T-USPEX method for crystal structure prediction at finite temperatures

Supported by the Russian Scientific Foundation grant No. 19072-30043 “Computational materials design laboratory” and
grant No. 19-73-00237 “Development of new methods for computational materials design using machine learning interatomic potentials”

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Crystal structure prediction methods

U_xH_y

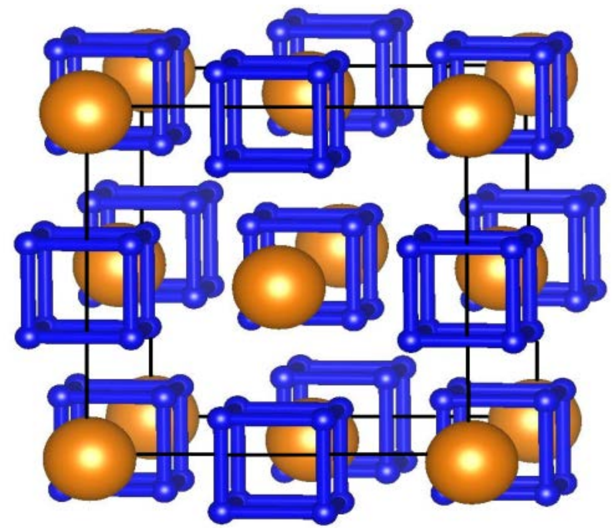
0, 100, ...GPa

T-USPEX

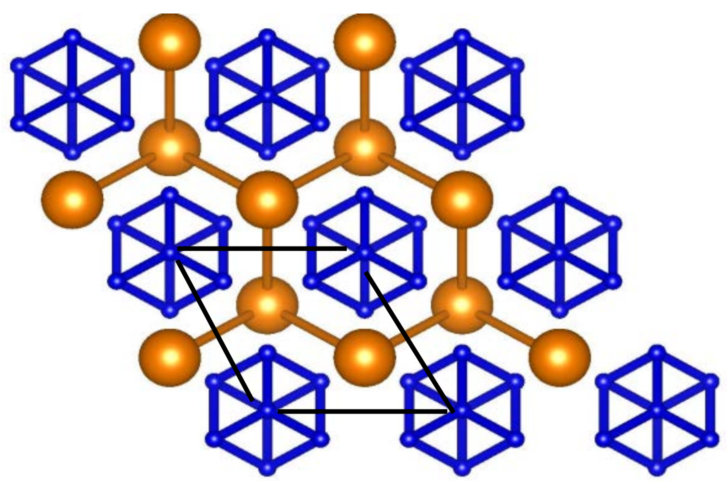
CALYPSO

AIRSS

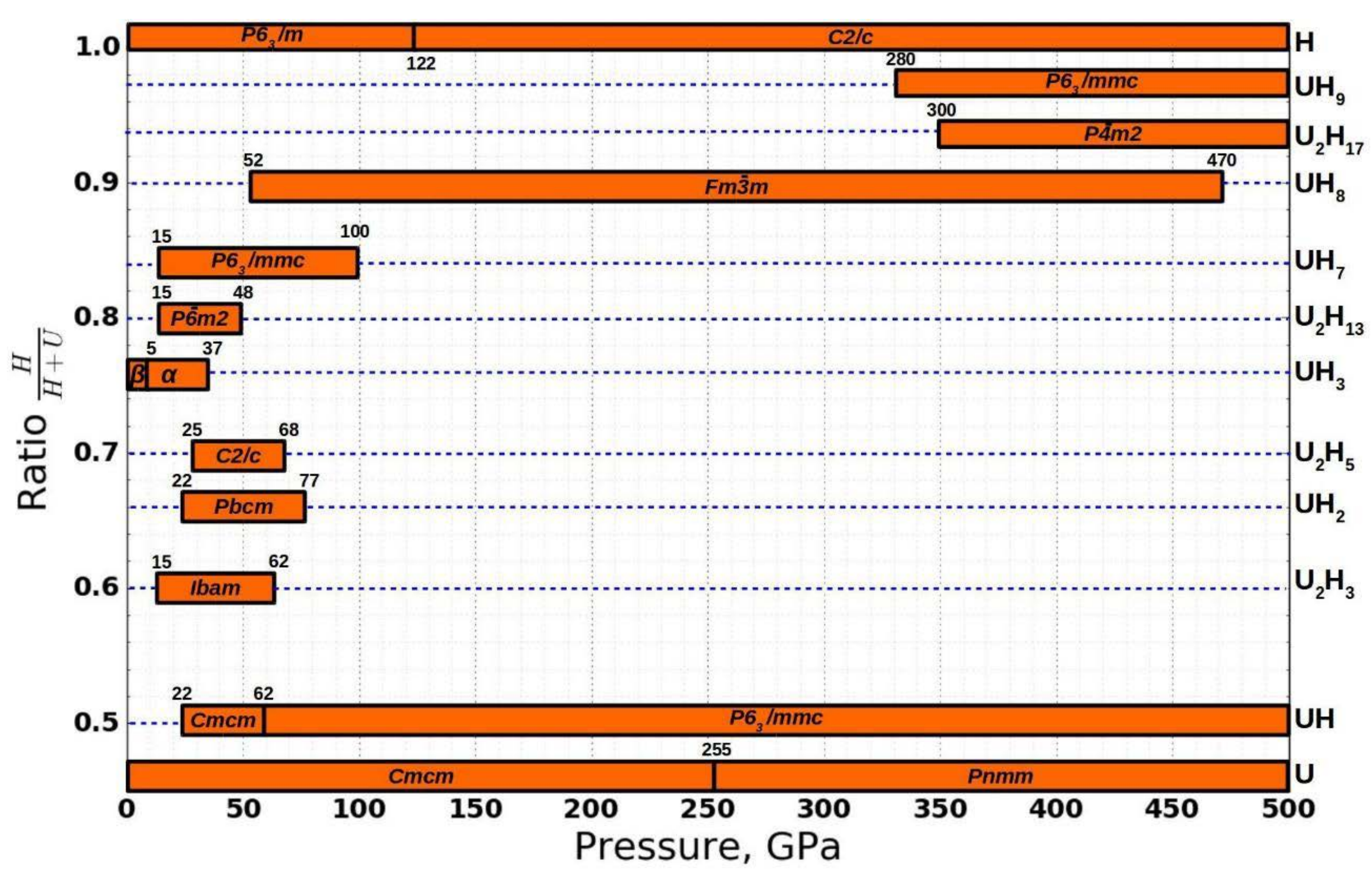
…

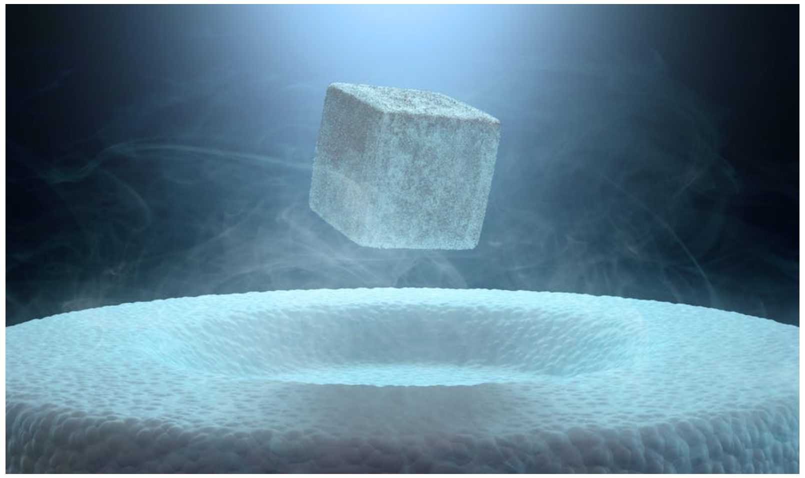


UH$_8$



UH$_7$





Plan of presentation

- **USPEX predictions**:

- BS

- U-H

- **Interatomic (machine learning) potentials:**

- Molecular crystals

- Al and U

- **T-USPEX predictions:**

- Al

- $MgSiO_3$

- WB, WC

- **Conclusions**

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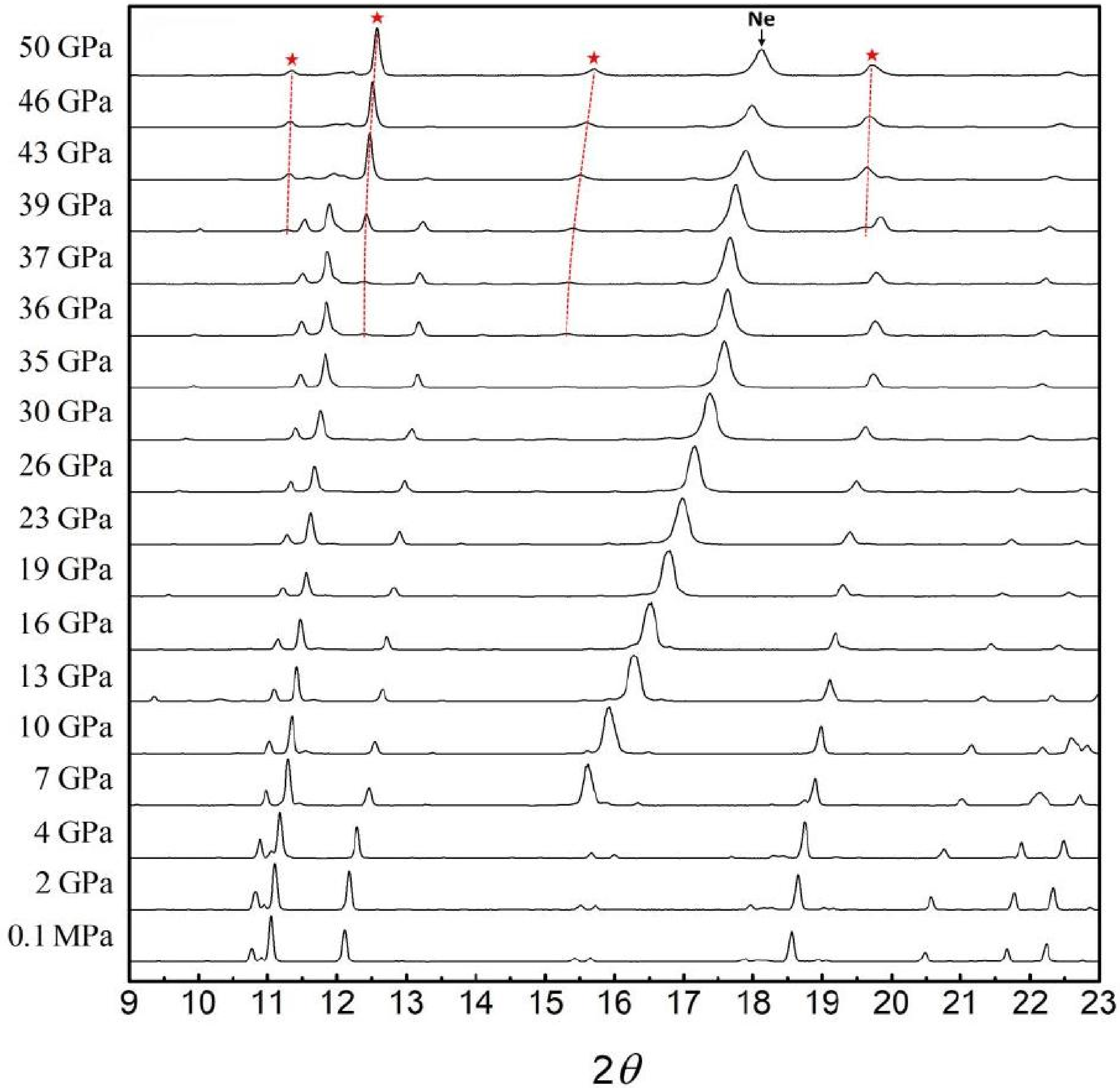
- MgSiO3
- WB, WC
- **Conclusions**

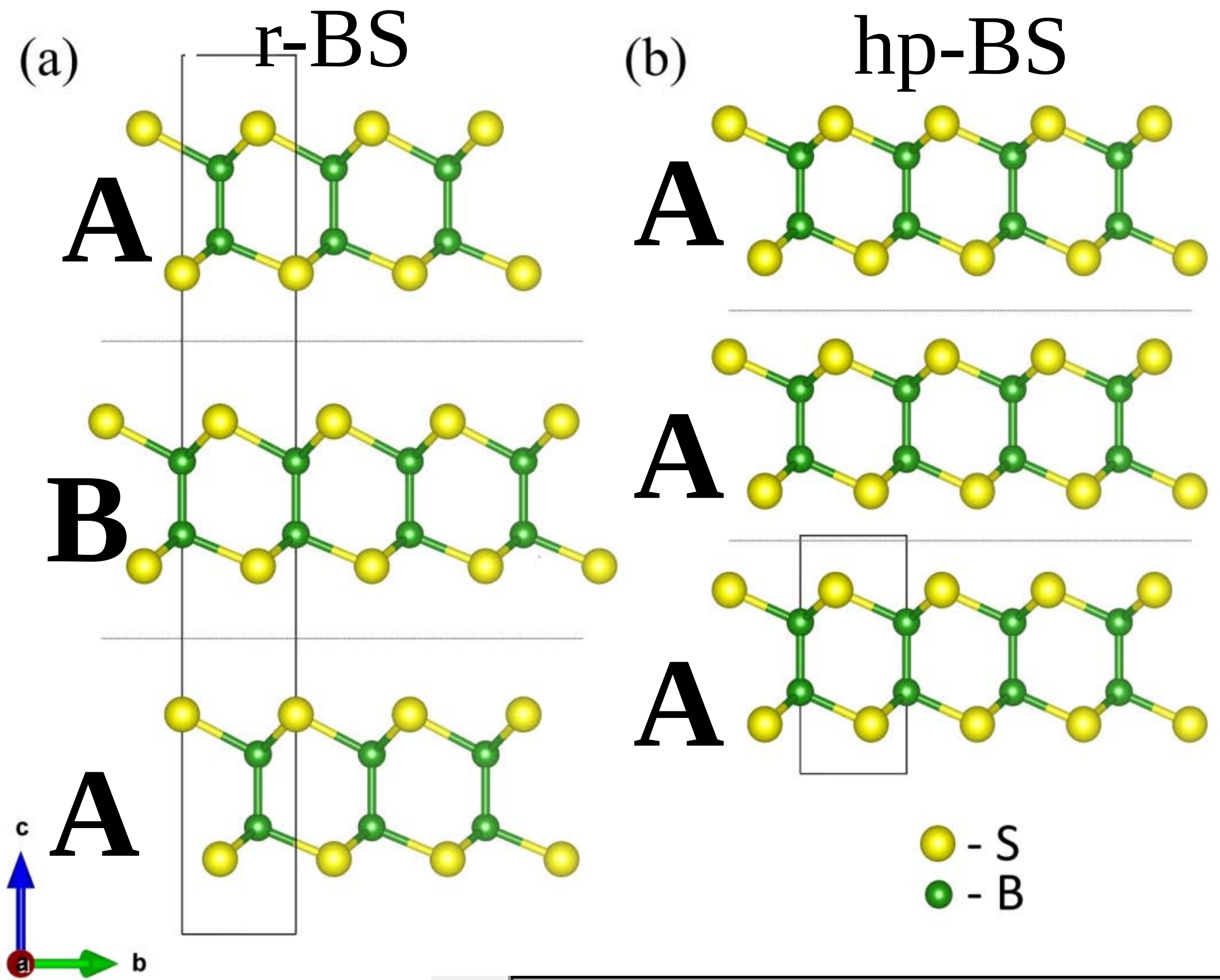
Phase transition in BS at P = 36 GPa

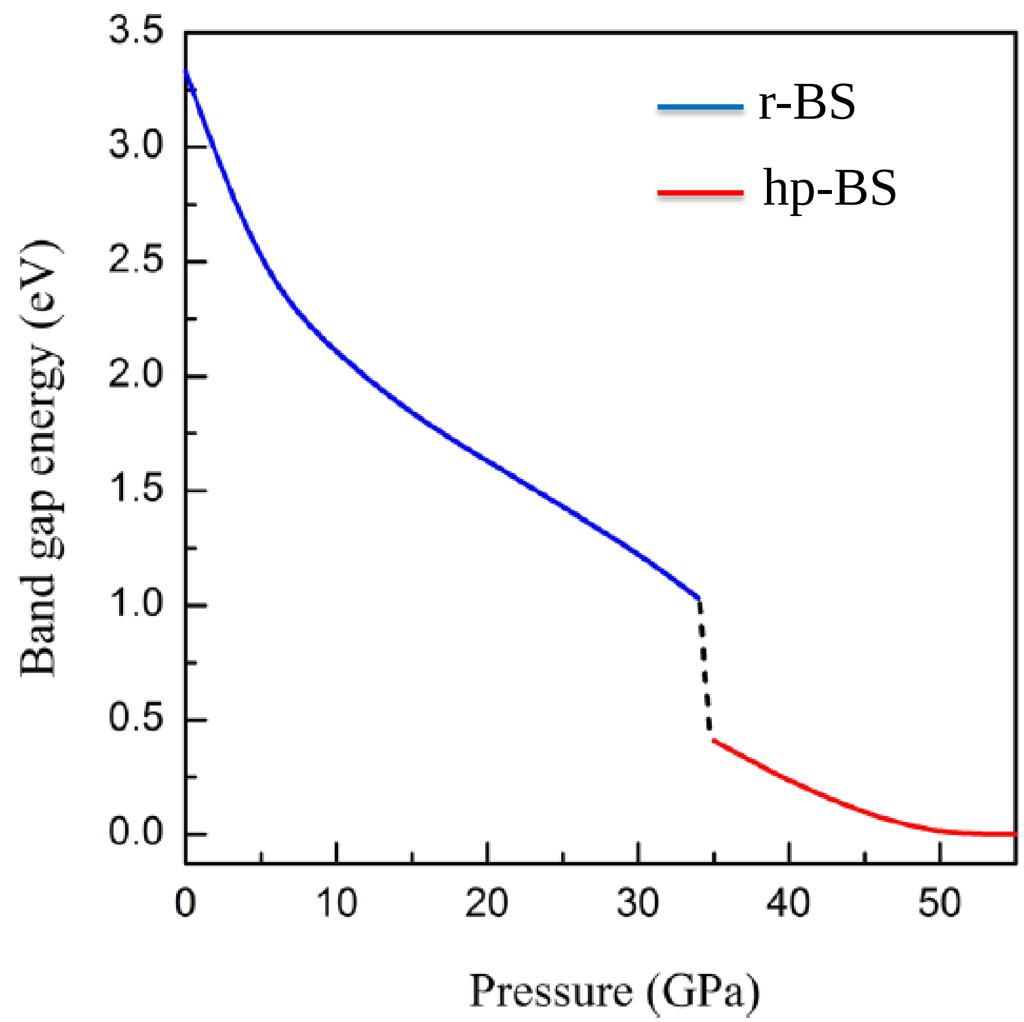
[Sasaki et al, Phys. Status Sol. B , 2001], [Cherednichenko et al, J. App. Phys., 2015]

