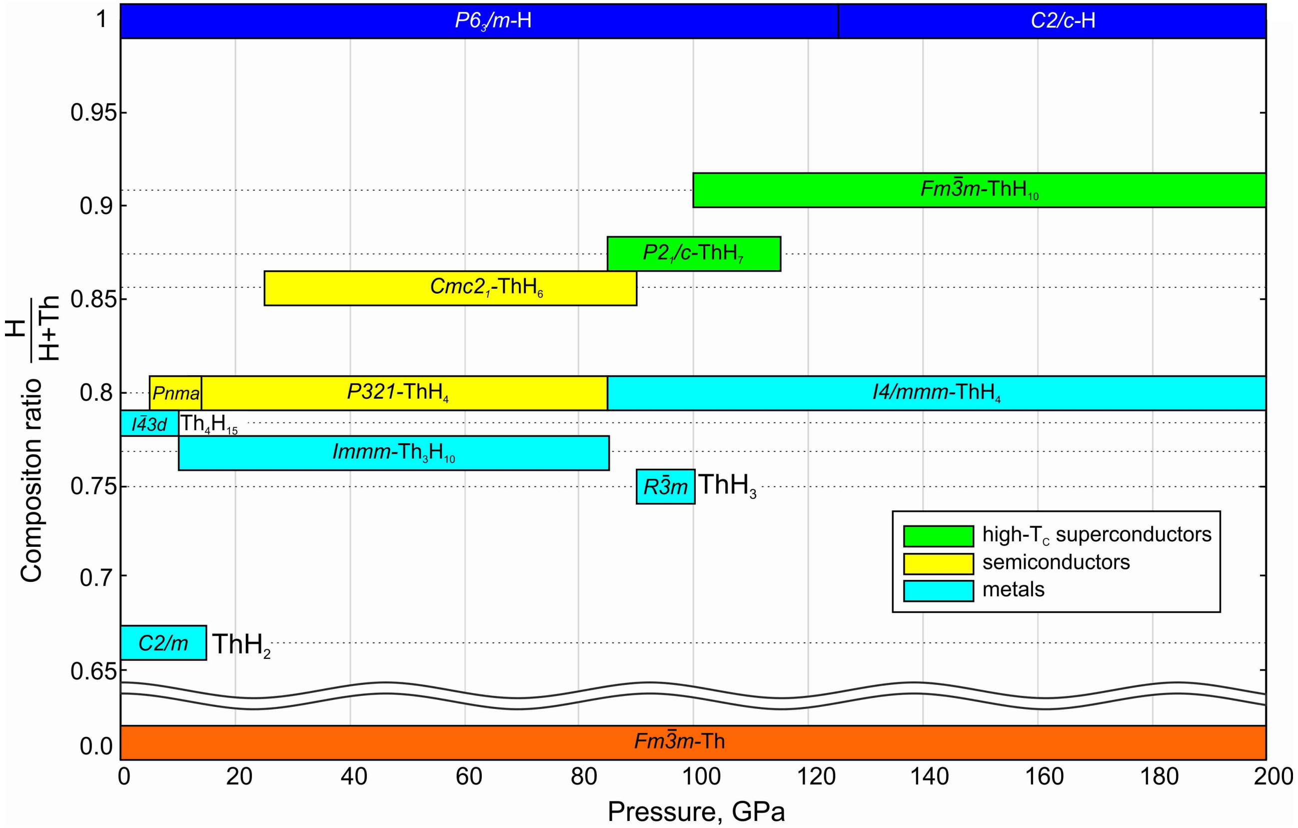
General rule



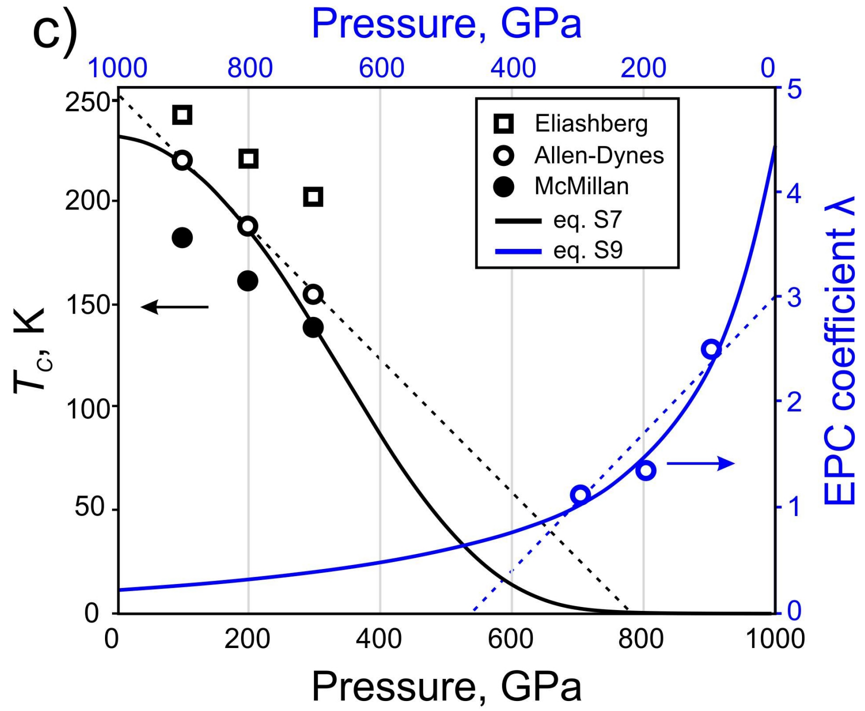
Th-H system







Stability field of thorium hydrides

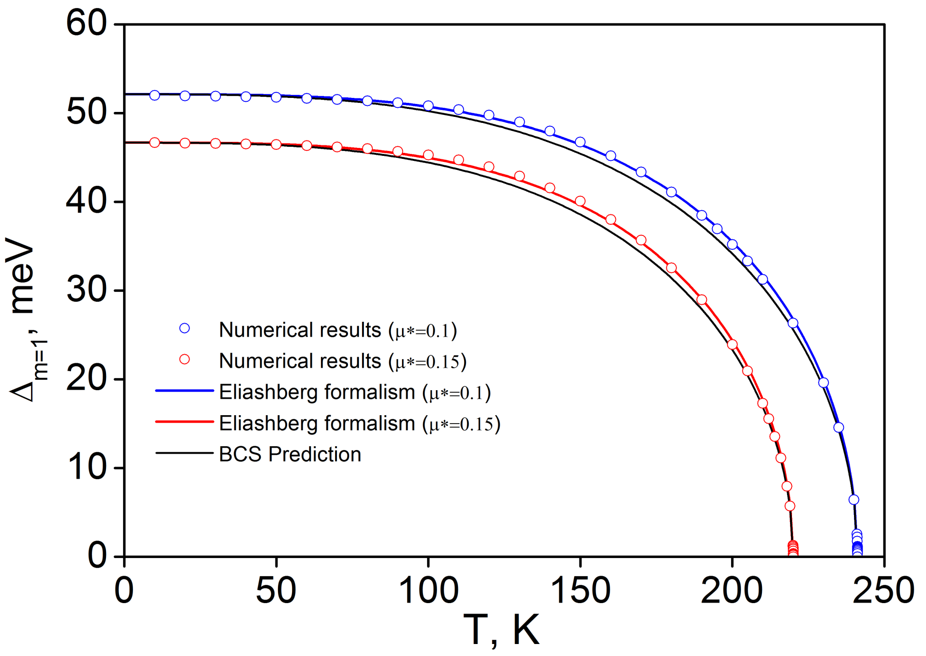


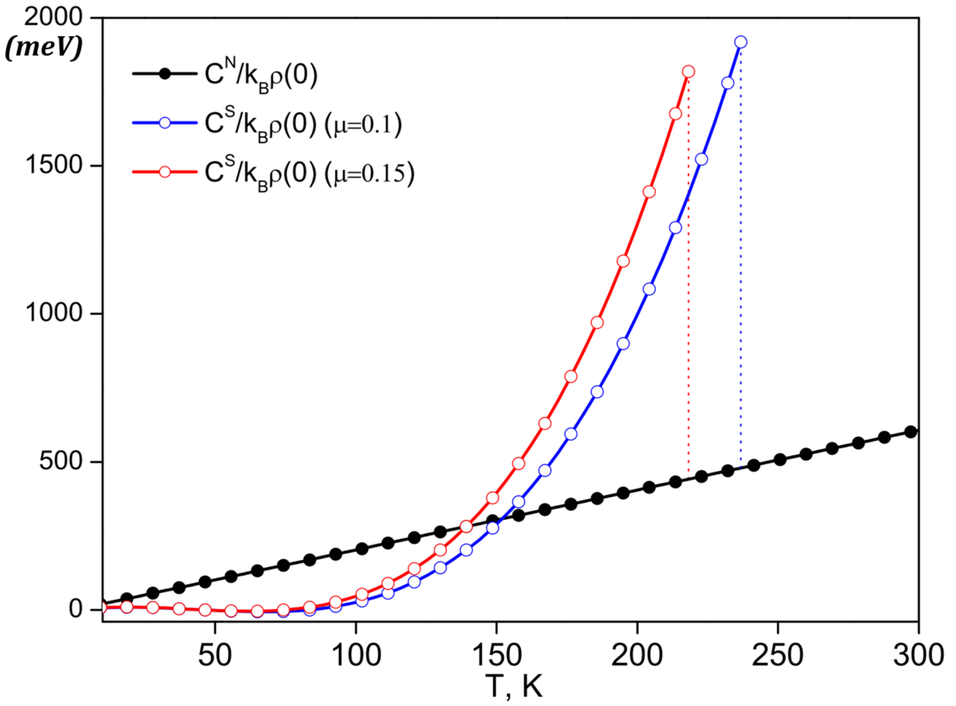
Max T_C is 241 K at 100 GPa for ThH_{10}

A.G. Kvashnin et al. ACS App. Mat. Interfaces, 2018, 10, 43809-43816

Th-H system

Compound	SC gap, meV	T_C, K
ThH_{10}	52	241
LaH_{10} [1]	68	286
YH_{10} [1]	77	326
H_3S [2]	42.7	203
BiH_6 [3]	18.1	100
PH_3 [4]	14.5	81
YH_3 [5]	8.4	45.9
H_3Se [6]	28.4	131
MgH_6 [7]	106.6	420
$YBa_2Cu_3O_{7-y}$ [8]	34	92
$NdBa_2Cu_3O_7$ [9]	30	95
$Bi_2Sr_2Ca_2Cu_3O_{10+y}$ [10]	45	111
$SmFeAsO_{0.9}F_{0.1}$ [11]	15	44
$Ba_{0.6}K_{0.4}Fe_2As_2$ [12]	12	37

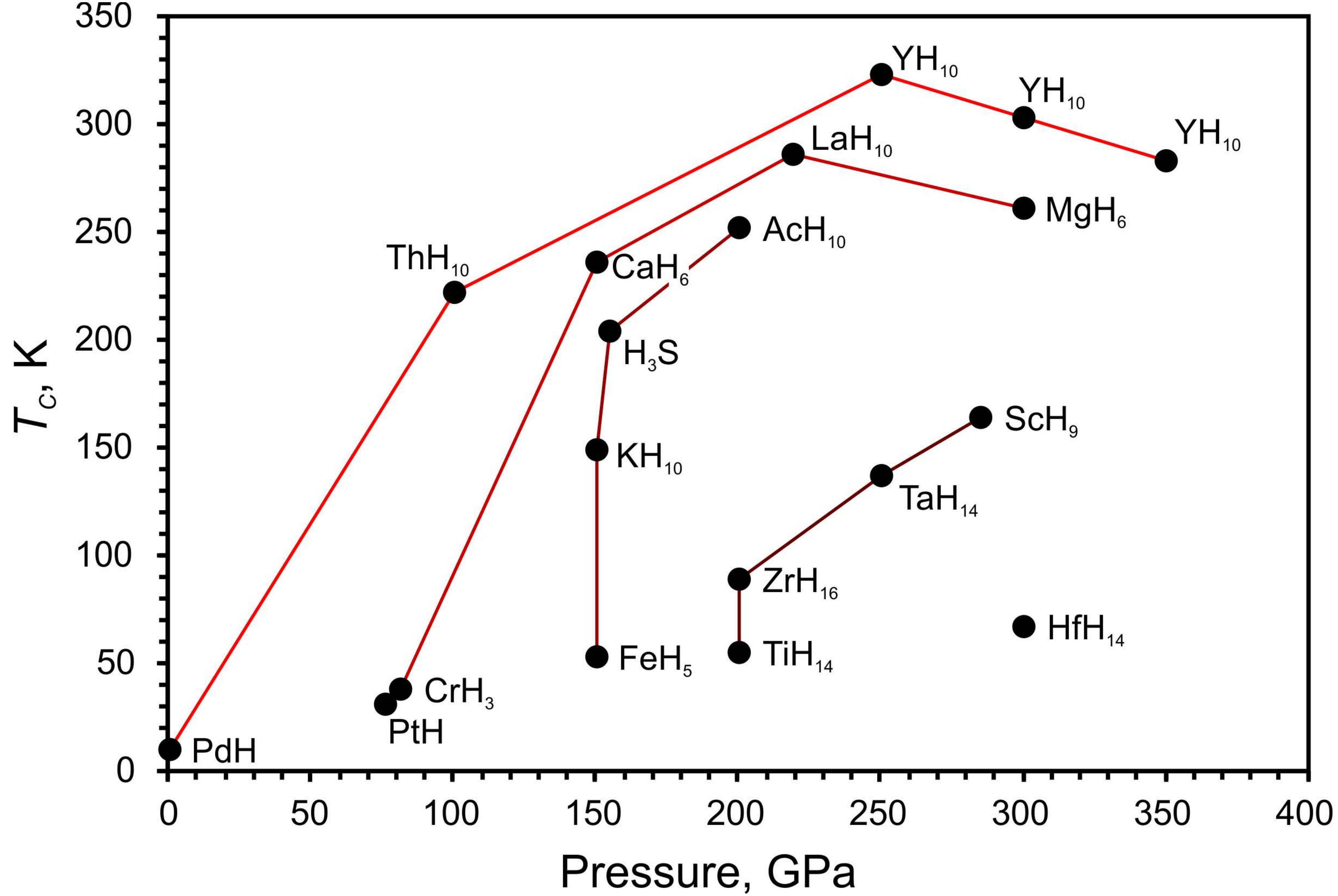




[1] H. Liu et al. PNAS **114**, 6990 (2017).
[2] A. P. Durajski et al. Annalen Der Physik **528**, 358 (2016).
[3] M. W. Jarosik et al. Solid State Communications **279**, 27 (2018).
[4] A. P. Durajski Scientific Reports **6**, 38570 (2016).
[5] M. W. Jarosik et al. Solid State Communications **250**, 5 (2017).
[6] J. Flores-Livas et al. Eur. Phys. J. B **89**, 63 (2016).
[7] R. Szczęśniak et al. Front. Phys. **11**, 117406 (2016).
[8] K. Nakayama et al. Phys. Rev. B **79**, 140503 (2009).
[9] M. Nishiyama et al. J. Supercond. Novel Magn. **15**, 351 (2002).
[10] M. Kugler et al. J. Phys. Chem. Sol. **67**, 353 (2006).
[11] T. Kondo et al. Phys. Rev. Lett. **101**, 147003 (2008).
[12] H. Ding et al. EPL **83**, 47001 (2008).