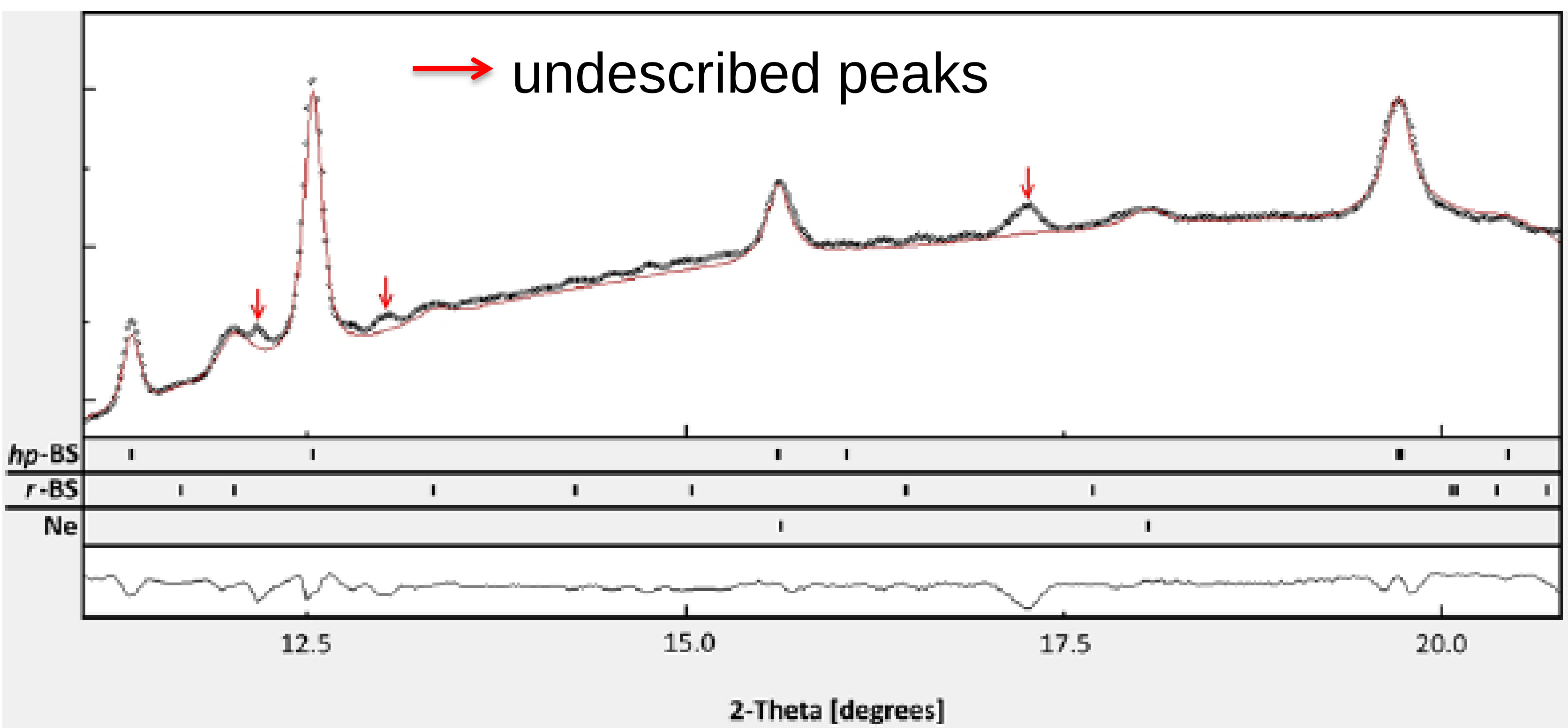
BS is a $A^{III}B^{IV}$-type semiconductor (like Ga(In)S(Se))



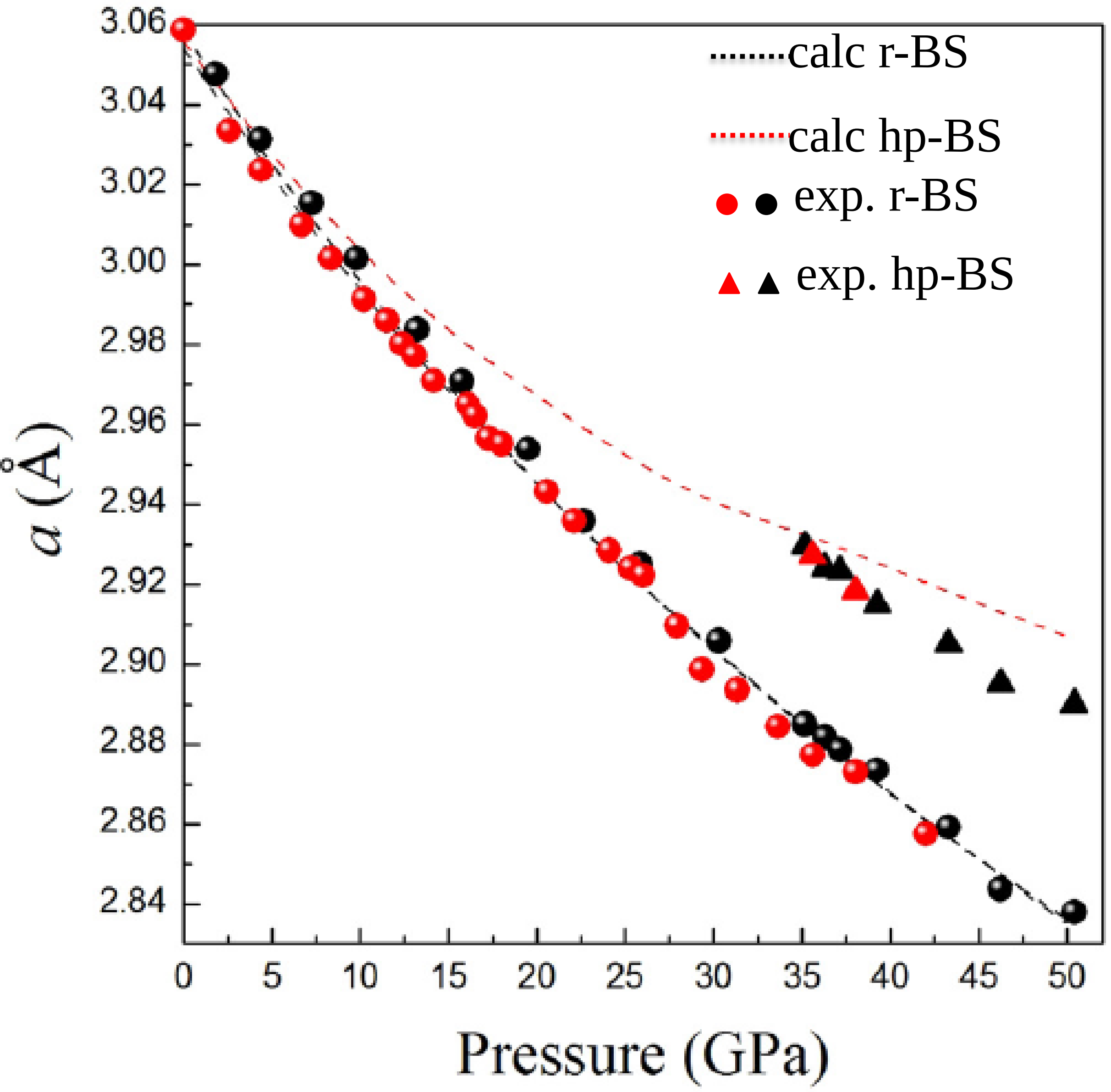
New high-pressure phase of BS

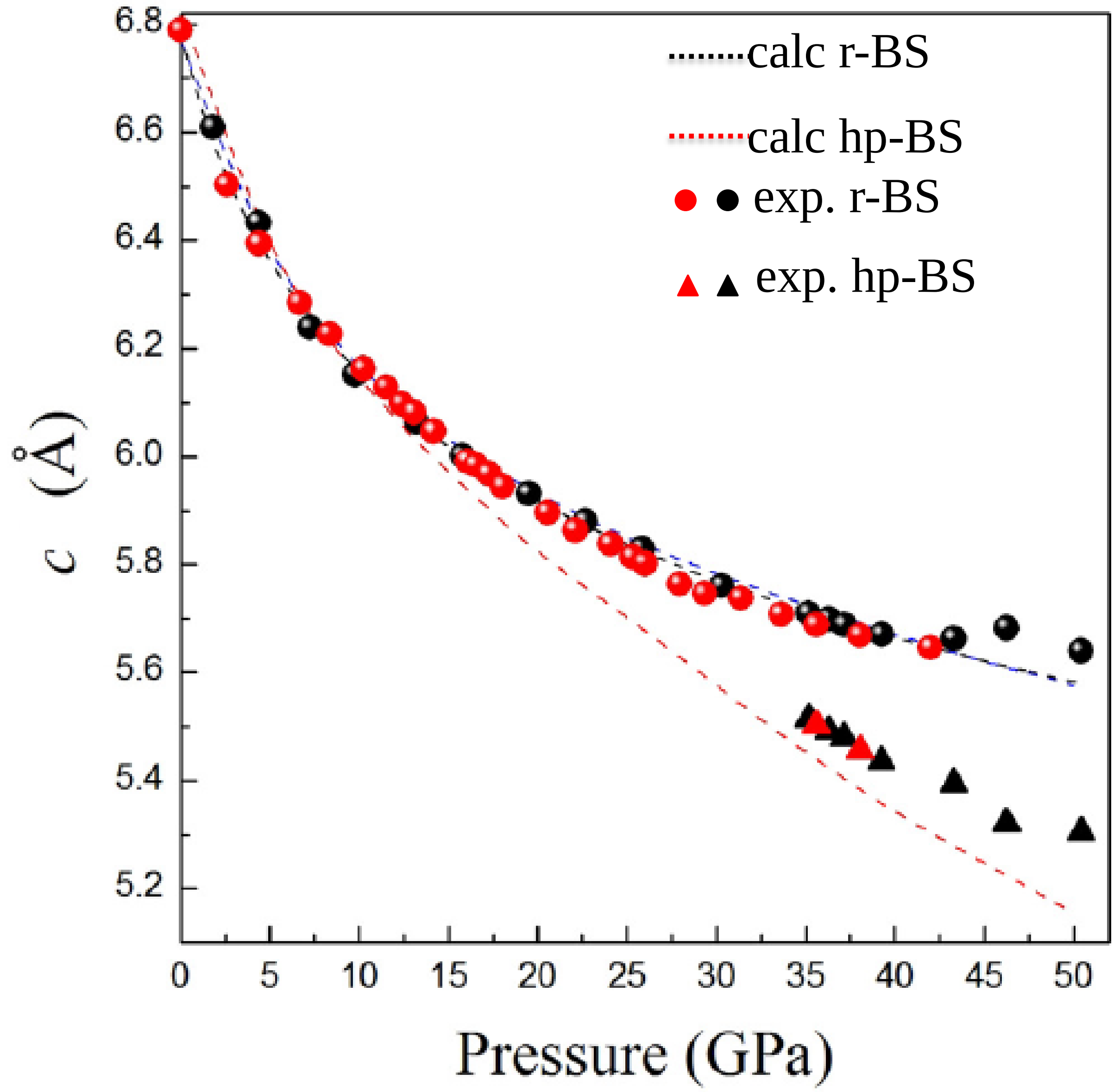






Lattice parameters of BS



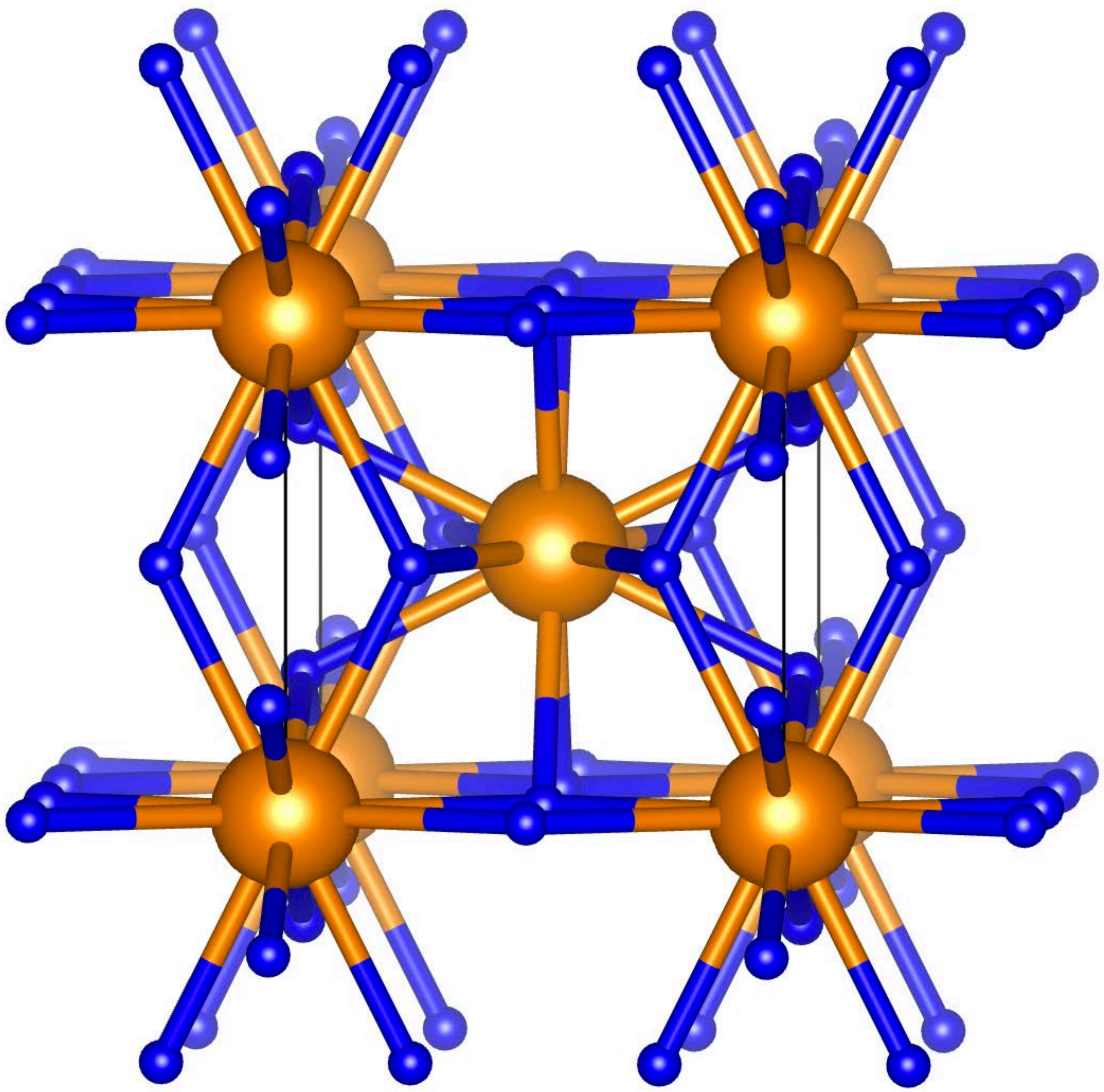


Experimental and theoretical lattice parameters of BS phases are in good agreement with each other

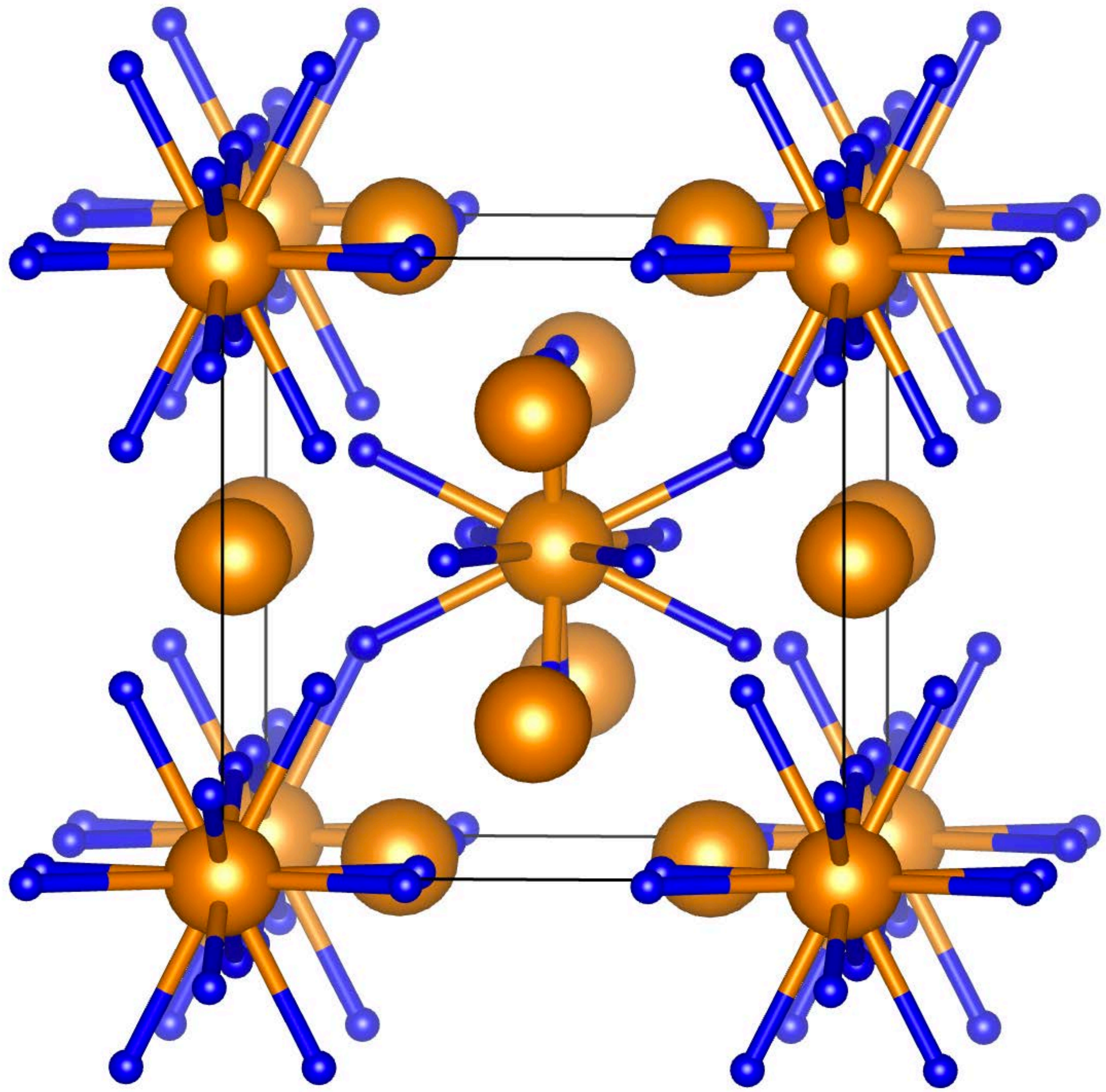
[Cherednichenko, Kruglov et al, JAP, 2018]

Uranium hydrides

αUH_3

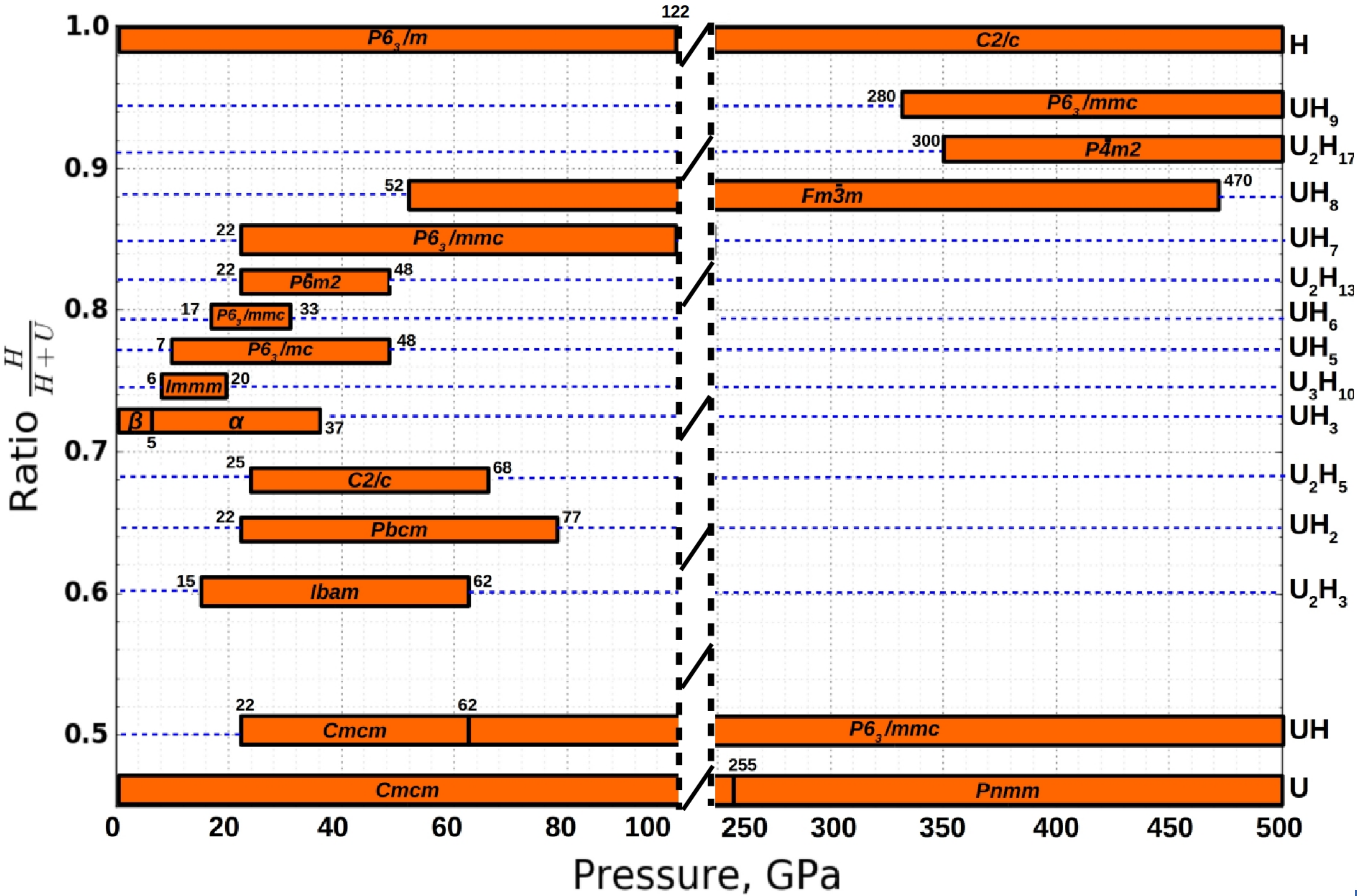


βUH_3

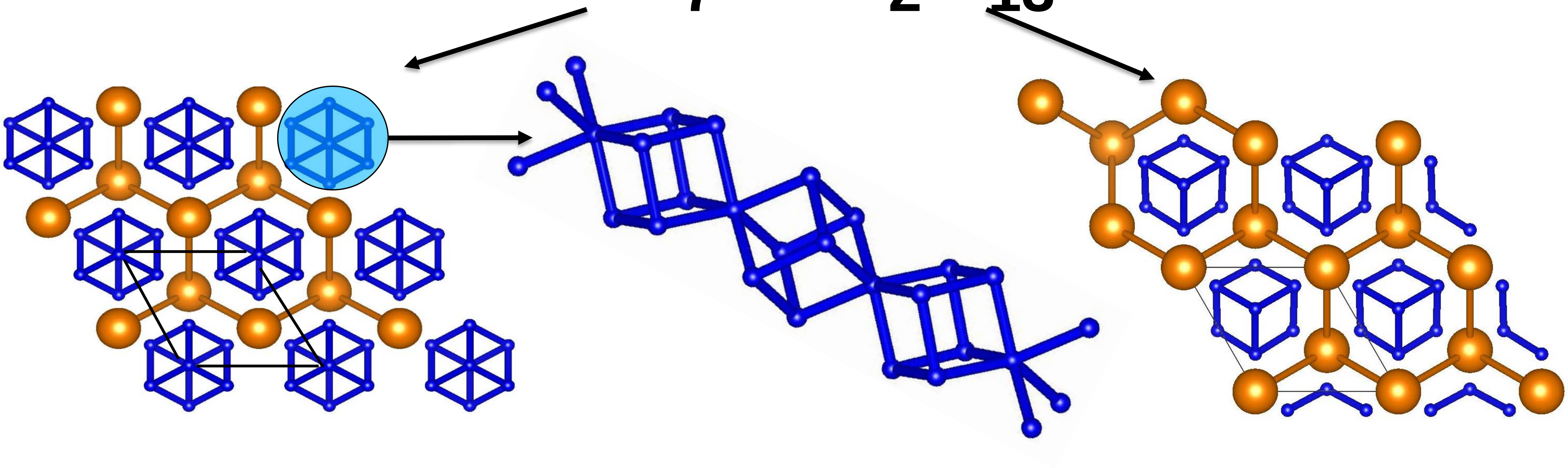


Are there any other uranium hydrides at higher pressures?

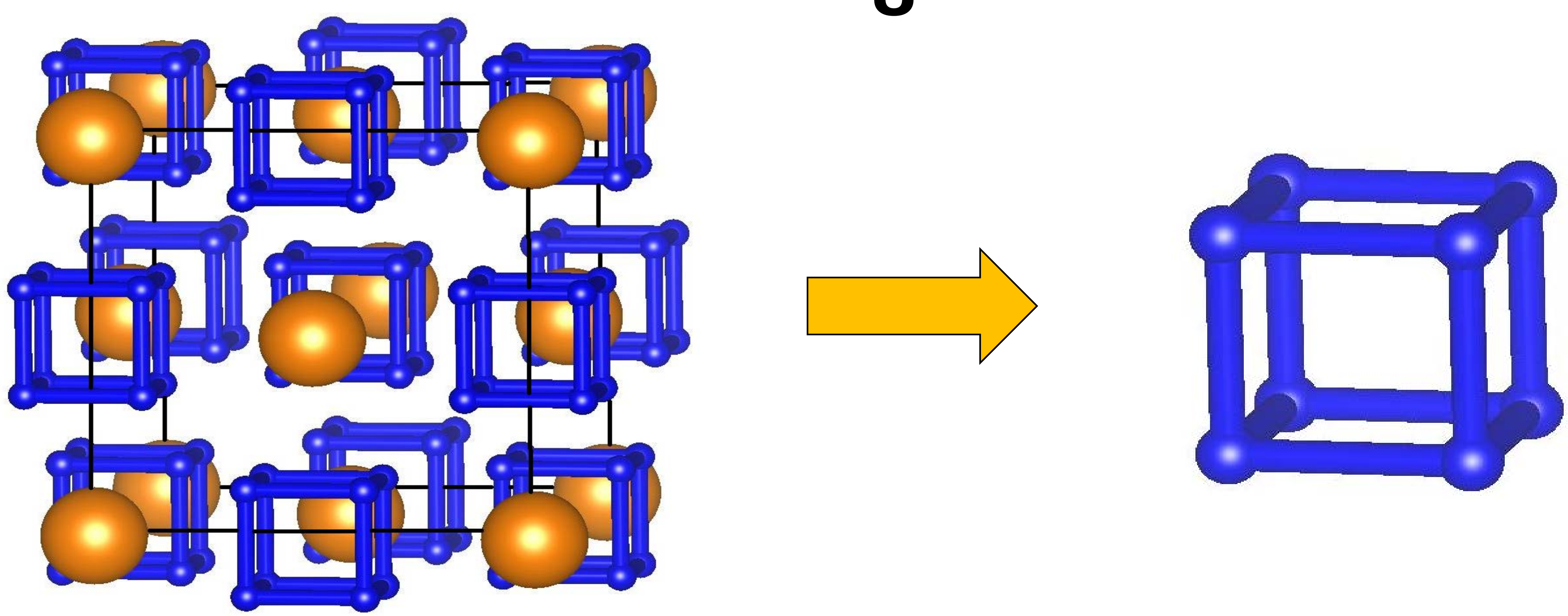
Phase diagram of U-H



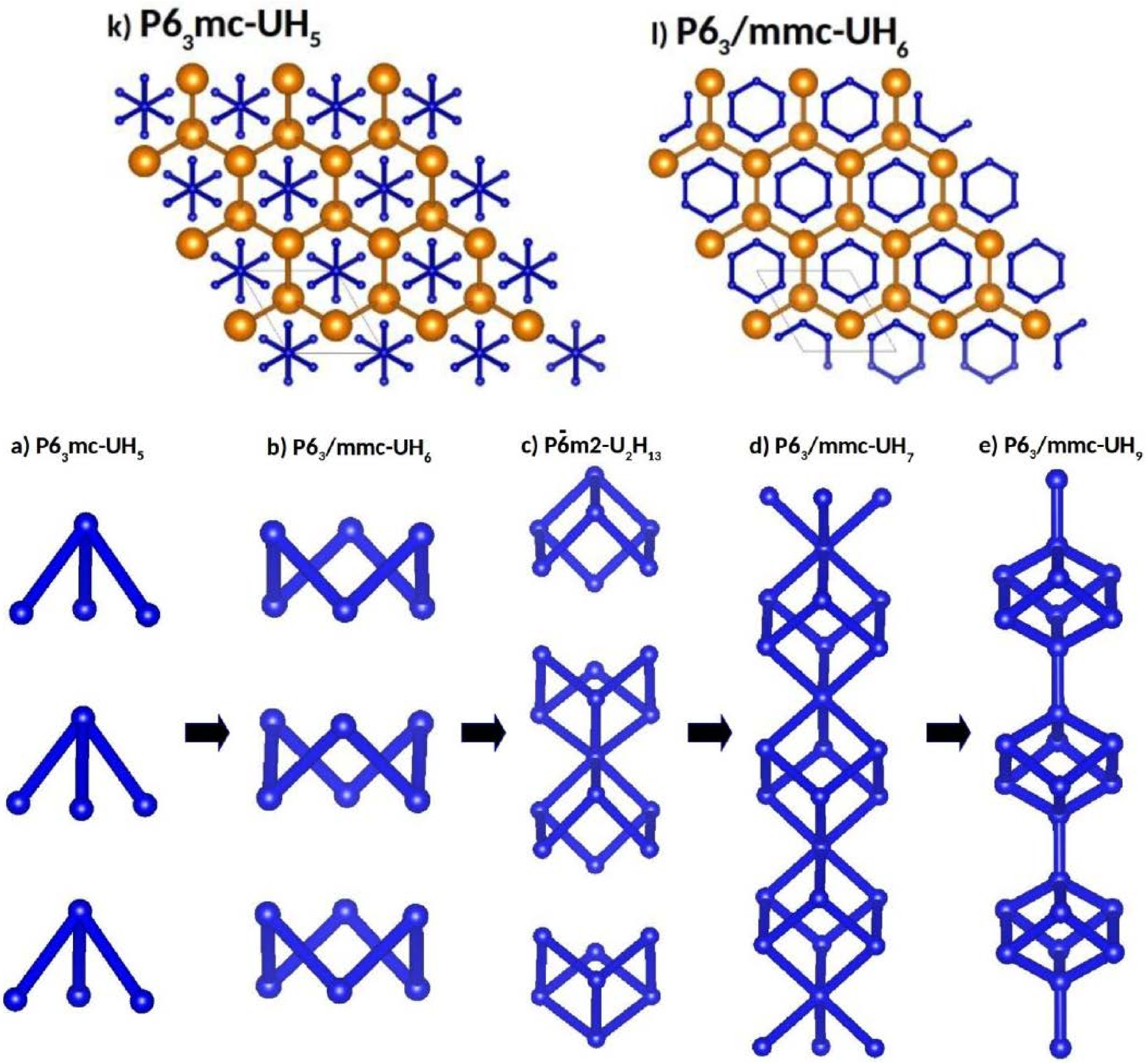
UH_7 и U_2H_{13}



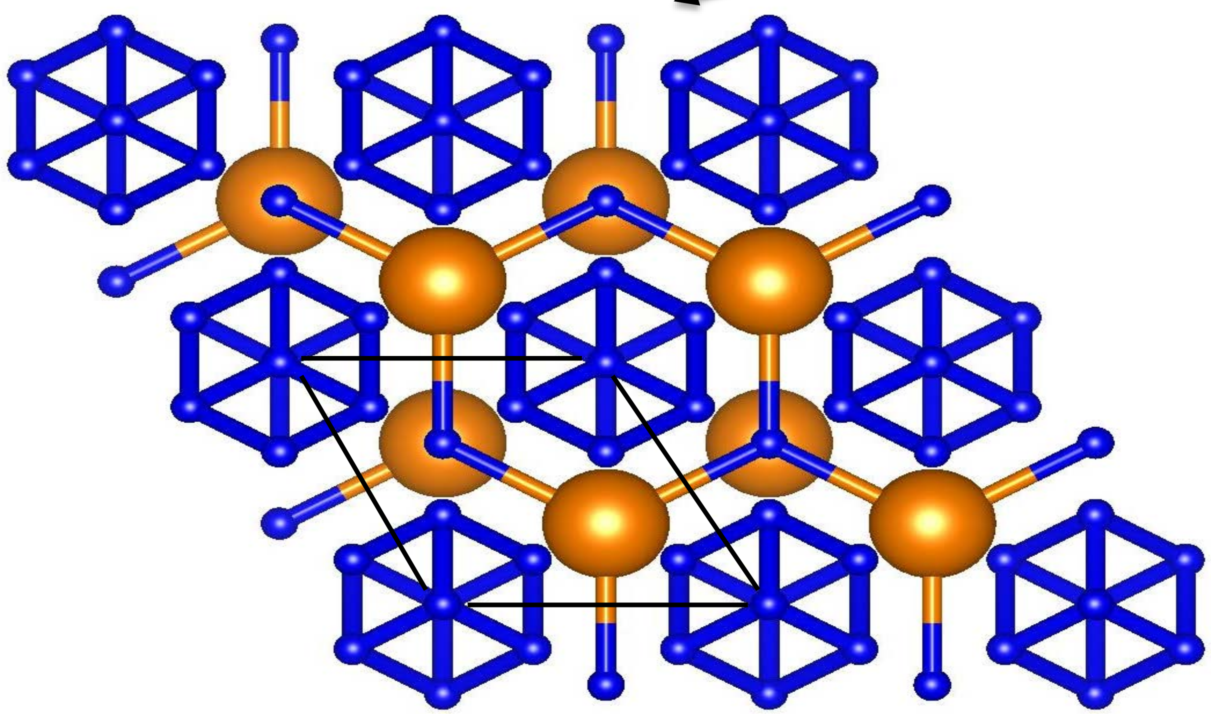
UH_8

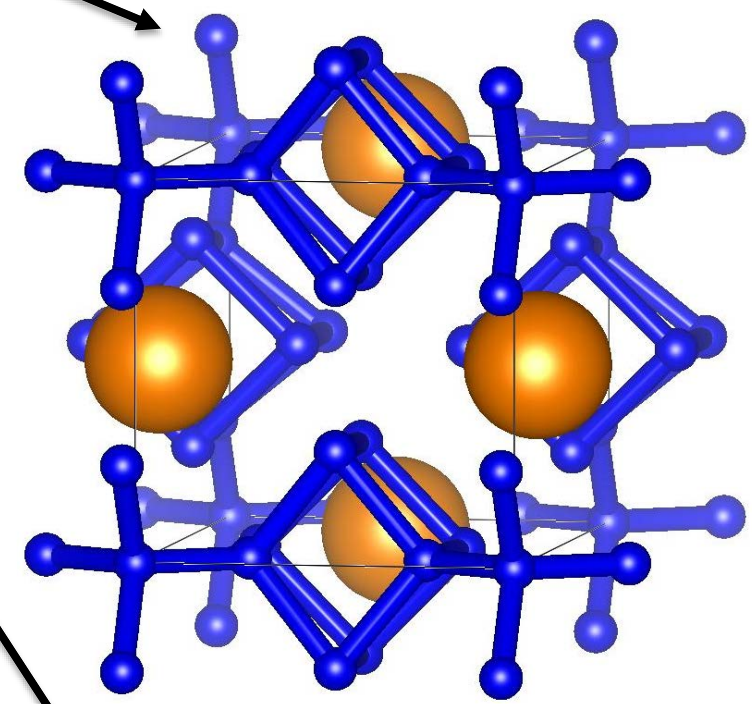


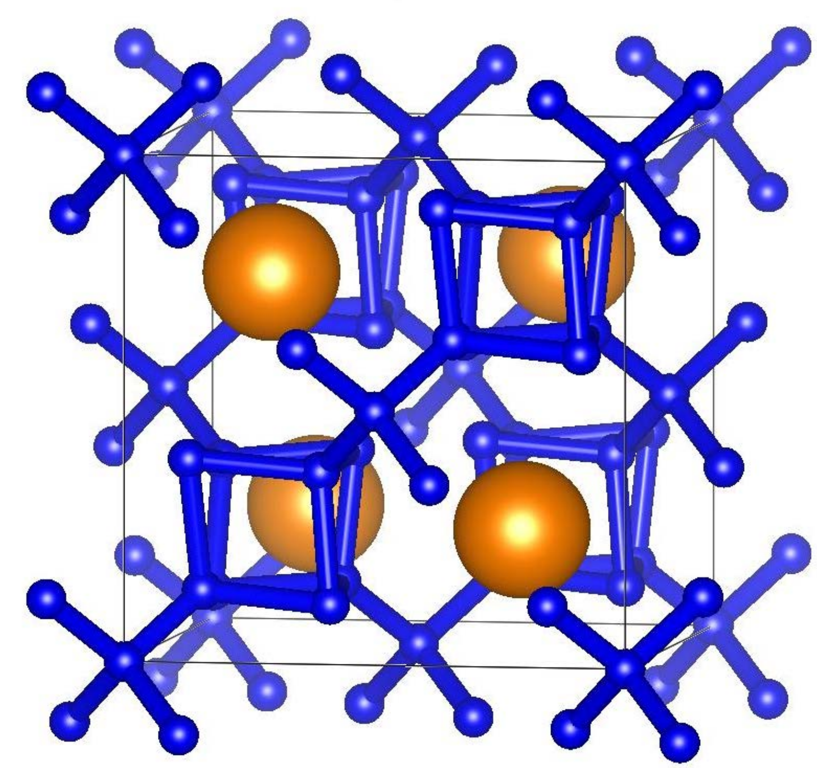
UH_5 и UH_6


k) P6₃mc-UH₅
l) P6₃/mmc-UH₆
a) P6₃mc-UH₅
b) P6₃/mmc-UH₆
c) P-6m2-U₂H₁₃
d) P6₃/mmc-UH₇
e) P6₃/mmc-UH₉