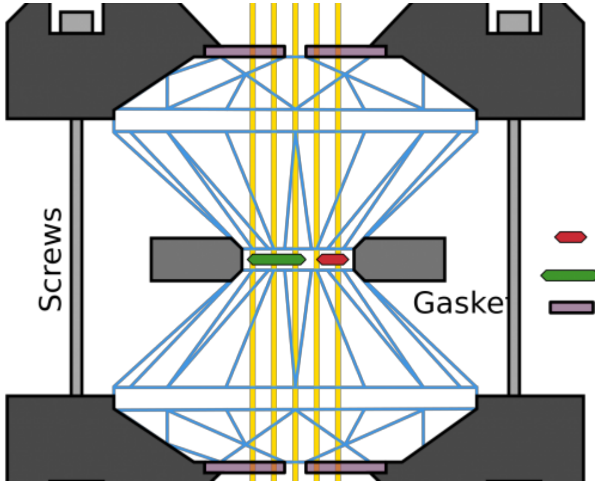
A.G. Kvashnin et al. ACS App. Mat. Interfaces, 2018, 10, 43809-43816

Ashby plot

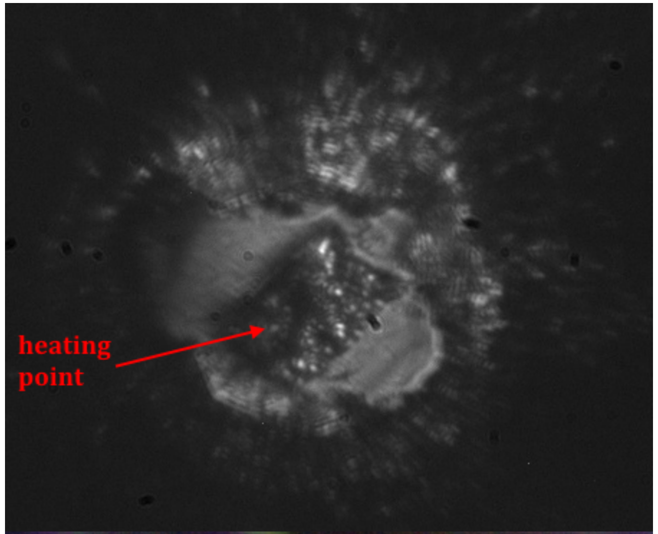


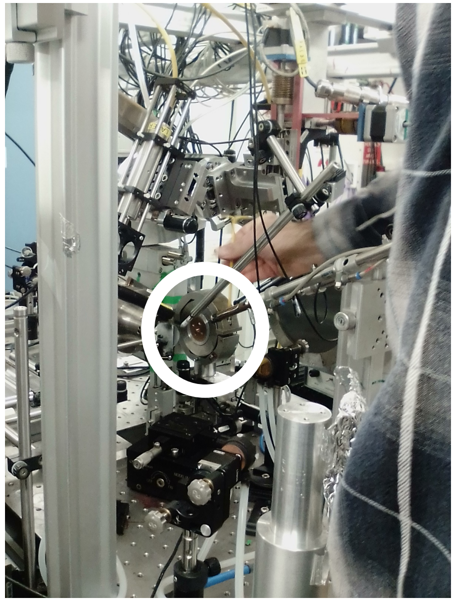
350
300
250
200
150
100
50
0
0
50
100
150
200
250
300
350
400
T_C, K
Pressure, GPa
YH10
YH10
YH10
LaH10
MgH6
AcH10
ThH10
CaH6
H3S
ScH9
KH10
TaH14
ZrH16
HfH14
FeH5
TiH14
CrH3
PtH
PdH