UH_9 и U_2H_{17}



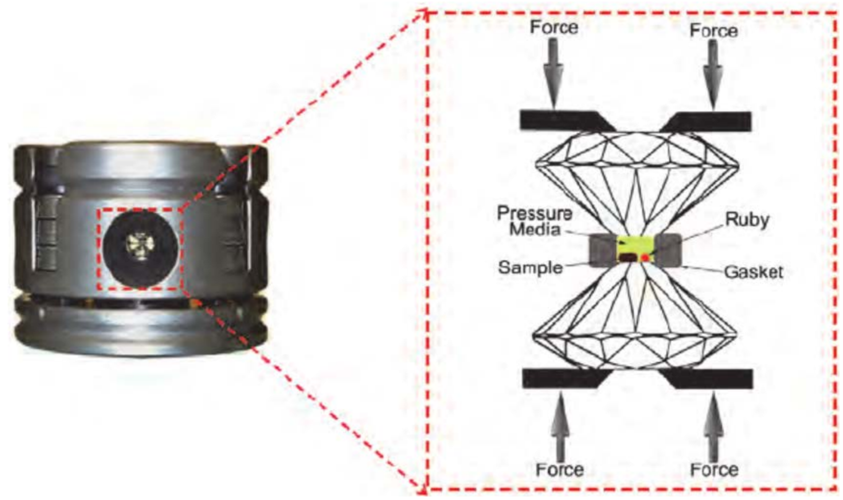


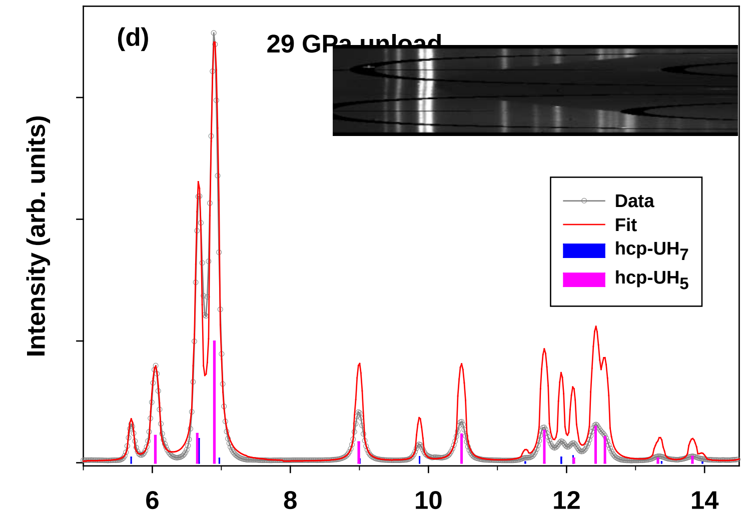


Phase	Space group	P, GPa	ω_{log}, K	λ	T_c, K
UH_7	$P\,6_3/mmc$	20	873.8	0.83	54.1 43.7
		0	764.9	0.95	65.8 56.7
UH_8	$Fm\bar{3}m$	50	873.7	0.73	33.3 23.4
		0	450.3	1.13	55.2 46.2
UH_9	$P\,6_3/mmc$	300	933.4	0.67	31.2 19.9

Experimental synthesis of $UH_{5,7,8-9}$

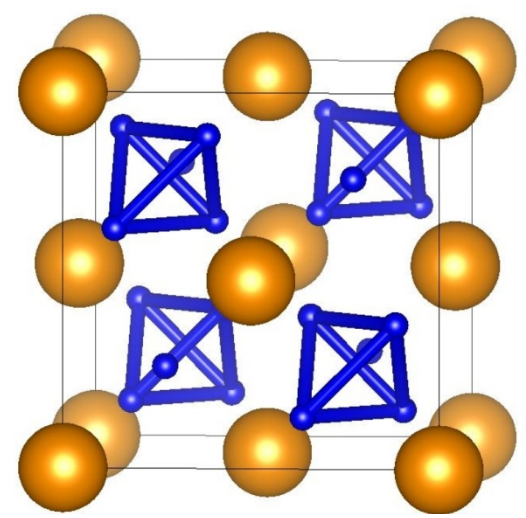
$U+H_2$





0 GPa: mixture of α- & β-UH_3

5 – 38 GPa: fcc UH_5



31 (22) GPa – : hcp UH_7

48 (52) GPa – : fcc UH_{8-9}

29 GPa – ?: hcp UH_5

P

P

[Kruglov et al, Science Advances, 2018]

Experimental synthesis of UH_x

Synthesis of UH_7 and UH_8 superhydrides: Additive-volume alloys of uranium and atomic metal hydrogen down to 35 GPa

PHYSICAL REVIEW B **102**, 014107 (2020)

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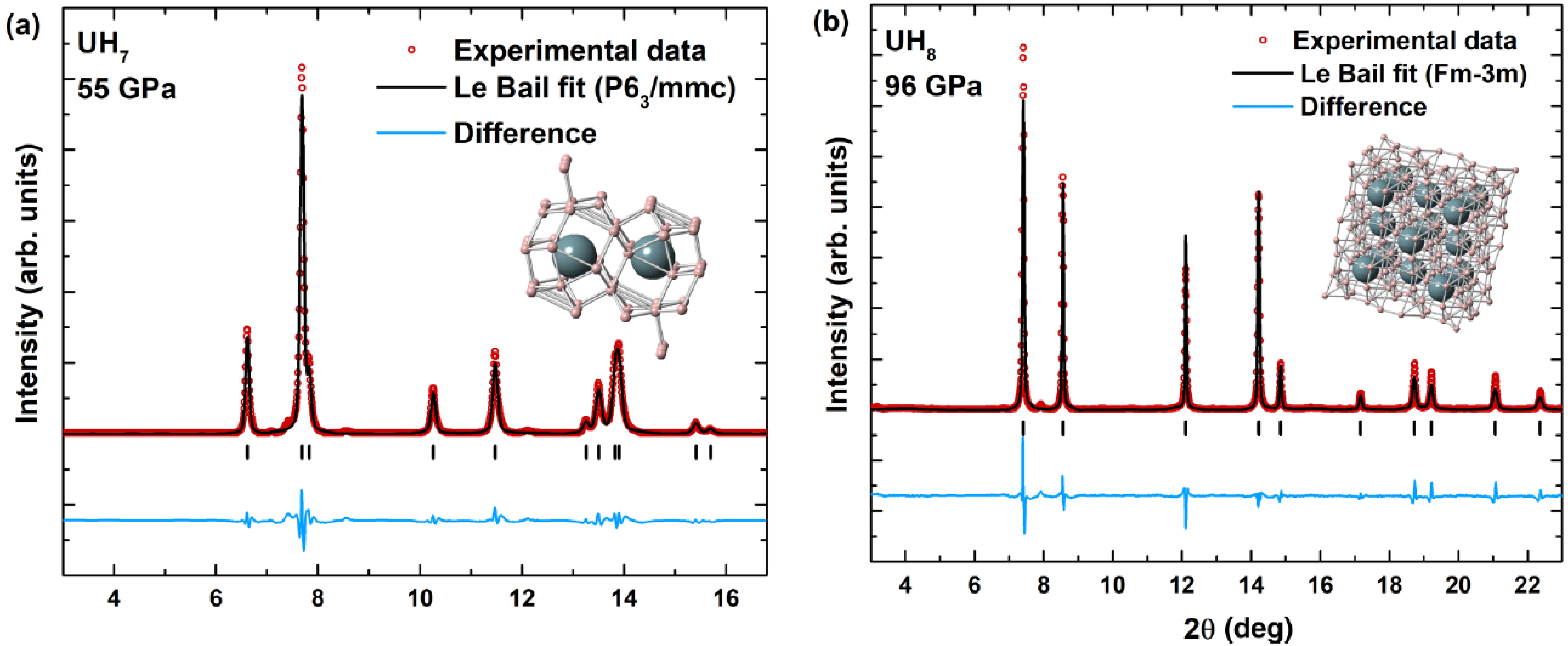
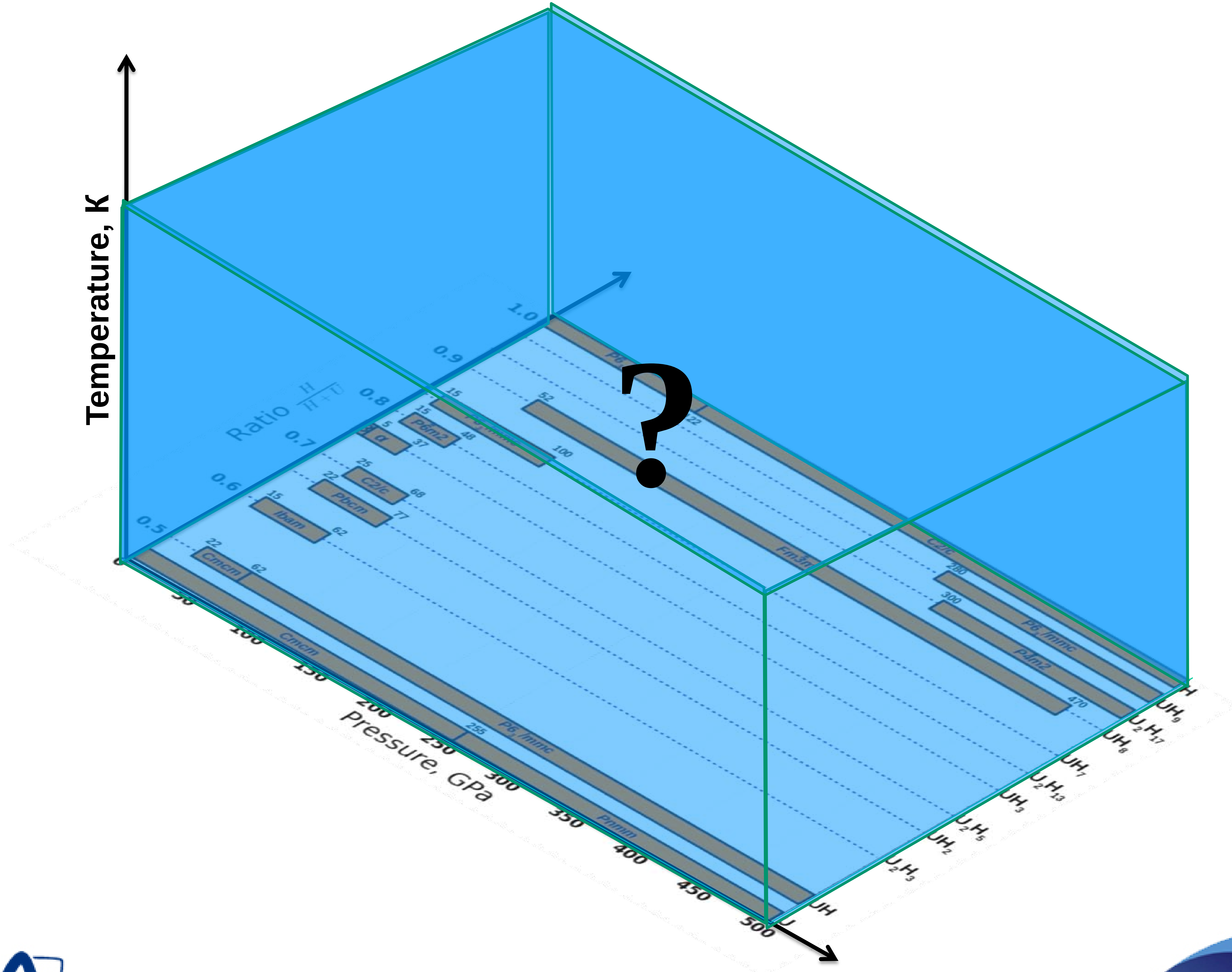
[2]*CEA, DAM, DIF, F-91297 Arpajon, France*

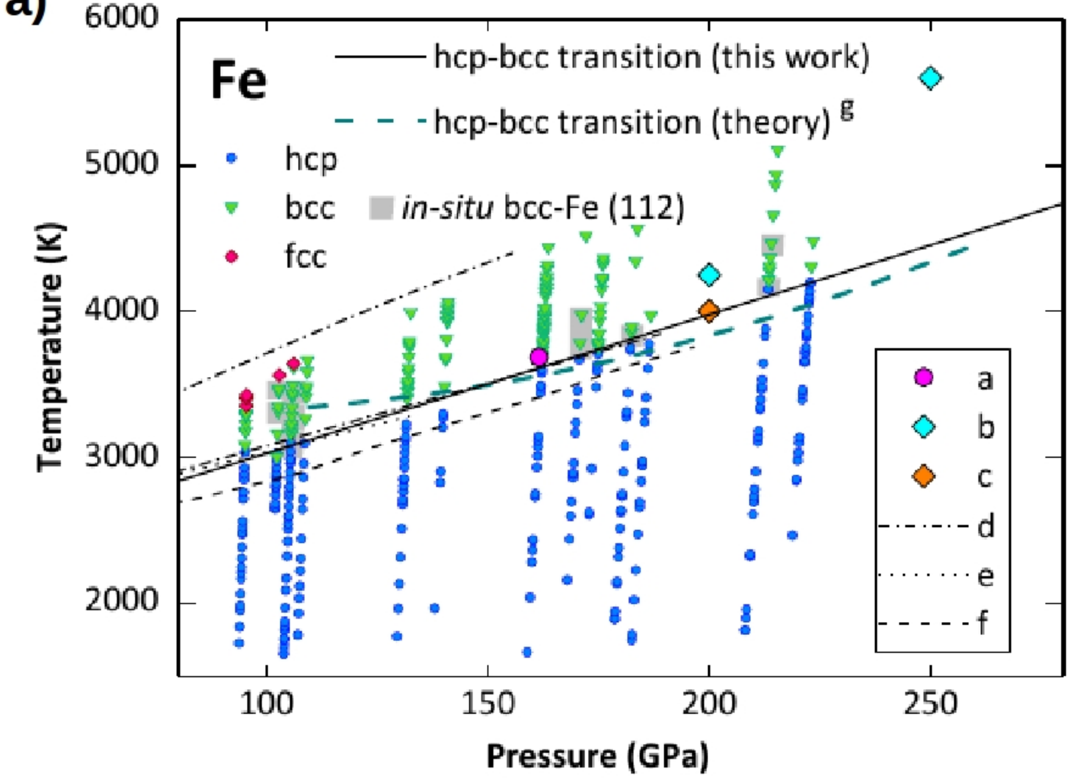




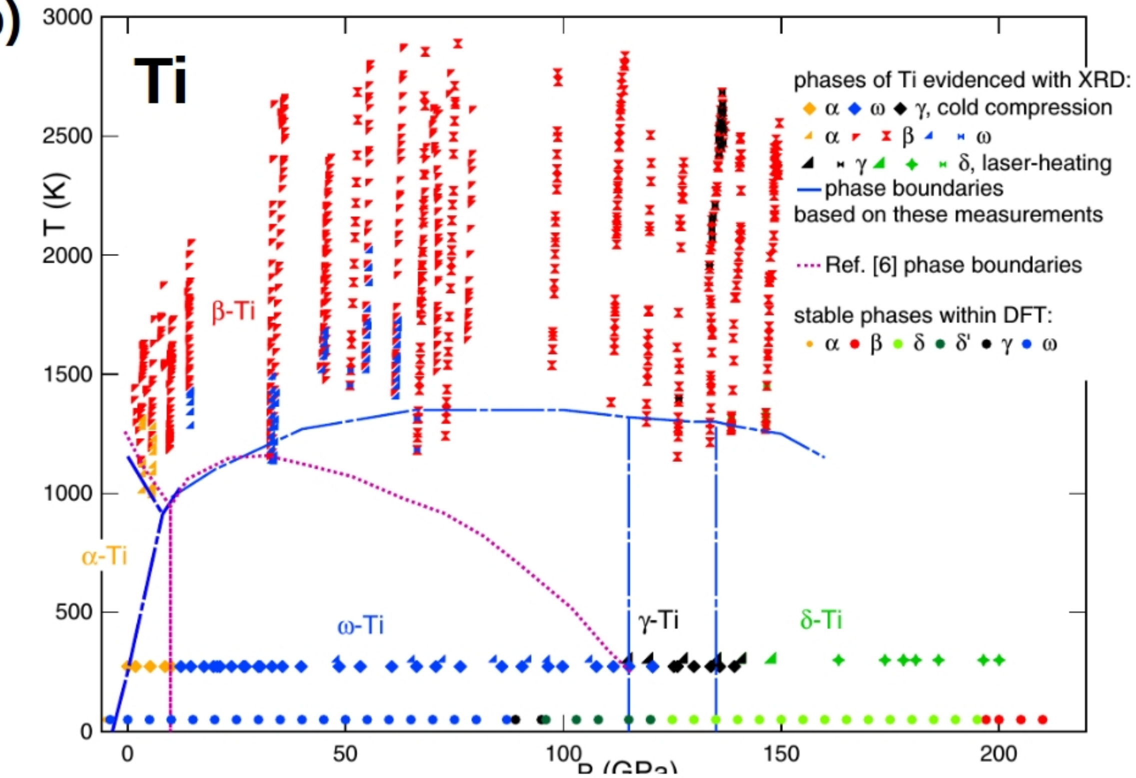
Temperature, K
?
Ratio
1.0
0.9
0.8
0.7
0.6
0.5
Pressure, GPa
50
100
150
200
250
300
350
400
450
500
Cmcm
Ibam
Pbcm
C2/c
P6m2
Fm3m
C2/c
P4m2
Pnmm
UH
U

High-temperature phases

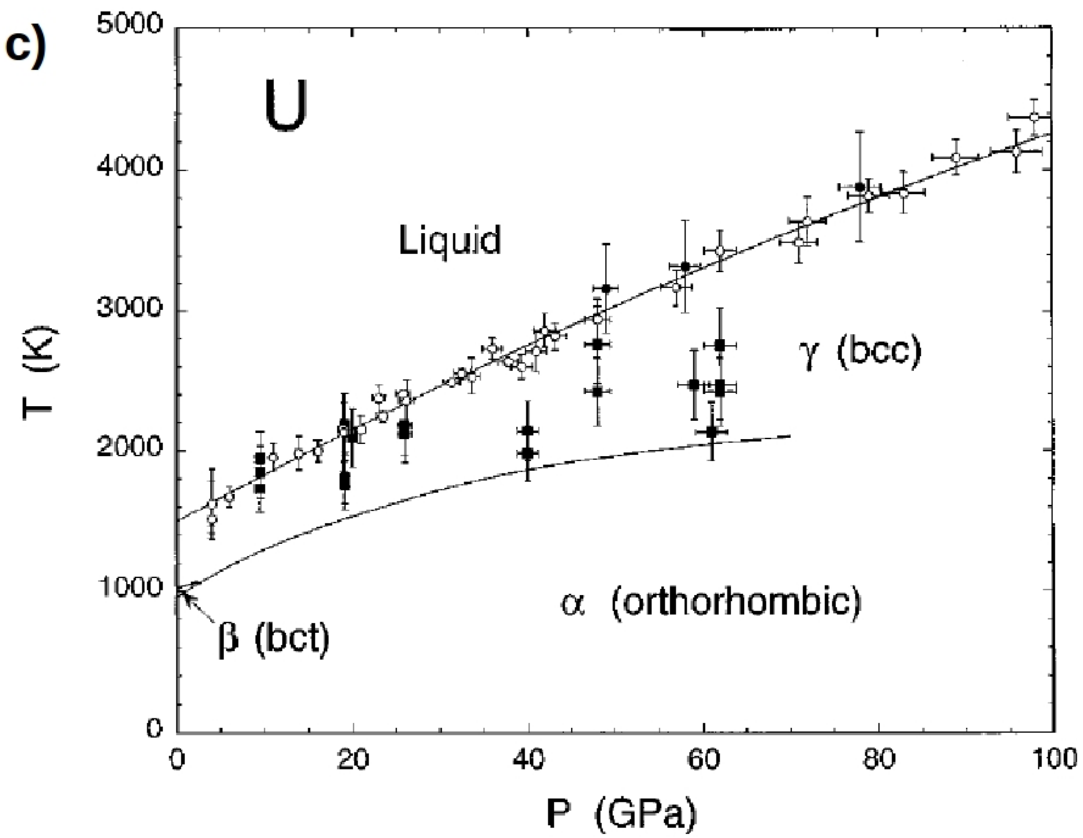
a)



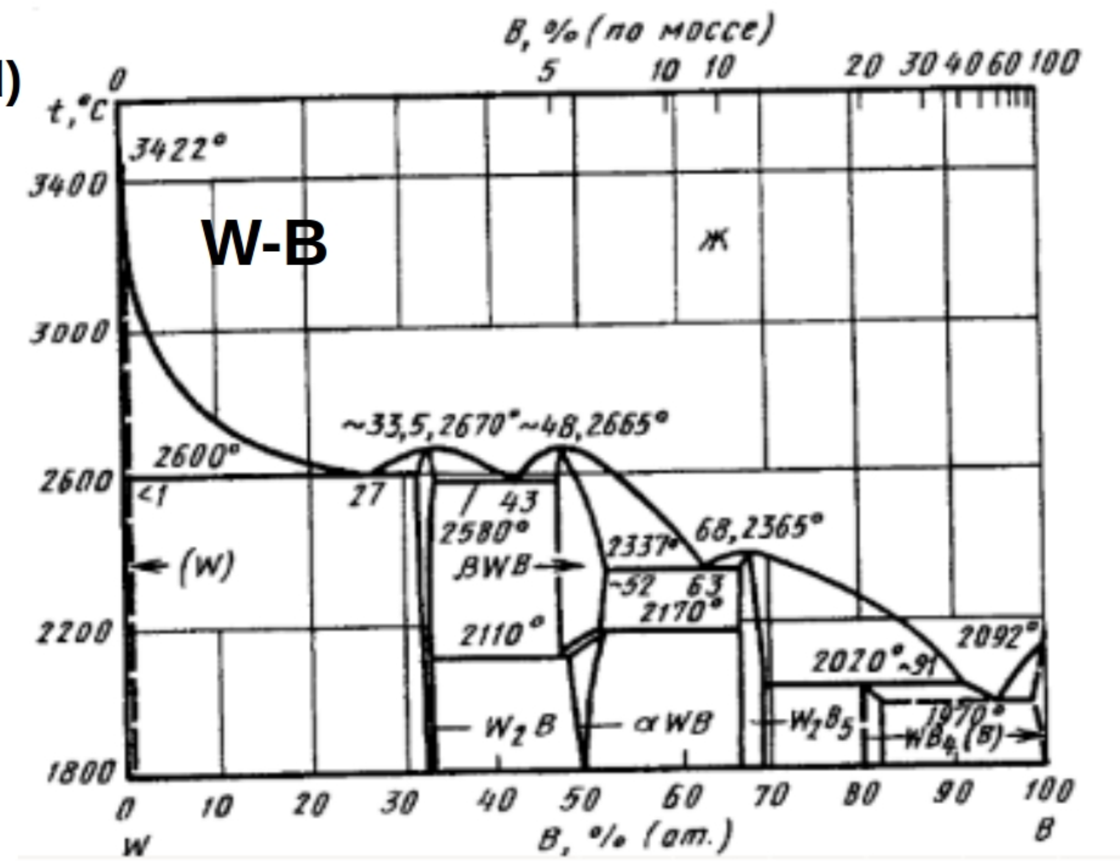
b)



c)

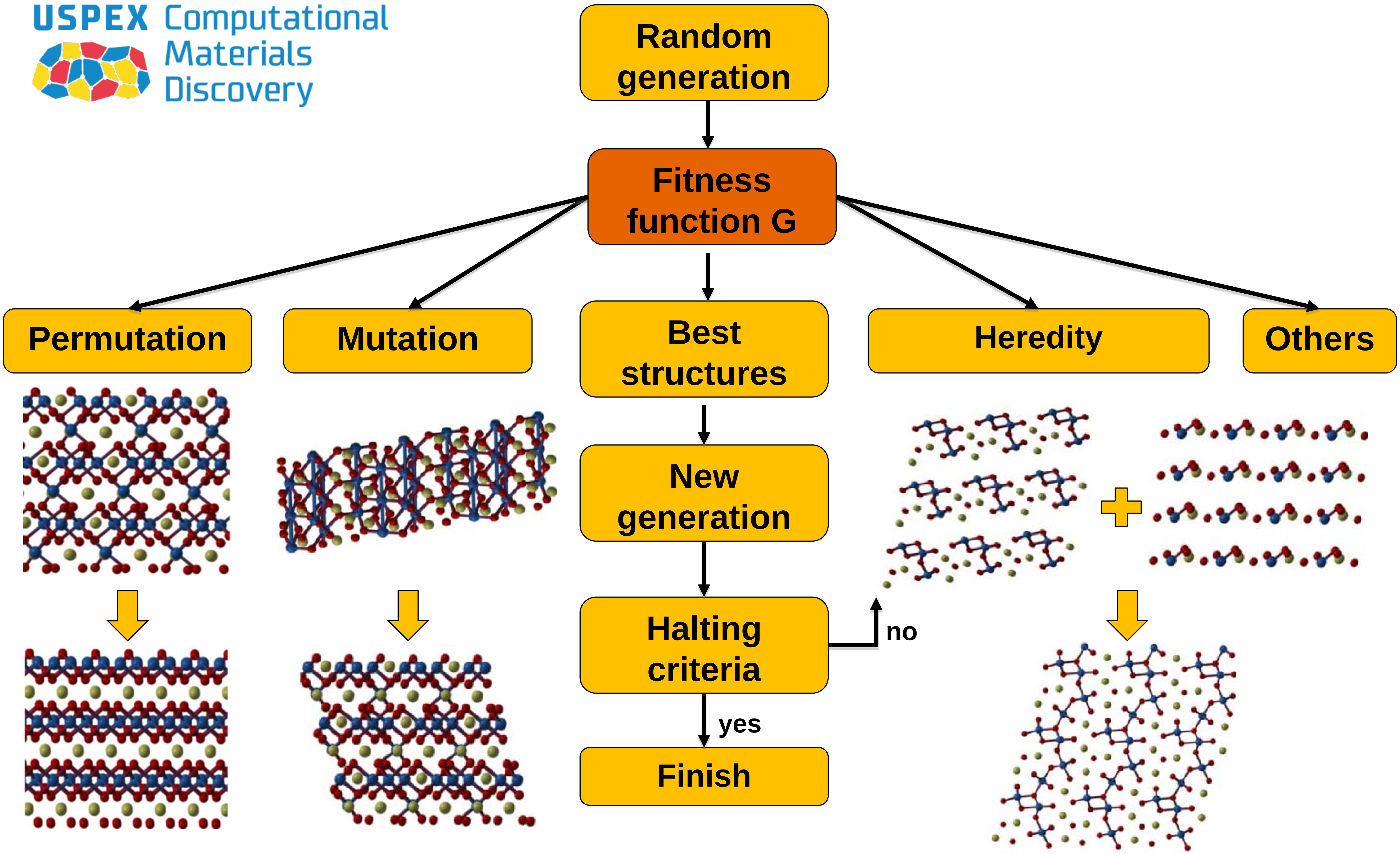


d)



T-USPEX scheme

USPEX Computational Materials Discovery



Difficulties

$$H=U+pV \Rightarrow G=U+pV-TS$$

How to calculate G?

- **Small displacement method (SMD)**
- **Self-consistent lattice dynamics (SCAILD)**
- **Using velocity autocorrelation function (VACF)**
- **Temperature-dependent effective potential (TDEP)**
- **Thermodynamic Integration (TI)**
- **…**

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- **Small displacement method (SMD)**
- **Self-consistent lattice dynamics (SCAILD)**
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- **Temperature-dependent effective potential (TDEP)**
- **Thermodynamic Integration (TI)**
  + includes anharmonic terms
  - requires big system (at least > 1000 atoms)

Interatomic potentials (machine learning)

Comparison of methods for G calculation

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Reproducibility of vibrational free energy by different methods

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[b] Material Modeling and Development Laboratory, NUST "MISiS", 119991 Leninskiy pr. 4, Moscow, Russia
[c] Moscow Institute of Physics and Technology, 141700 Institutskiy per. 9, Dolgoprudny, Moscow Region, Russia

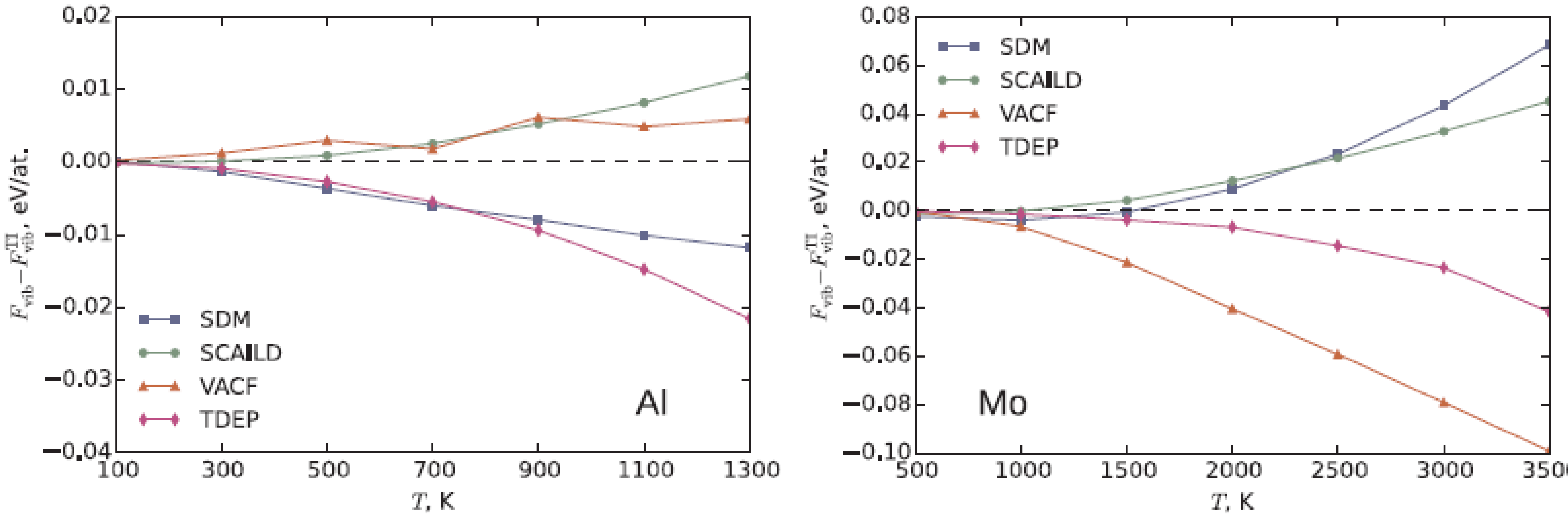

Fig. 3. Calculated vibrational free energy with respect to the result of thermodynamic integration.

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- **Conclusions**

Interatomic potential

Classic potentials

ML potentials

- **LJ**

$$E = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad r < r_c$$

- **Buckingham**

$$E = Ae^{-r/\rho} - \frac{C}{r^6} \qquad r < r_c$$

- **EAM**

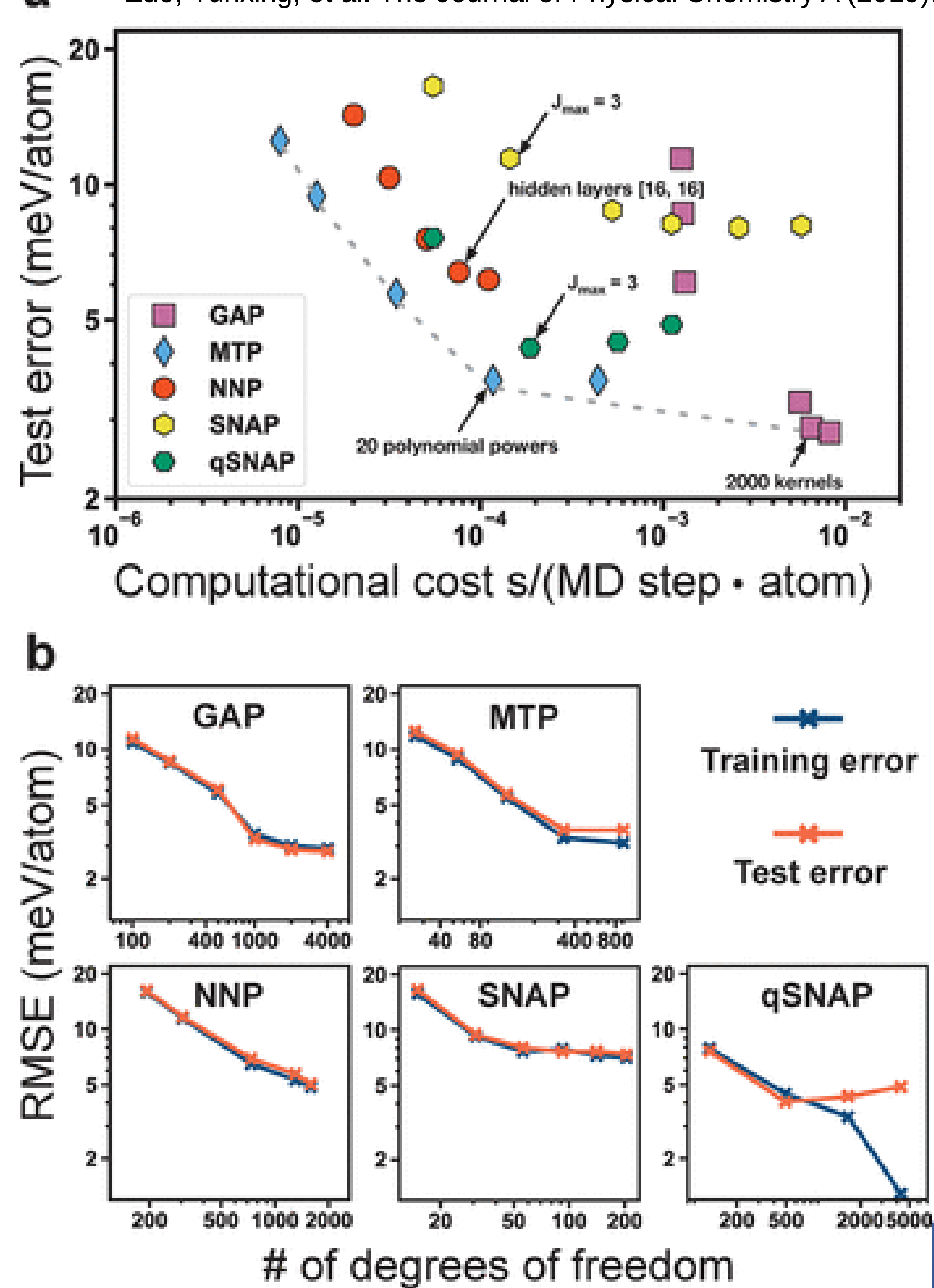
$$E_i = F_\alpha\left(\sum_{j \neq i} \rho_\beta(r_{ij})\right) + \frac{1}{2}\sum_{j \neq i}\phi_{\alpha\beta}(r_{ij})$$

NIST

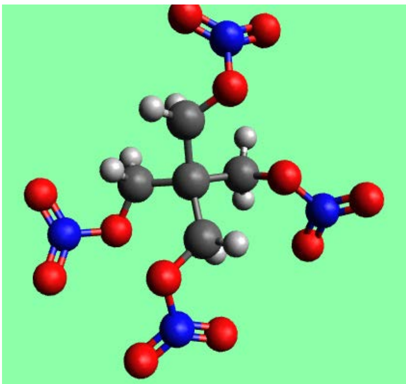
IPR Interatomic Potentials Repository

- **NNP**
- **GAP**
- **SNAP**
- **MTP**

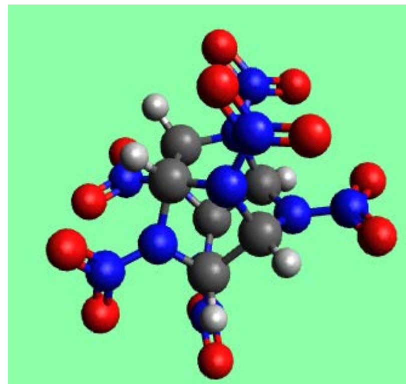
Zuo, Yunxing, et al. The Journal of Physical Chemistry A (2019).