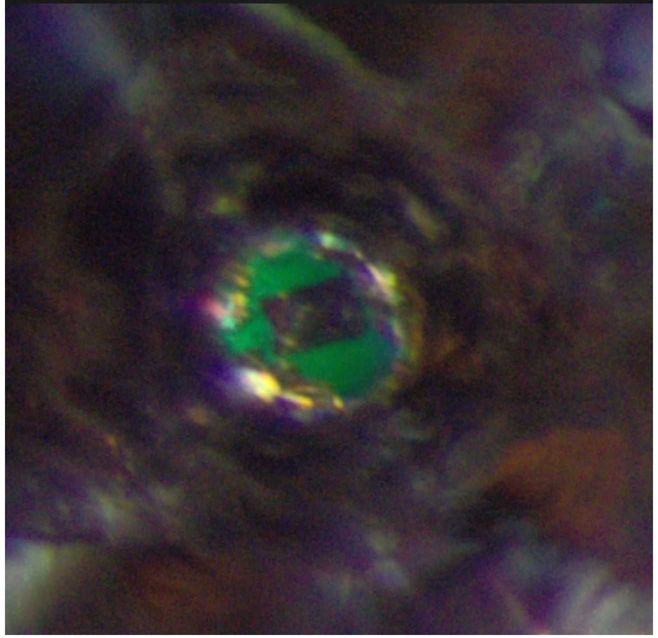
Synthesis

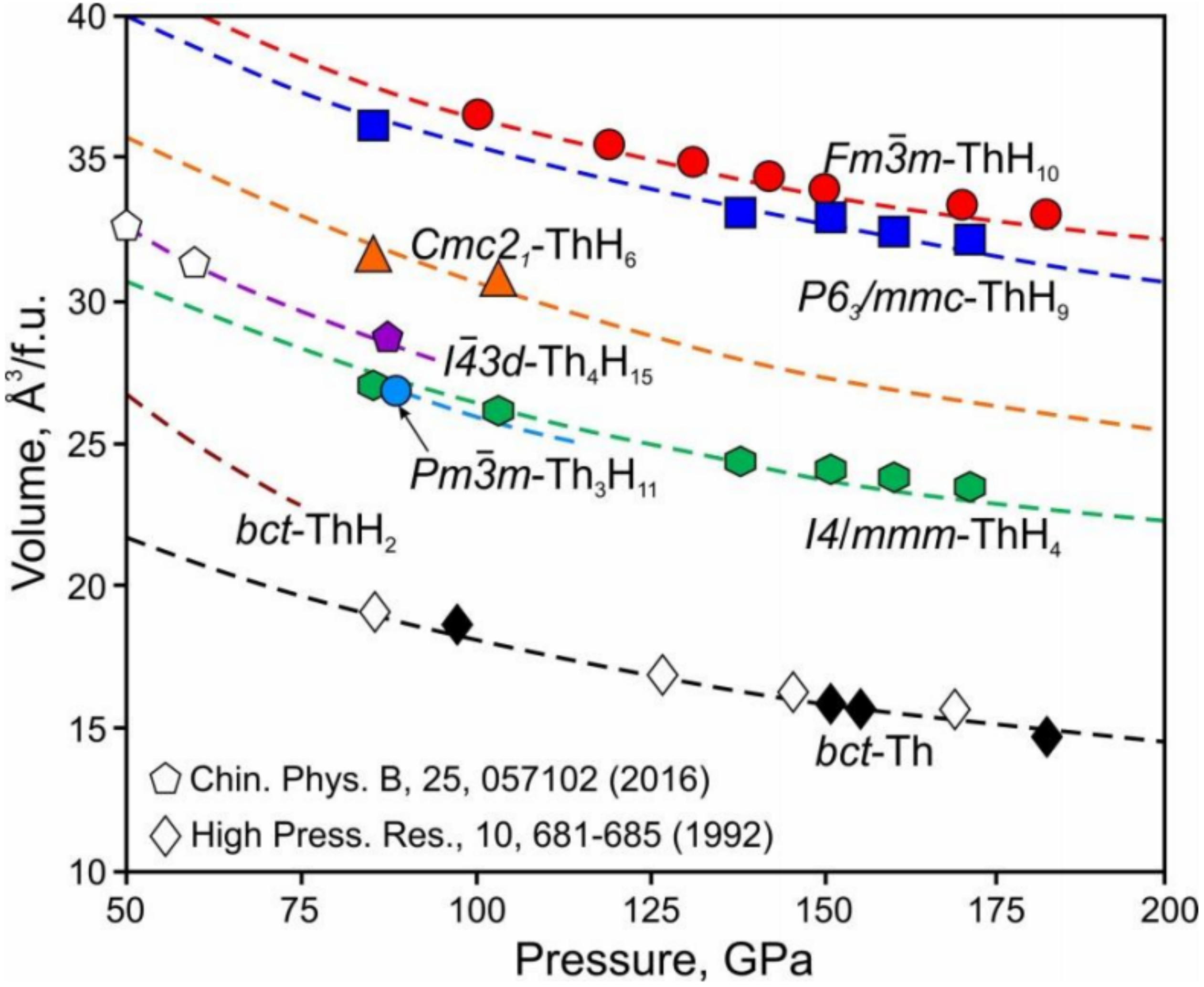


Optical images after heating





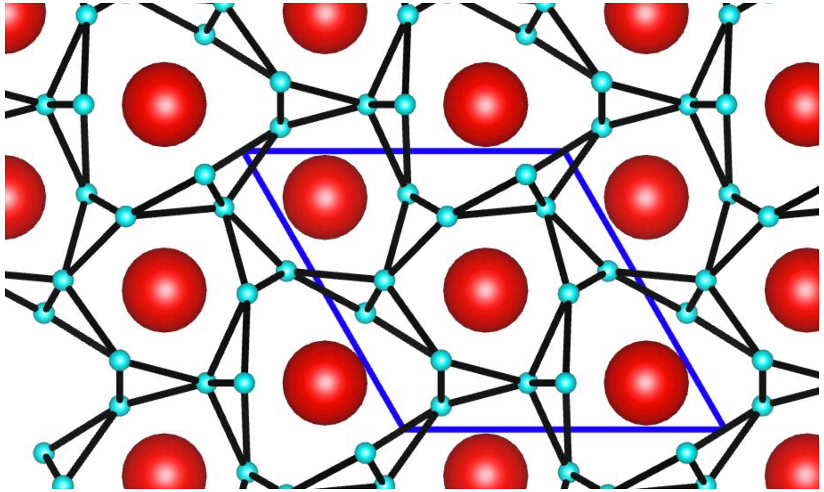


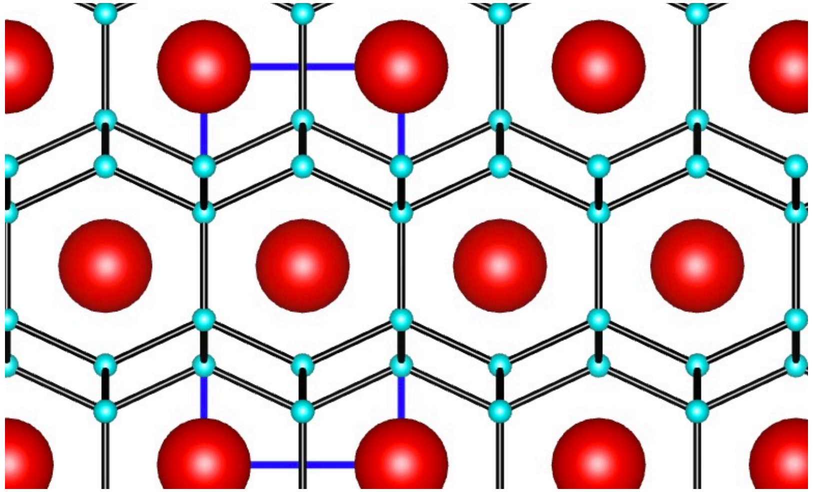


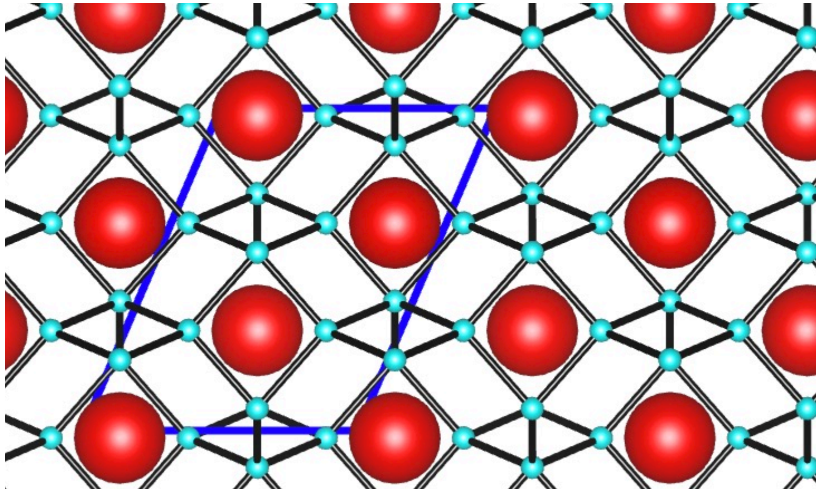
Synthesis of ThH_4

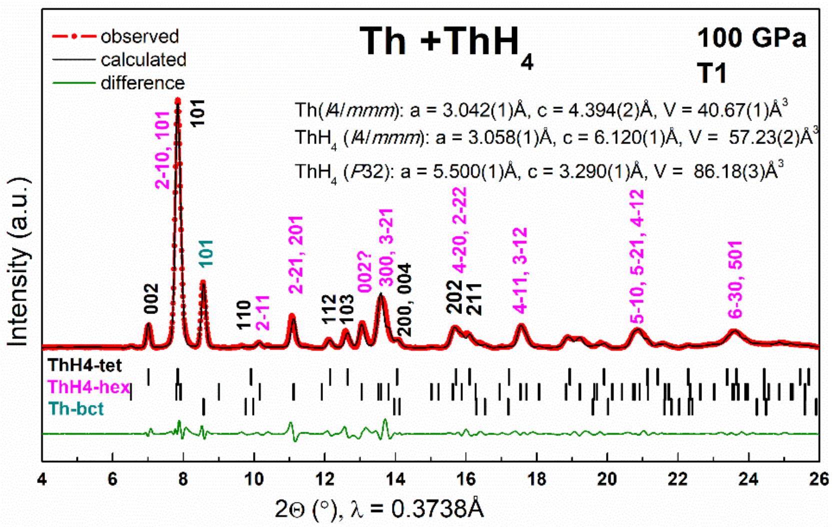
P321 → ***I4/mmm*** → ***Fmmm***

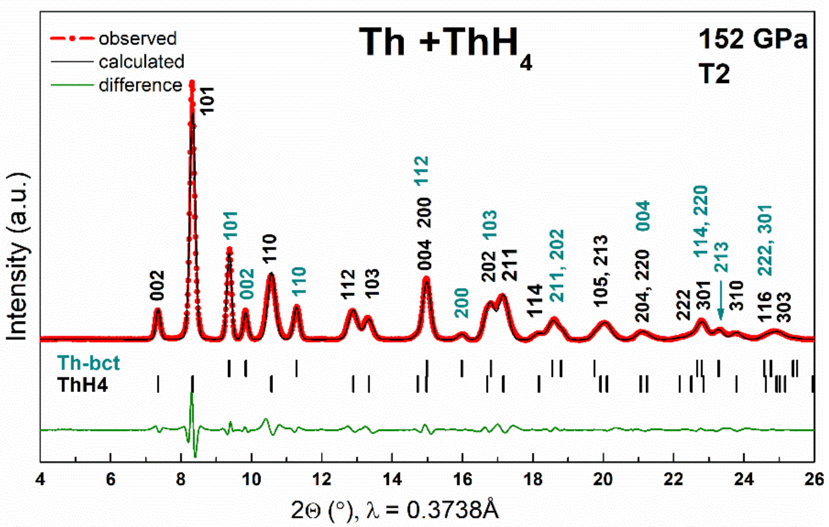
1800 K, 100 GPa | 1400 K, 152 GPa | 2000 K, 152 GPa