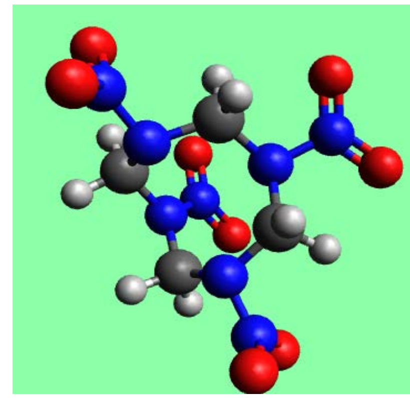
Molecular crystals of energetic materials



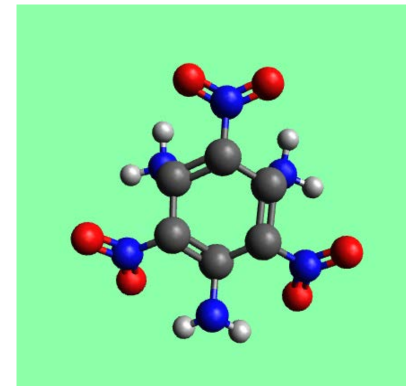
PETN



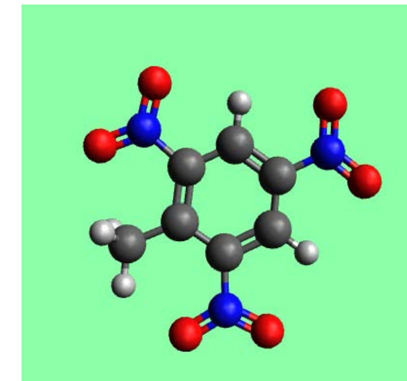
CL-20



HMX



TATB



TNT

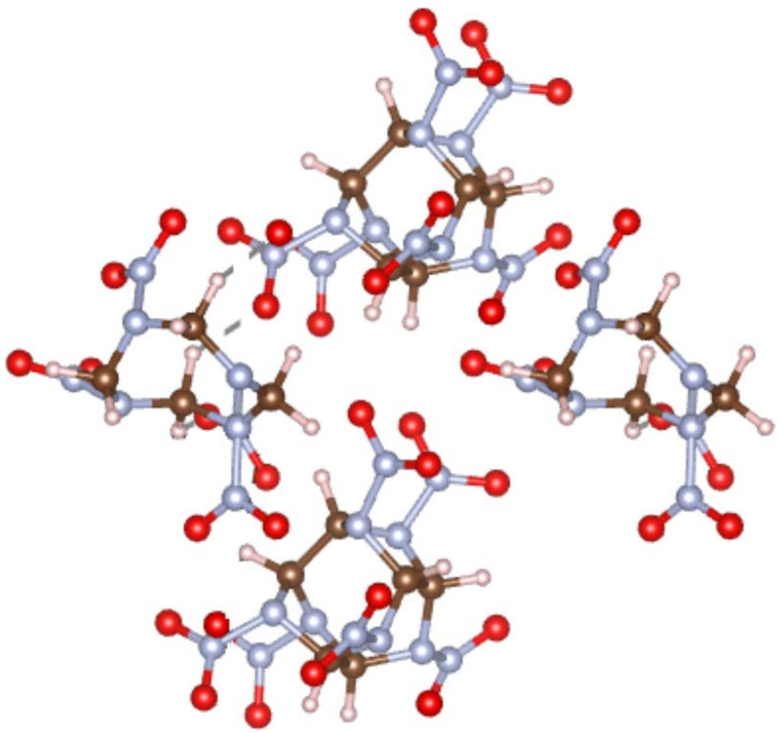
USPEX Computational Materials Discovery

LAMMPS

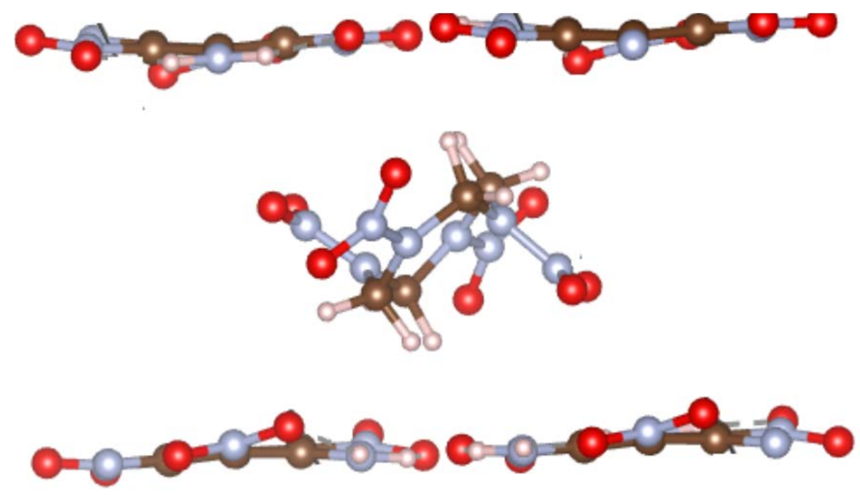
ReaxFF

	PETN	TNT	CL-20	TATB	HMX
Energy/molecule, kcal mol^{-1}					
ReaxFF, exp	−2949	−2516	−3683	−2783	−2752
ReaxFF, USPEX	−2948	−2516	−3685	−2783	−2751
Density, g cm^{-3}					
ReaxFF, exp	1.81	1.83	1.99	1.93	1.99
ReaxFF, USPEX	1.81	1.84	2.00	1.93	1.98

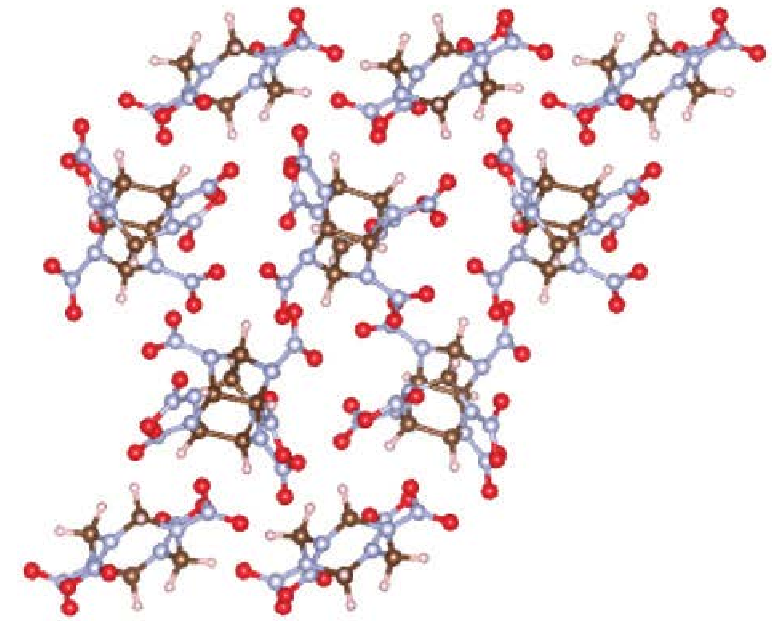
Cocrystals of energetic materials



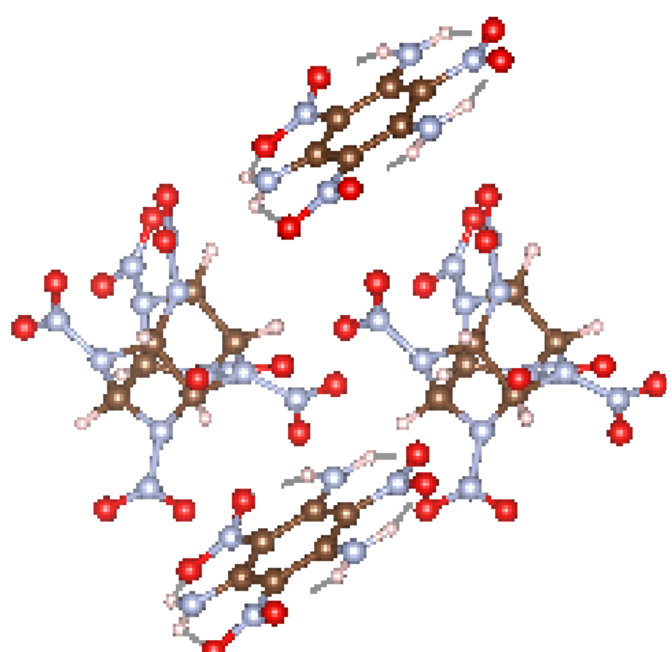
a) 1 Cl-20 : 1 HMX



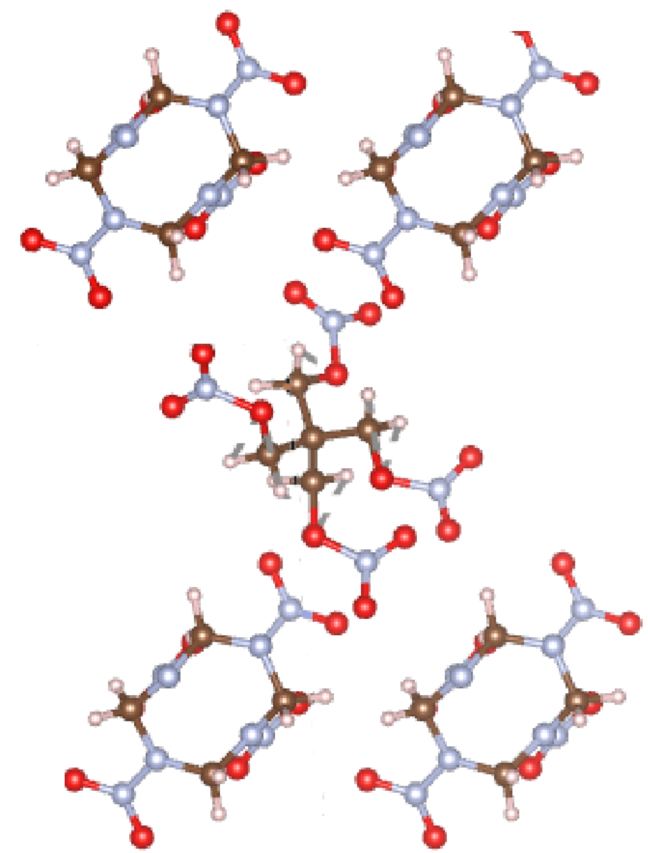
d) 2 TATB : 1 HMX



a)



f) 1 CL-20 : 1 TATB

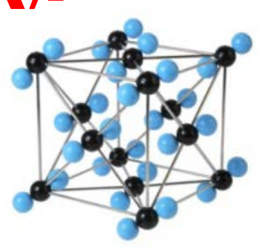
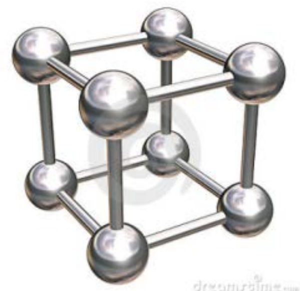
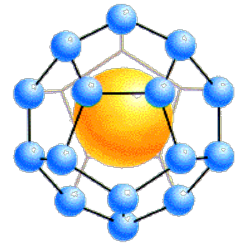


e) 1 PETN : 1 HMX

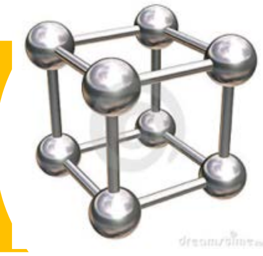
[Pakhnova et al, PCCP 2020]

Machine learning

Vector $(x^i_1, x^i_2, \ldots, x^i_n)$, $i = 1..K$, property y^i $\quad f(X) \rightarrow Y$

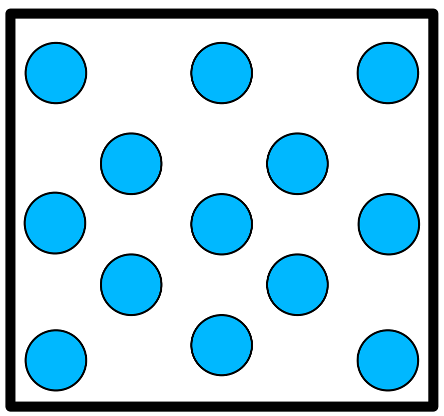




Energies,
Forces, …

F() → E

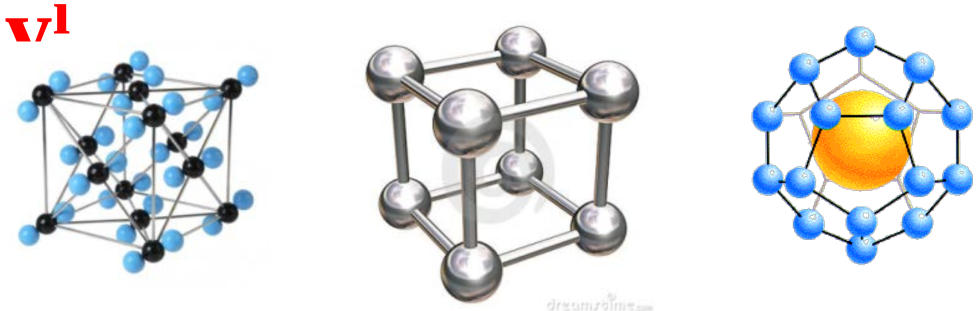
ML interatomic potential

Feature vector:

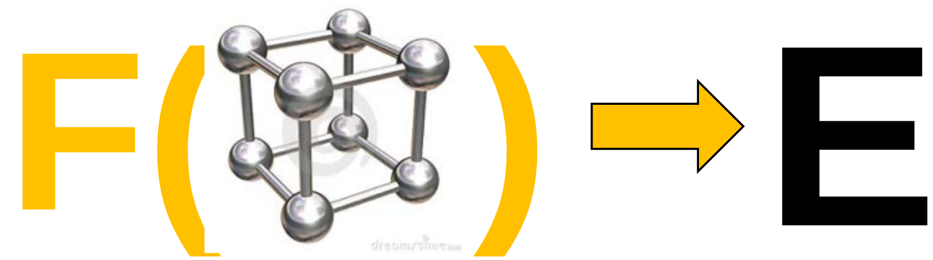


Machine learning

Vector $(x^i_1, x^i_2, \ldots, x^i_n)$, $i = 1..K$, property y^i $\quad f(X) \rightarrow Y$

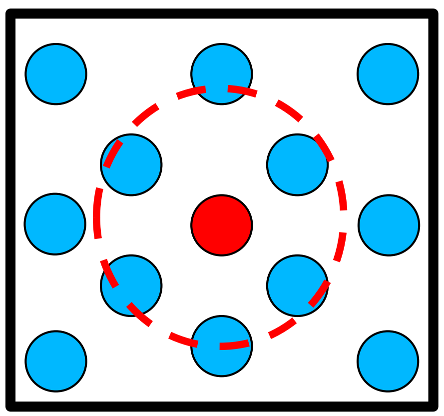


Energies,
Forces, …



ML interatomic potential

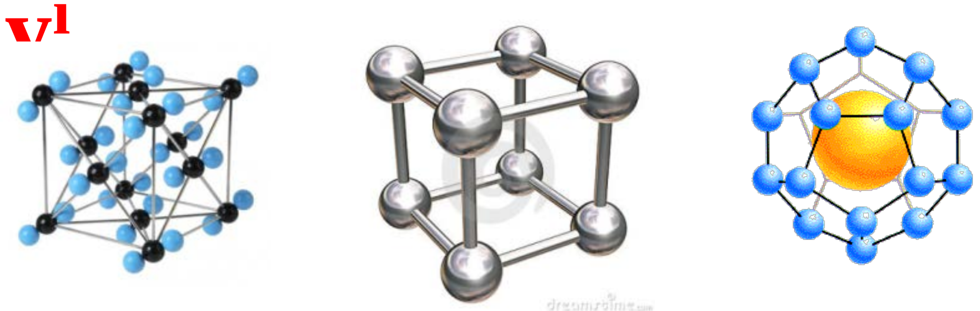
Feature vector:



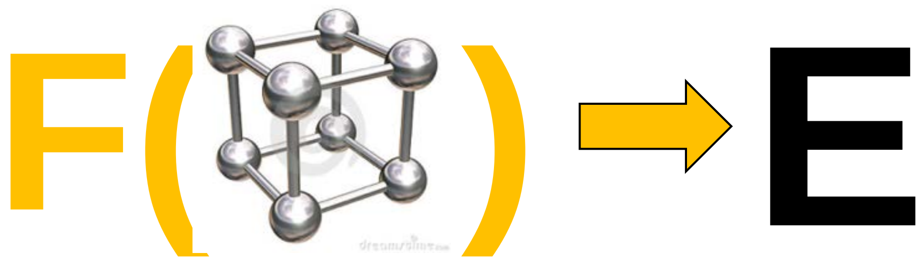
Machine learning

Vector $(x^i_1, x^i_2, \ldots, x^i_n)$, $i = 1..K$, property y^i

$$f\,(X) \rightarrow Y$$



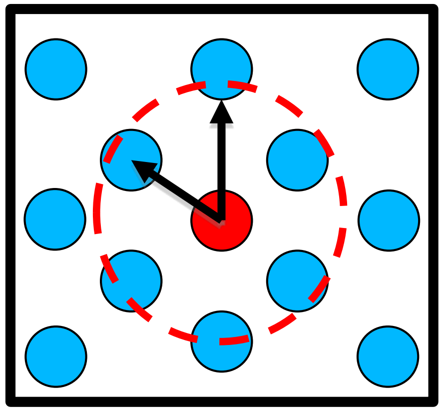
Energies,
Forces, …



ML interatomic potential

Feature vector:

[Li, Z. et al, PRL, 2015]



$$X_E = \sum_{i=1}^{N_{at}} \sum_{j=1}^{N_{neigh,i}} exp\left[-\left(\frac{|\vec{r_{ij}}|}{r_{cut}(k)}\right)^{p(k)}\right]$$

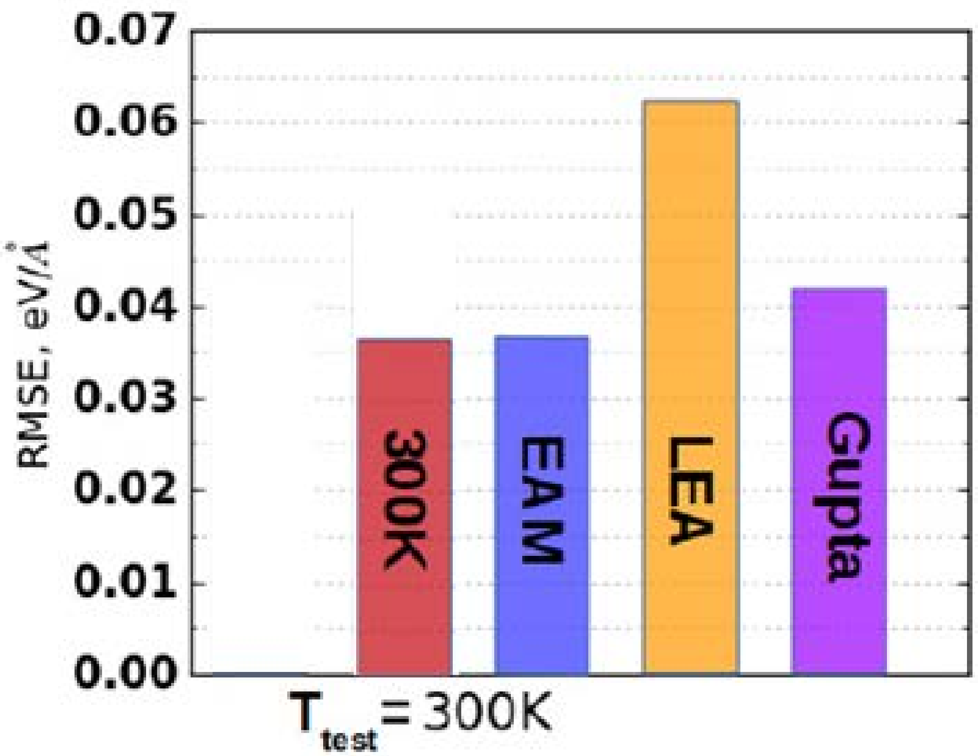
$$E = \Theta X_E + \Theta_0 \quad F_{x,i} = -\frac{\partial E}{\partial x_i} = -\Theta \frac{\partial X_E}{\partial x_i} = \Theta X_F$$

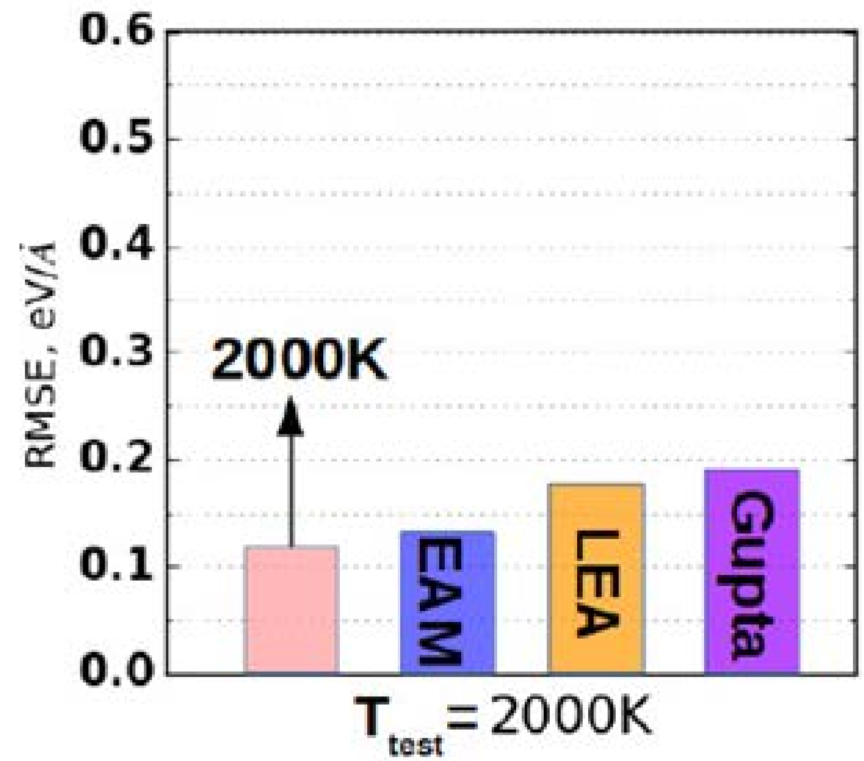
$$\Theta = (X_E^T X_E)^{-1} E, \Theta = (X_F^T X_F)^{-1} F$$

Θ → Interatomic potential

[Kruglov et al, Sci. Rep., 2017]

Machine learning potential for Al



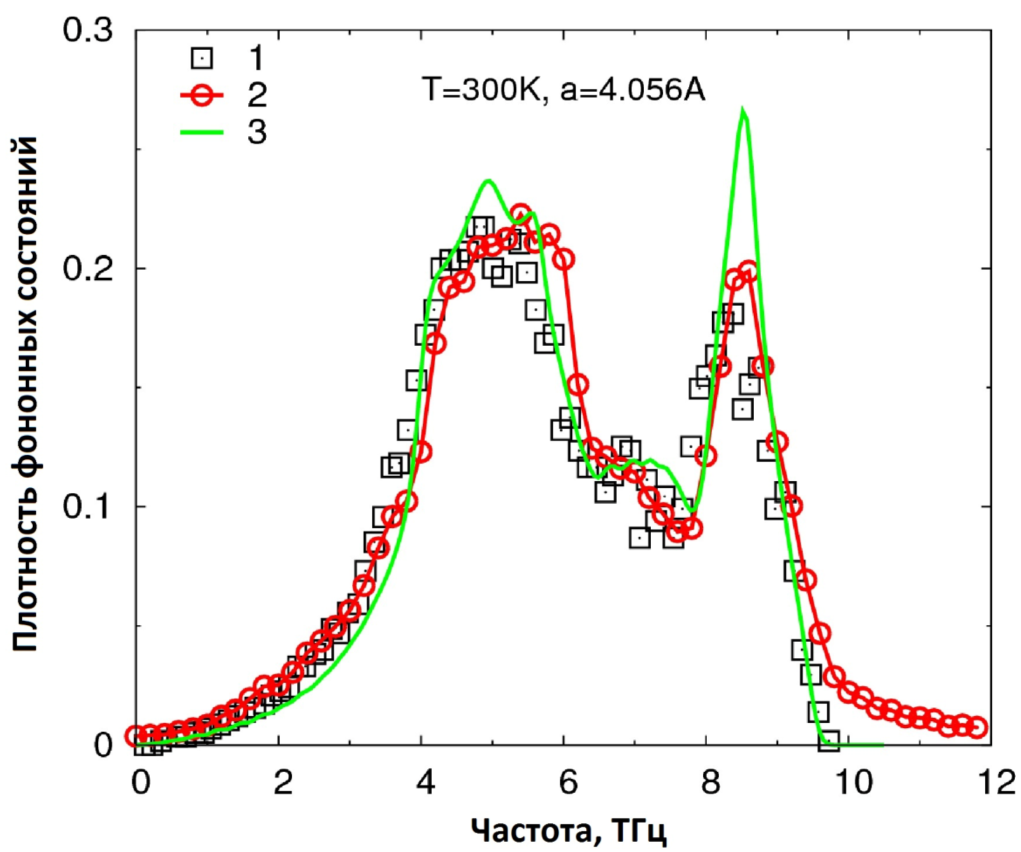


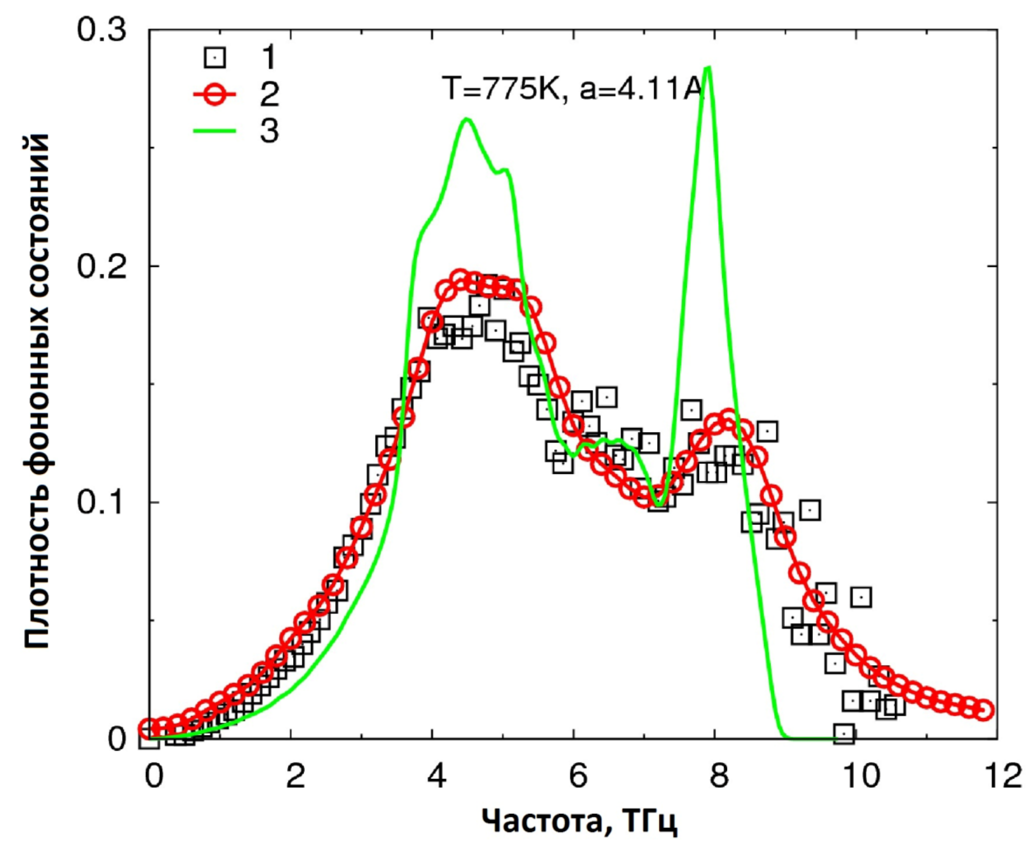
'LEA': [Liu et al, Model. Simul. Mater. Sci. Eng., (2004)] **'Gupta'** : [Winey et al, Model. Simul. Mater. Sci. Eng., (2009)]

Exp

Phonopy

VACF

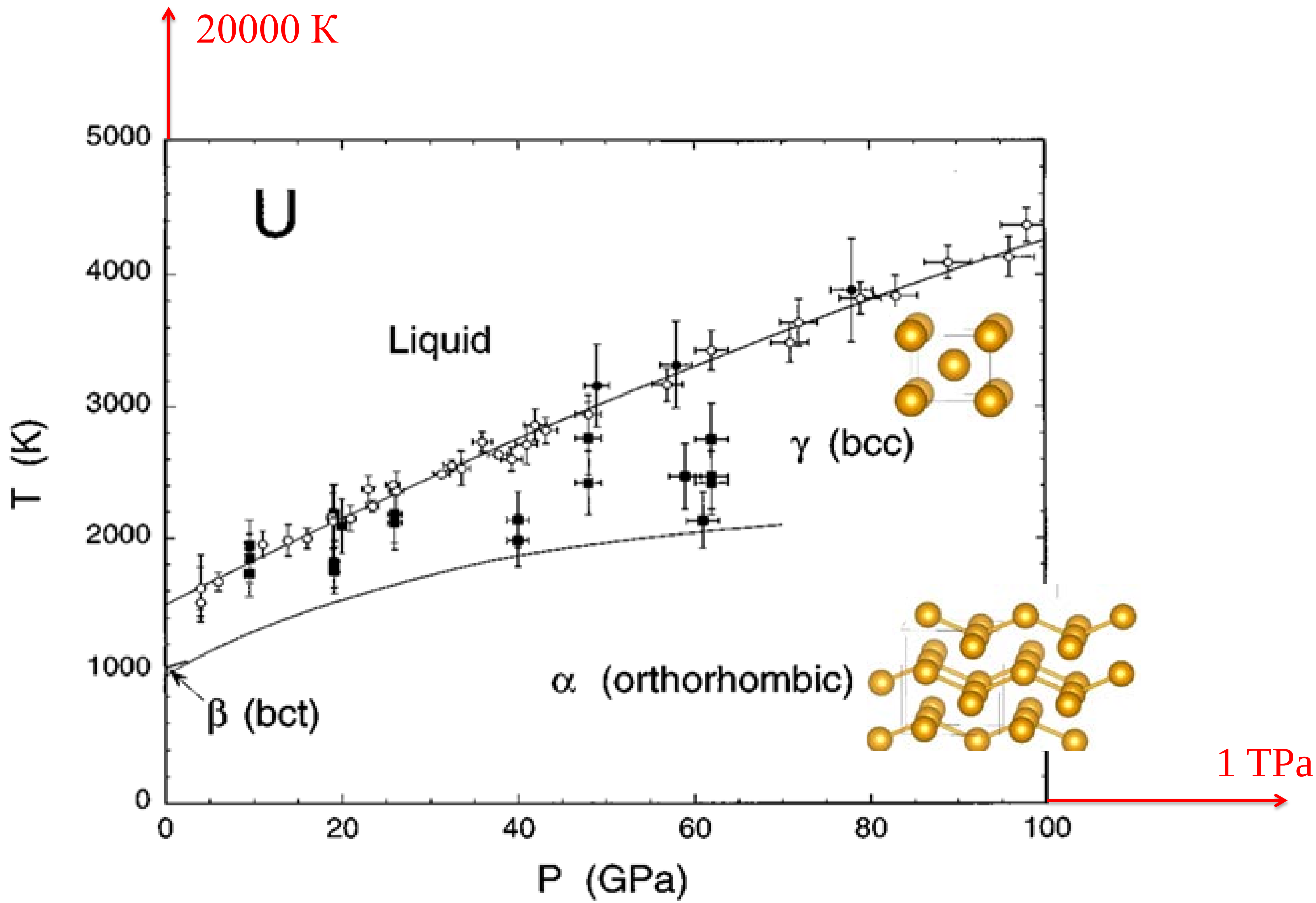




	T_{melt}, K
Exp.	933
MLP	925
EAM	915

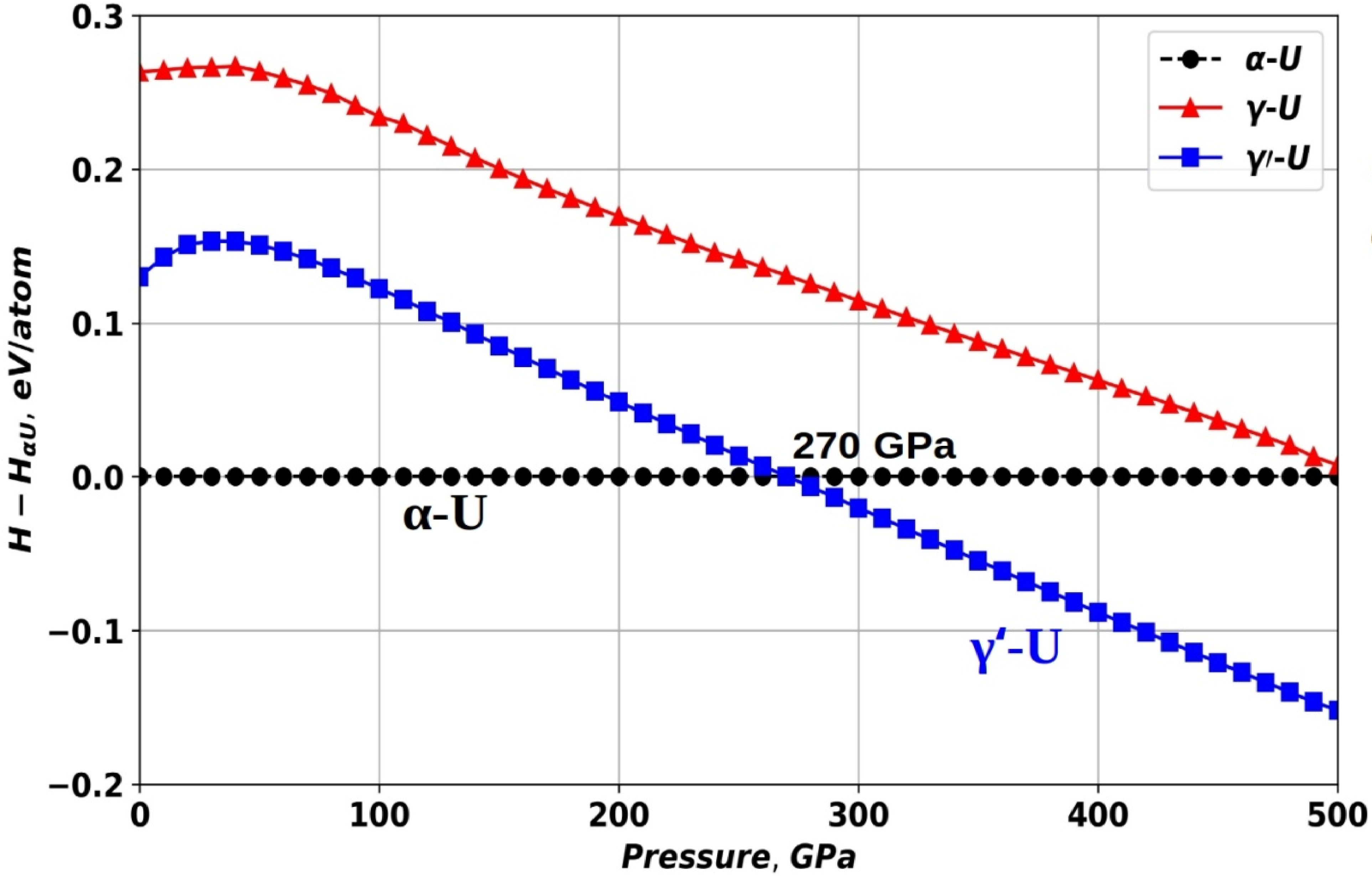
[Kruglov et al, Sci. Rep., 2017]

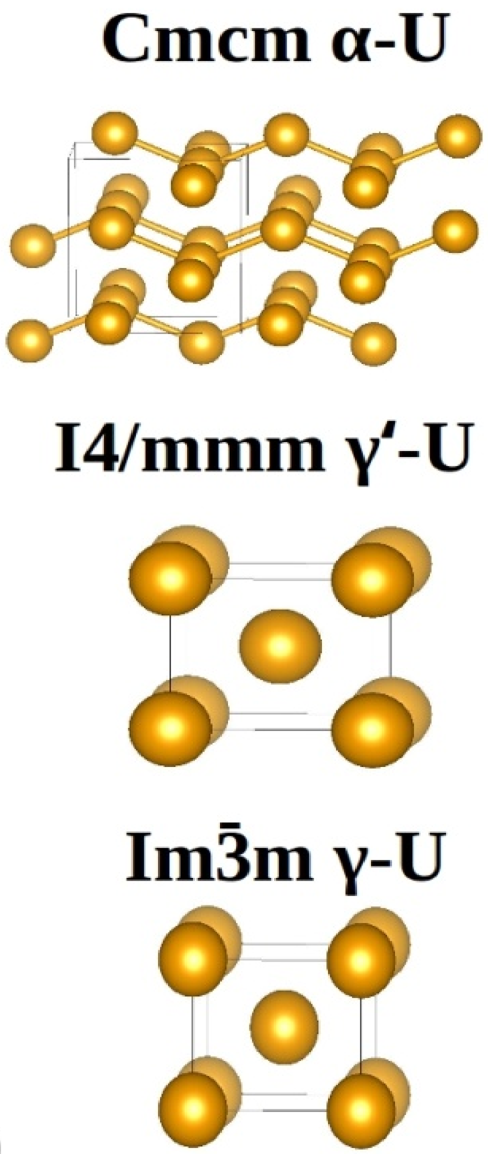
U phase diagram from experiment



[C.S. Yoo et al, PRB, 1998]