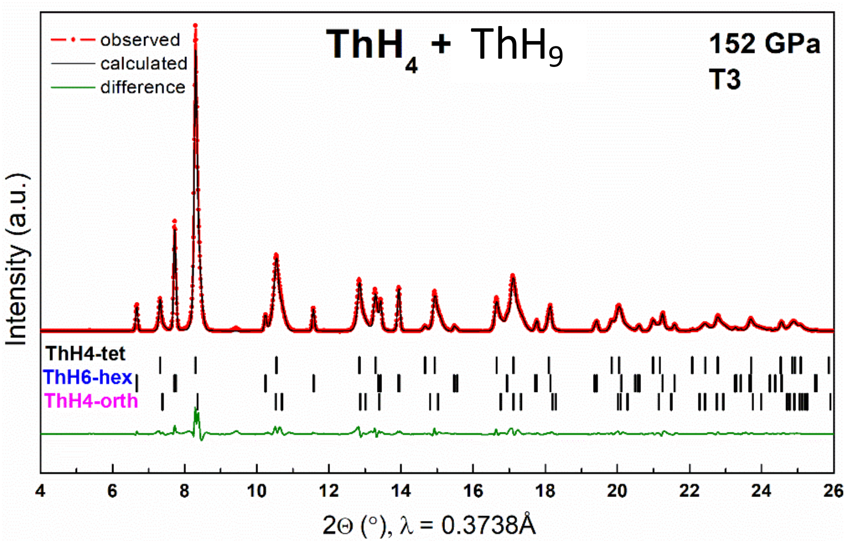








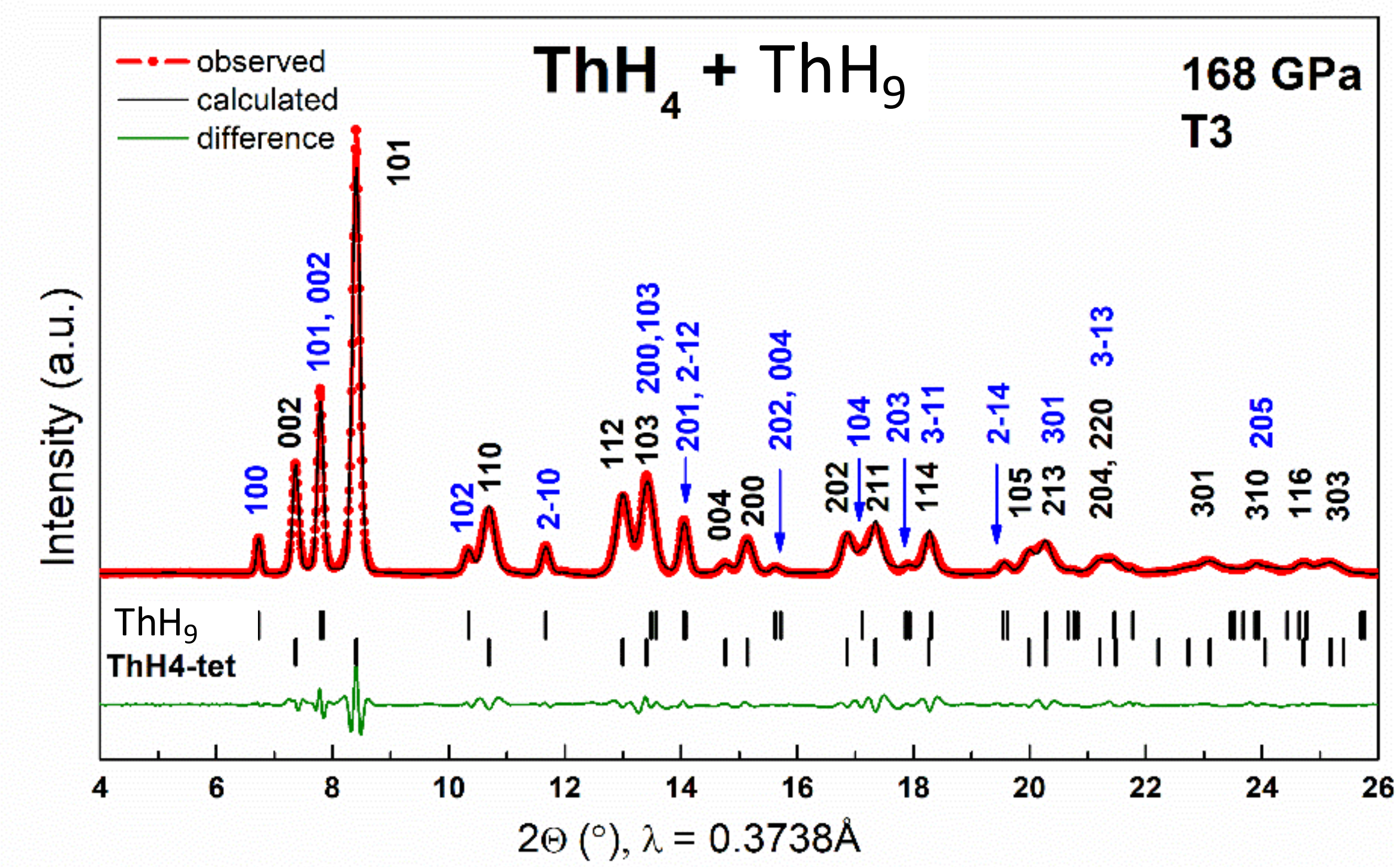


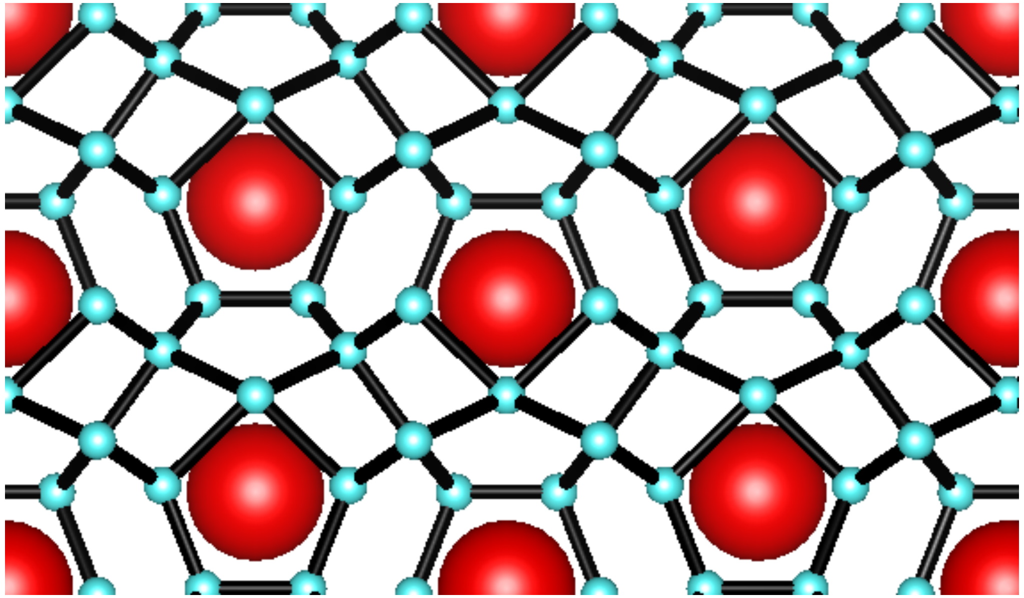


Synthesis of ThH_9

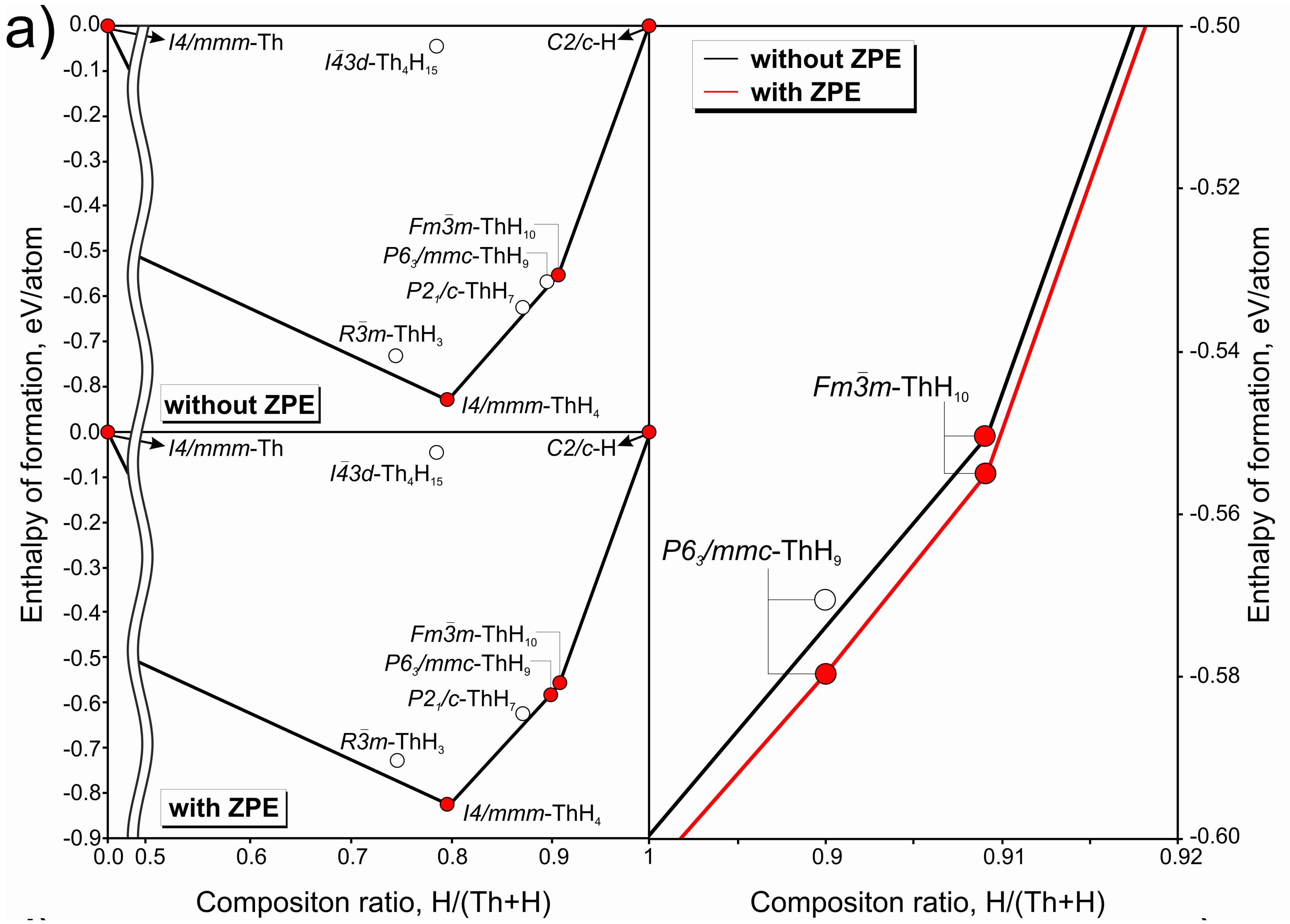
Further heating: 2100 K, 168 GPa, 2 laser impulses

Fmmm-ThH_4 → $P6_3/mmc$-ThH_9





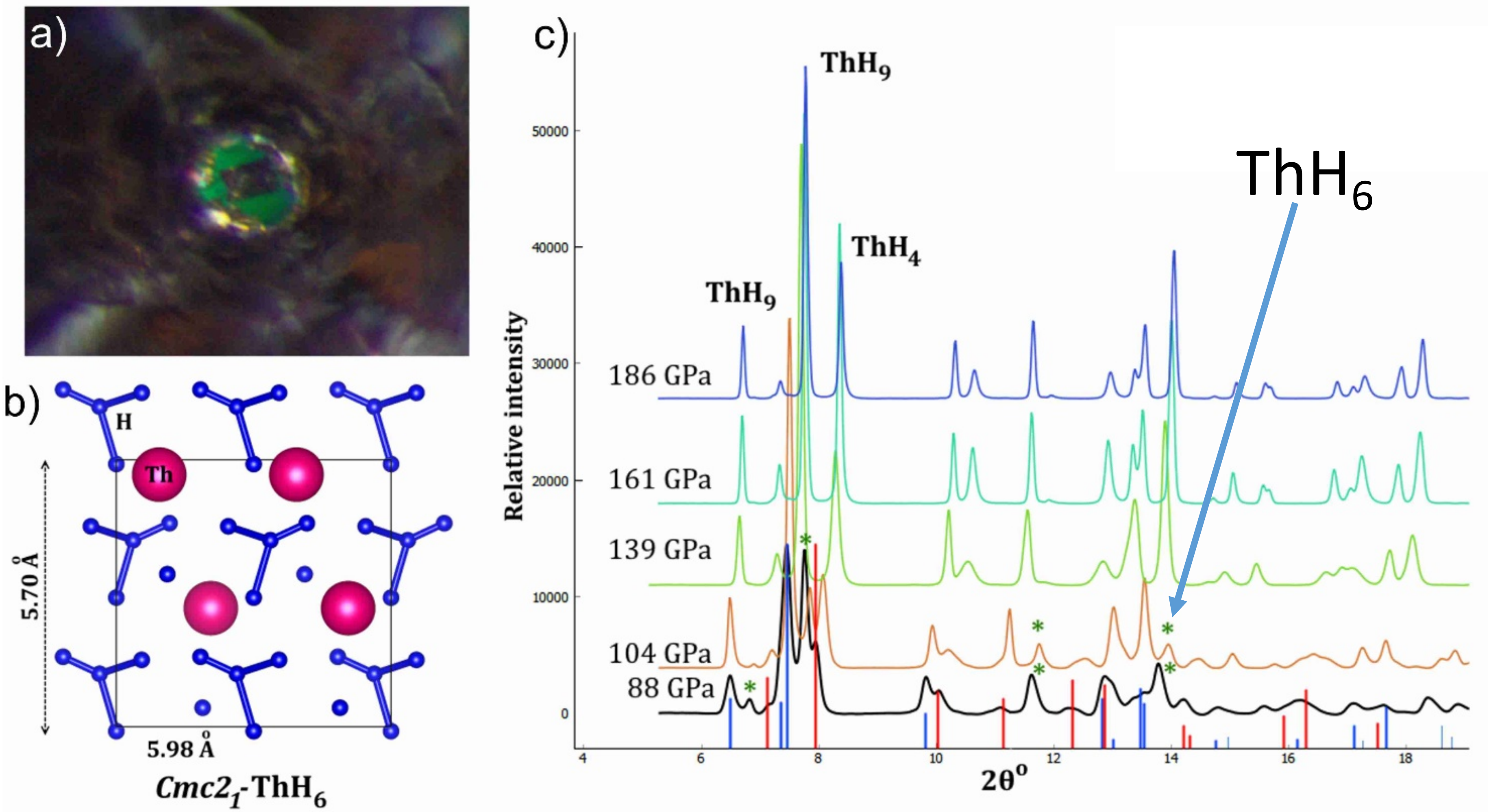
Stability of ThH_9. Effect of ZPE



Synthesis of ThH_6

Reduction of pressure from 168 to 68 GPa

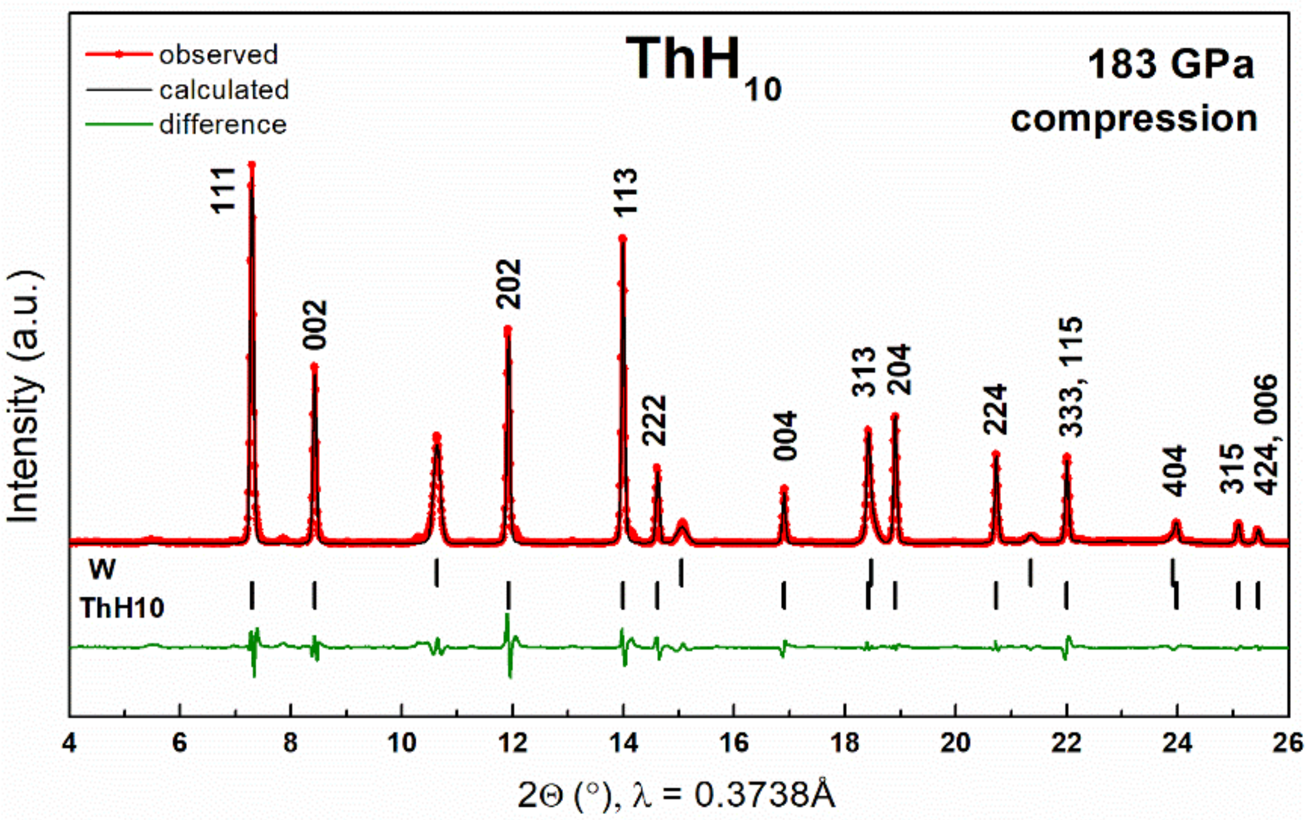
$Fmmm$-ThH_4 + $P6_3/mmc$-ThH_9 → $Cmc2_1$-ThH_6

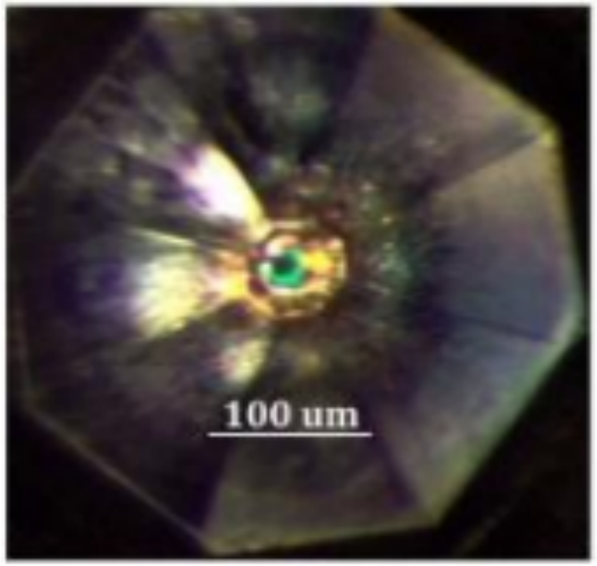


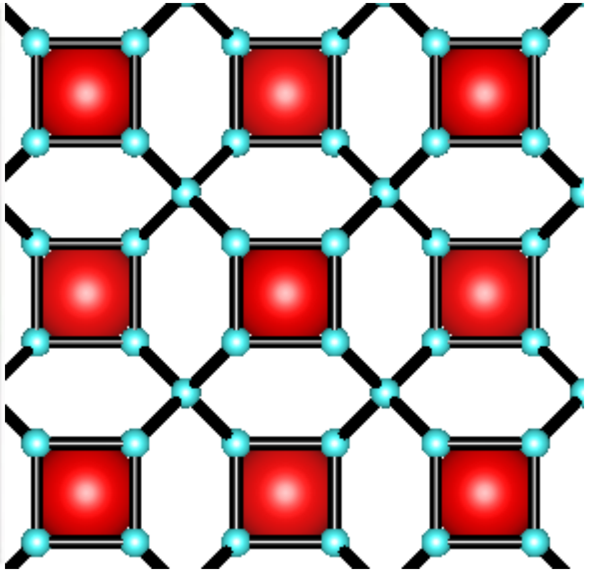
Synthesis of ThH_{10}

The formation of cubic ThH_{10} is observed

183 GPa, 1800 K



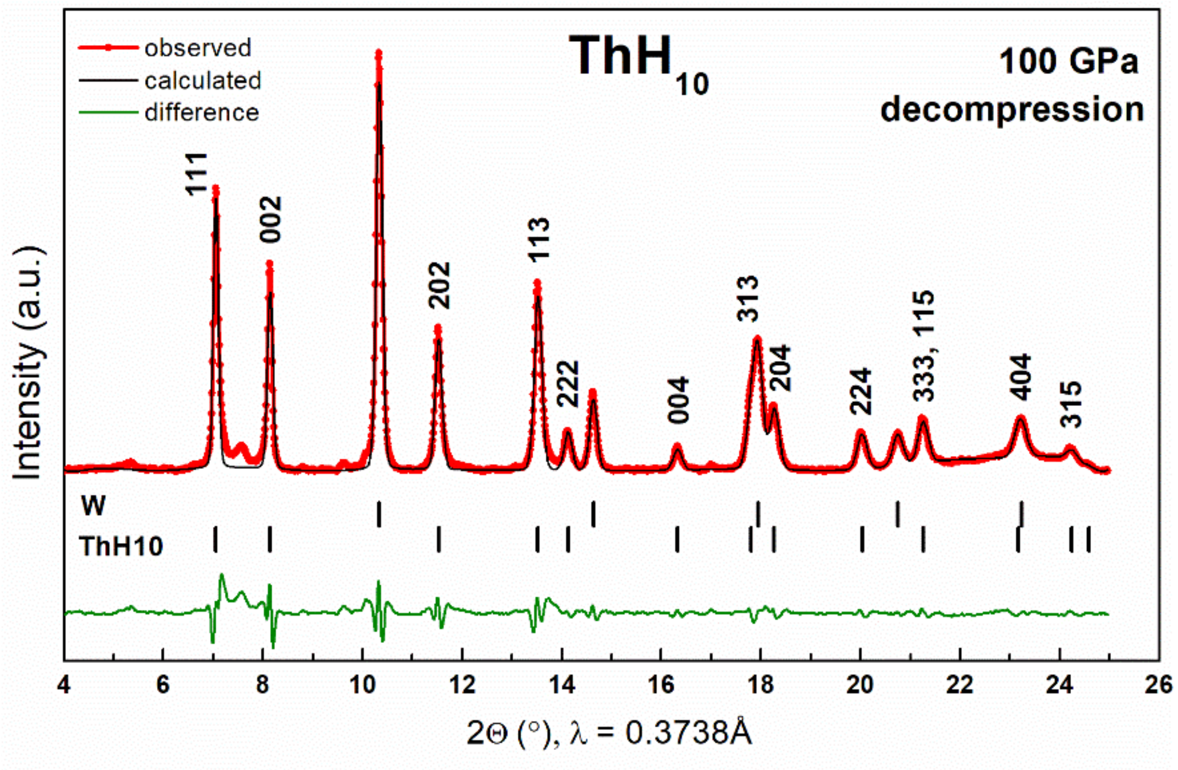


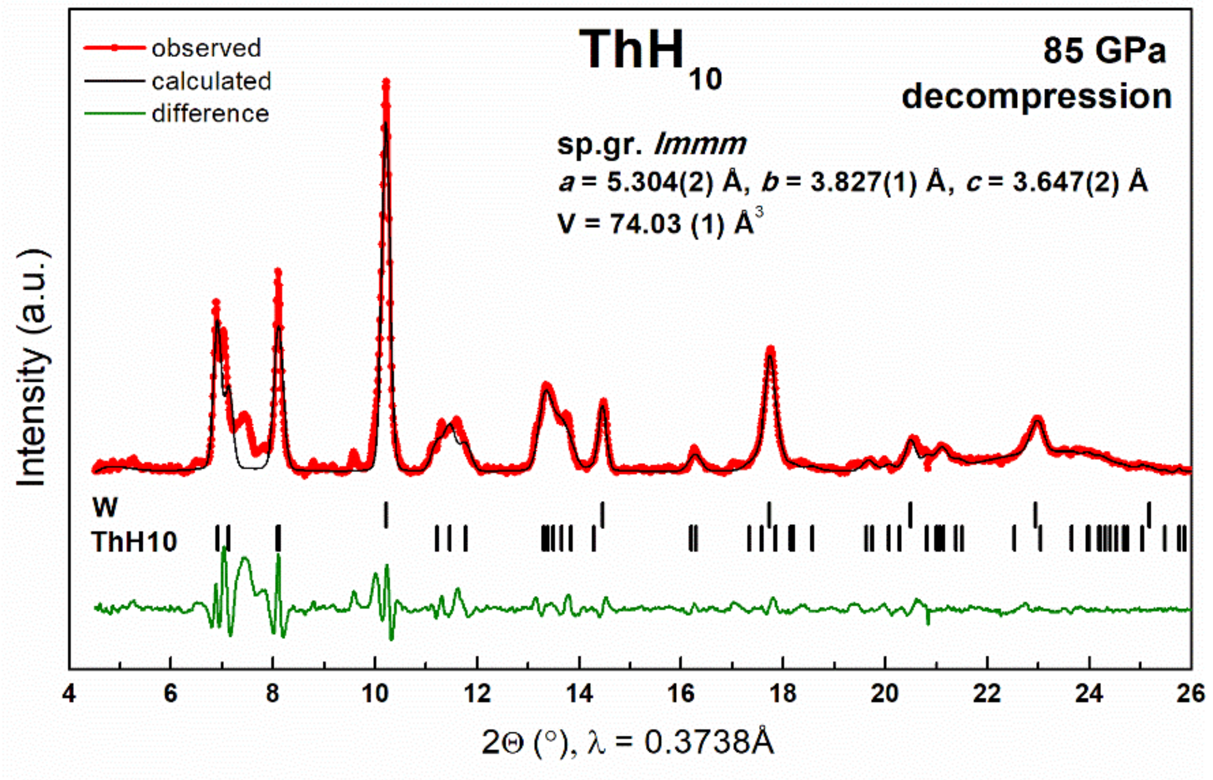


Synthesis of ThH_{10}

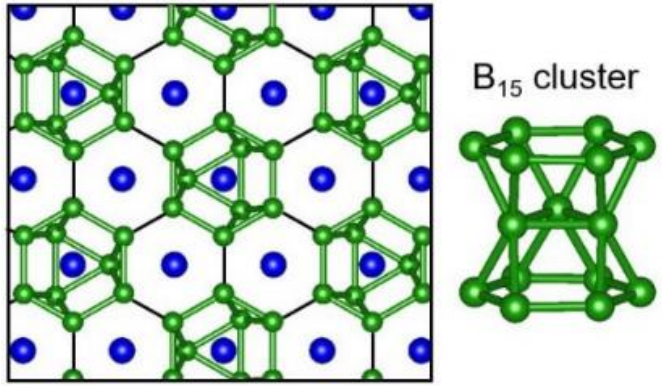
Decompression of ThH10 down to 80 GPa leads to orthorhombic distortion

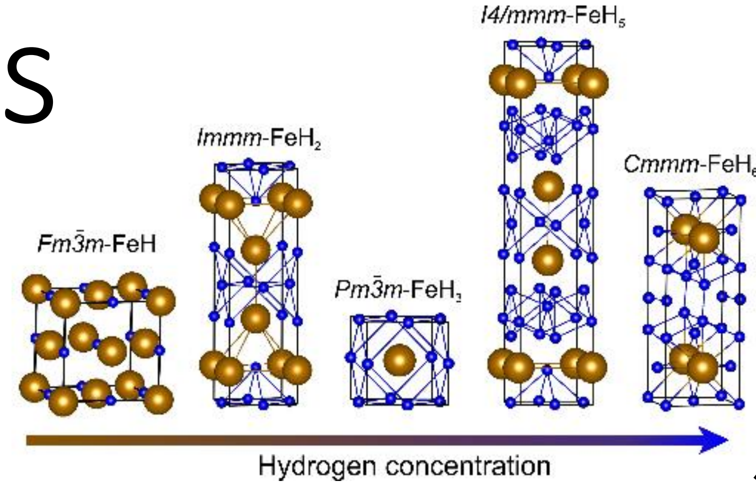
$$Fm\bar{3}m \rightarrow Immm \ \ \rightarrow ThH_9$$

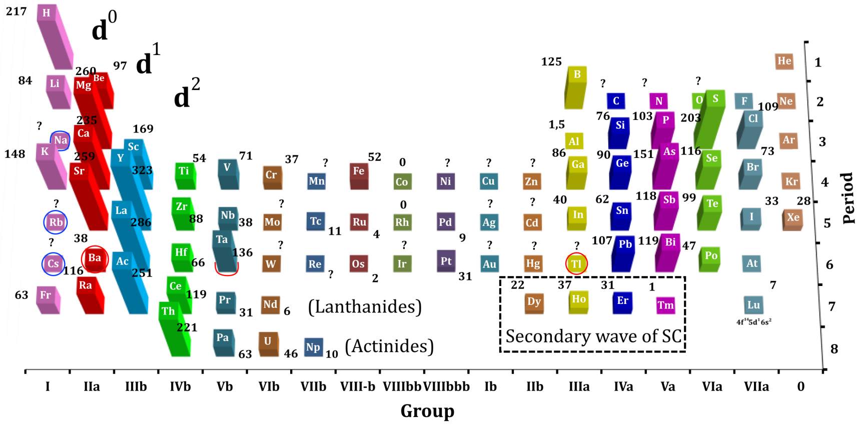


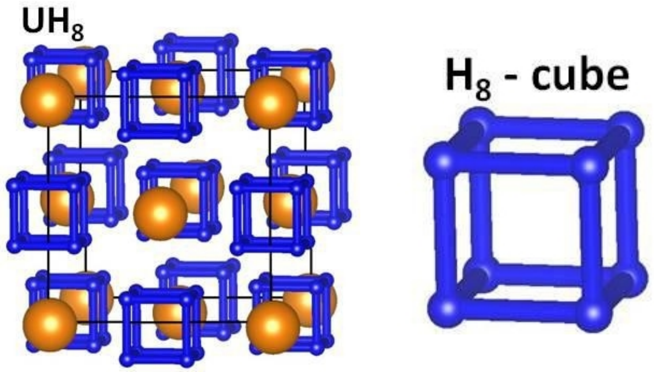


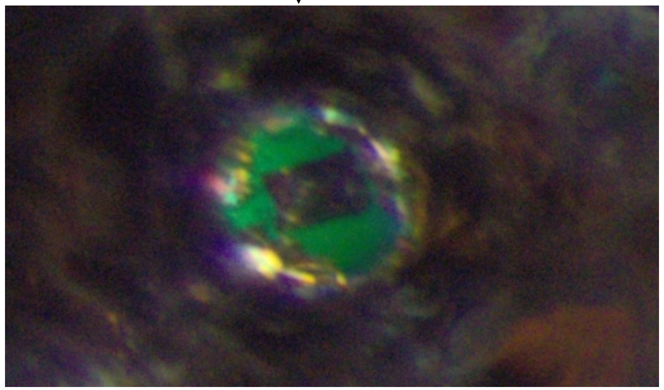
Conclusions

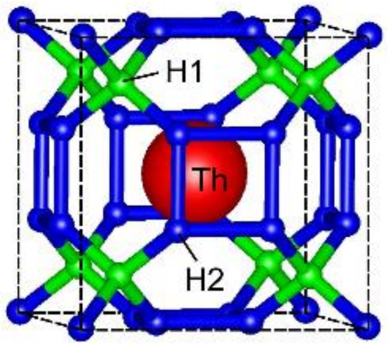


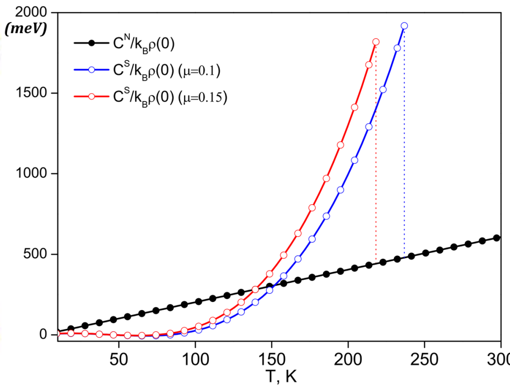


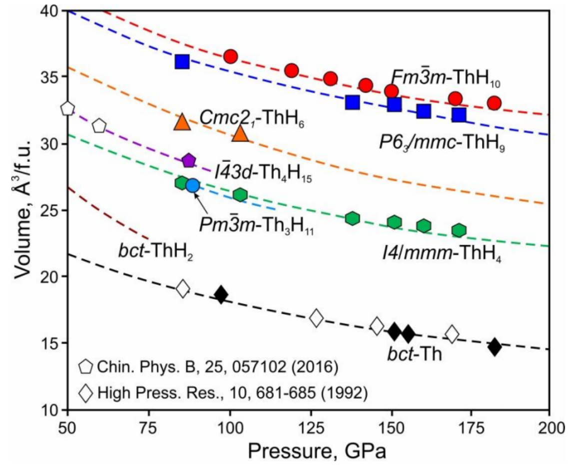












Acknowledgements

A.R. Oganov

V.V. Brazhkin

V.P. Filonenko

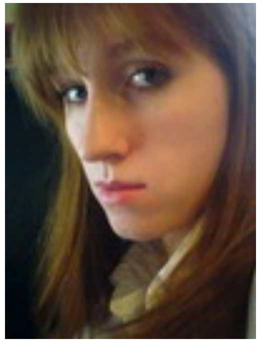
I.A. Troyan

A.A. Osiptsov

A.A. Zakaryan

C. Xie

Y.A. Kvashnina



D.V. Rybkovskiy

I.A. Kruglov

D.V. Semenok

РНФ | Российский научный фонд

№ 16-13-10459 № 17-73-20038

ГАЗПРОМ НЕФТЬ

Skoltech
Skolkovo Institute of Science and Technology

ФОНД СОДЕЙСТВИЯ ИННОВАЦИЯМ

ИНСТИТУТ ФИЗИКИ ВЫСОКИХ ДАВЛЕНИЙ
1958
РОССИЙСКАЯ АКАДЕМИЯ НАУК

ВНИИА

CARNEGIE SCIENCE | Geophysical Laboratory