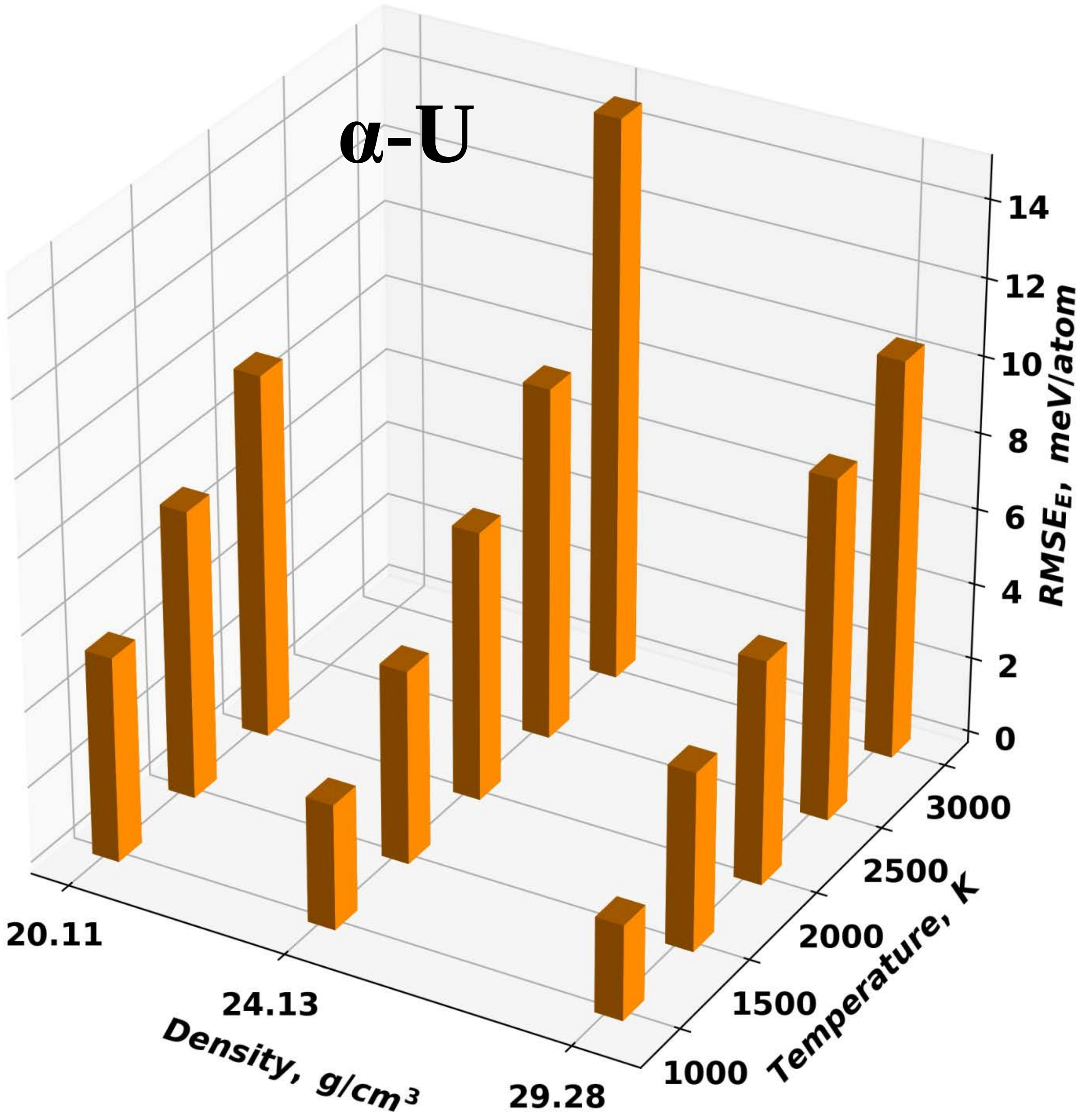
Phase transition at 0 K

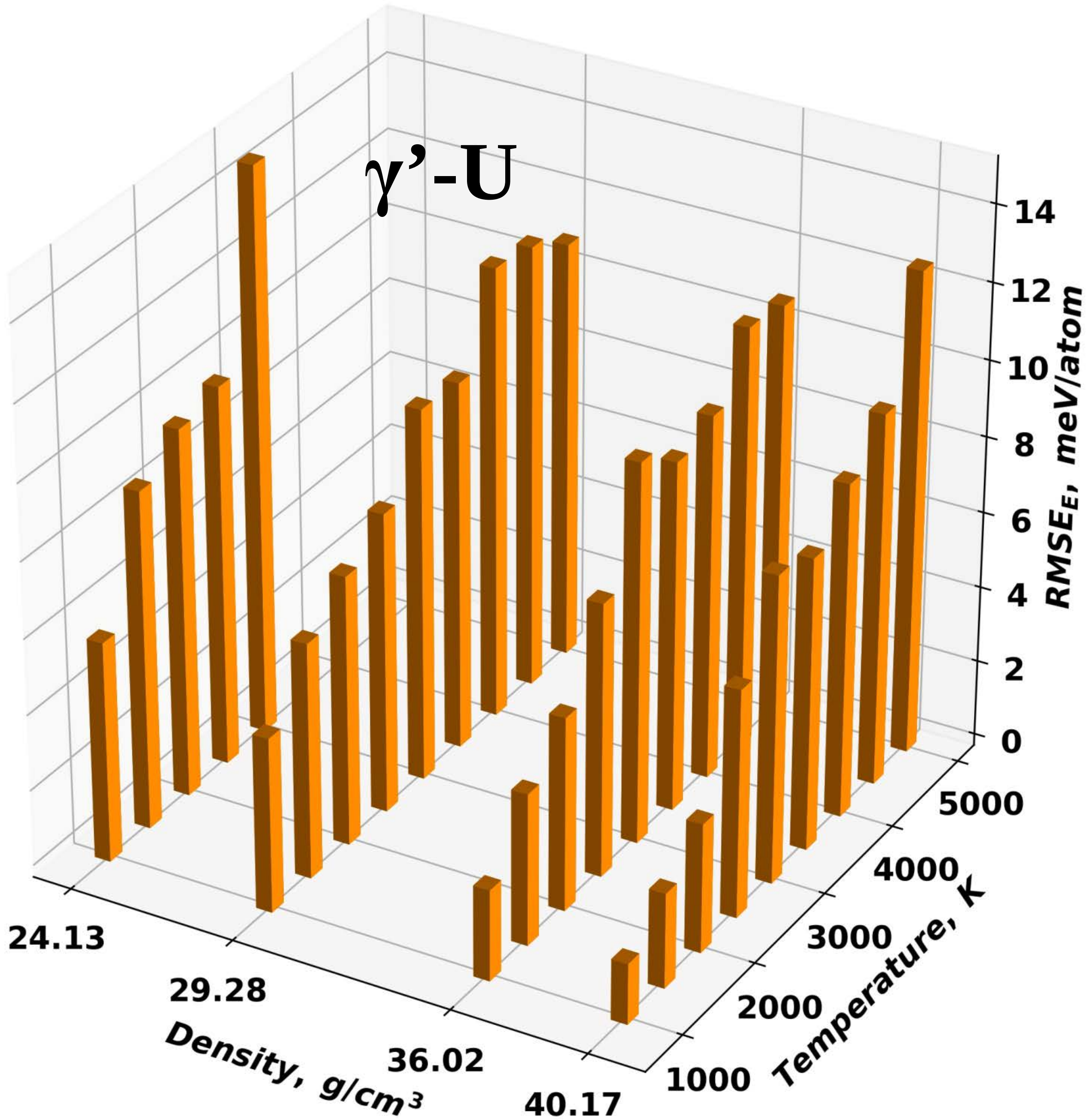




α-U transforms to *bct* γ'-U at 270 GPa

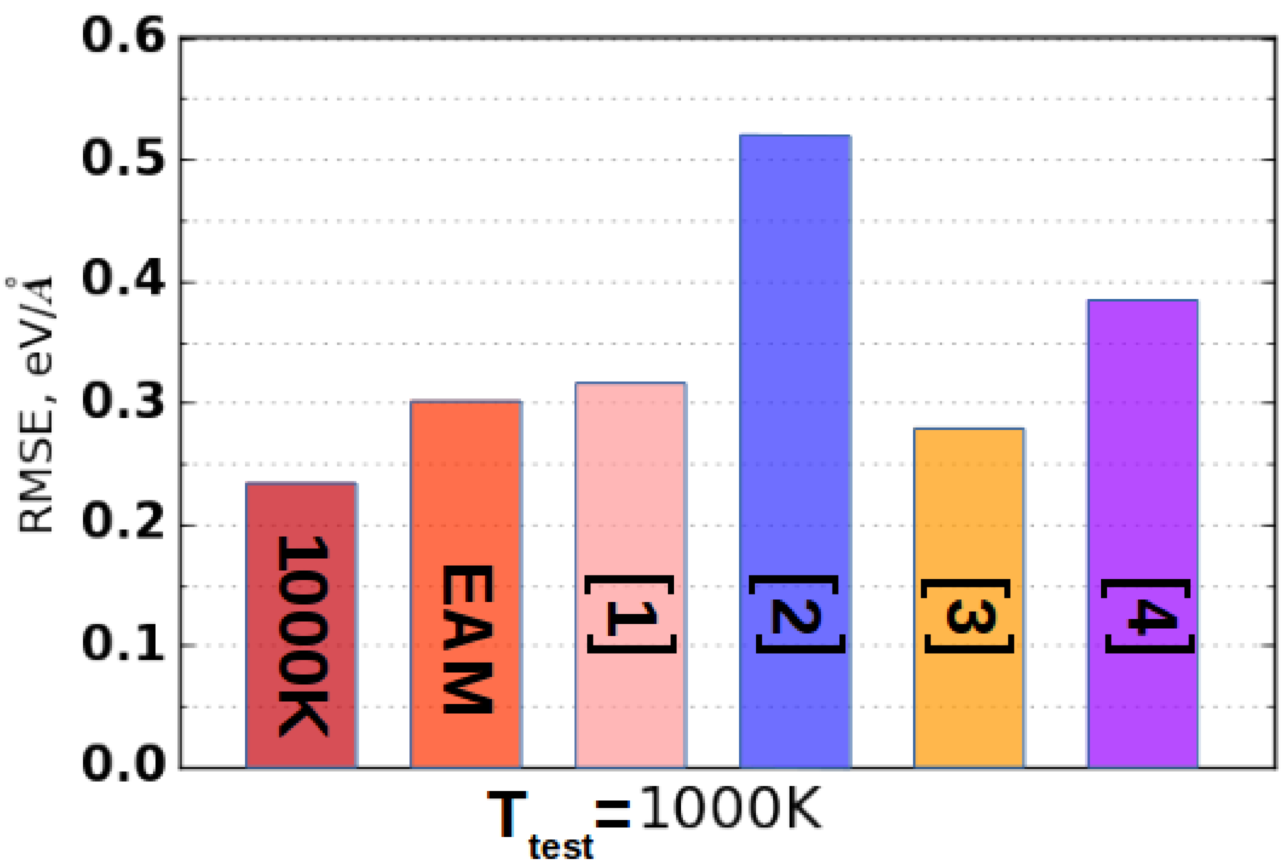
Accuracy of ML potential for U

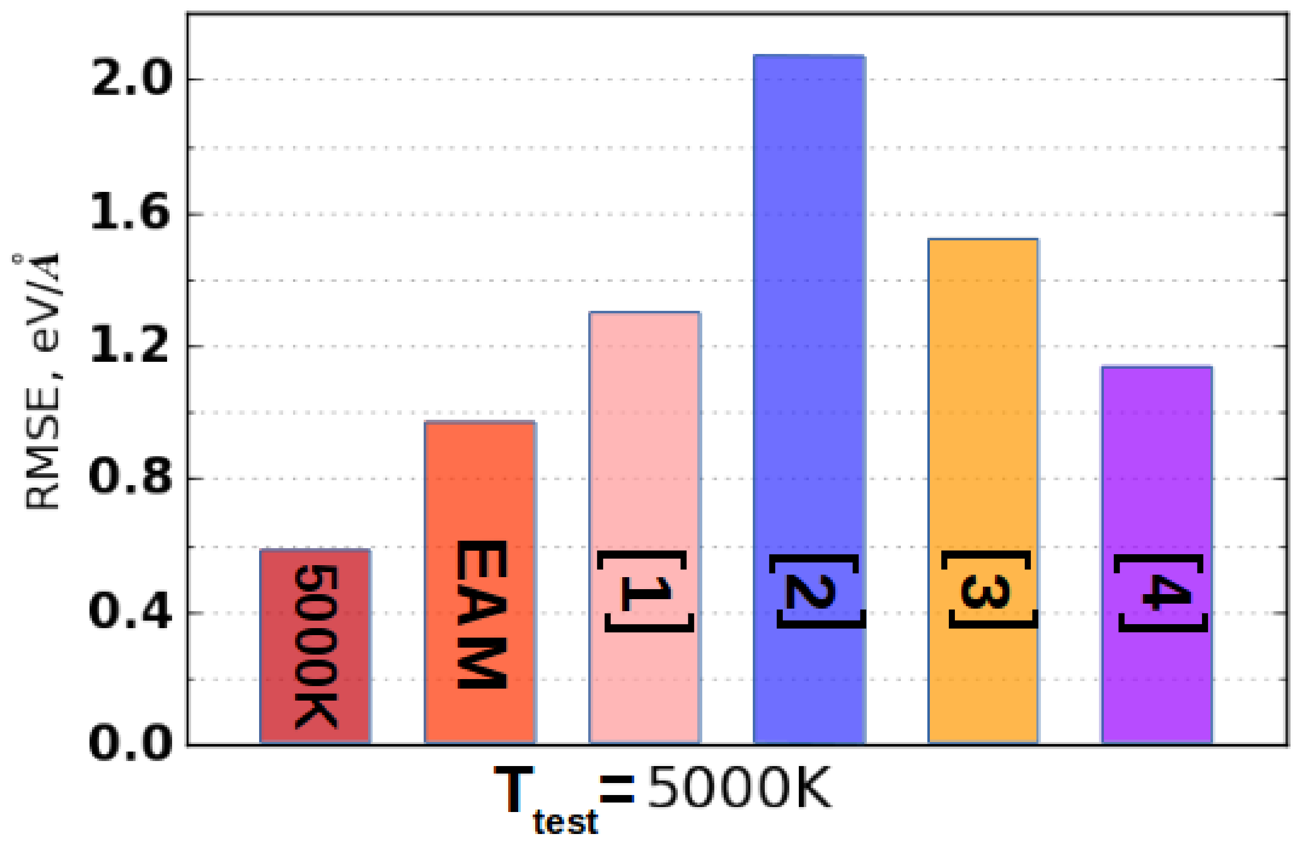




Average error in energy prediction ~ 10 meV/atom

Accuracy of ML potential for U





[1] D. Smirnova et al Journal of Physics: Condensed Matter, 2011

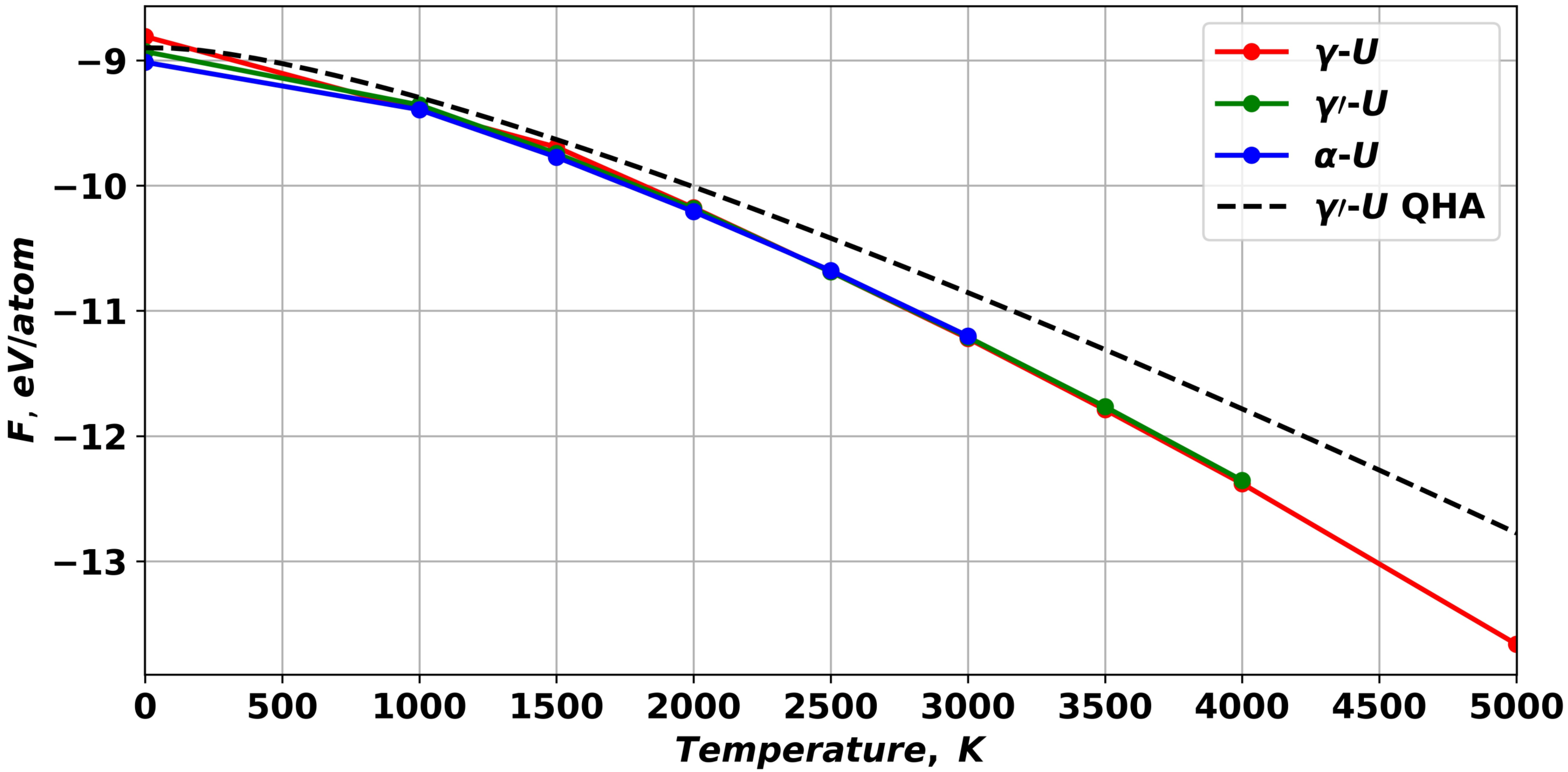
[2] D. Smirnova et al, Journal of Nuclear Materials, 2015.

[3] D. Smirnova et al, Model. and Sim. in Mat. Sci. and Eng. 2013

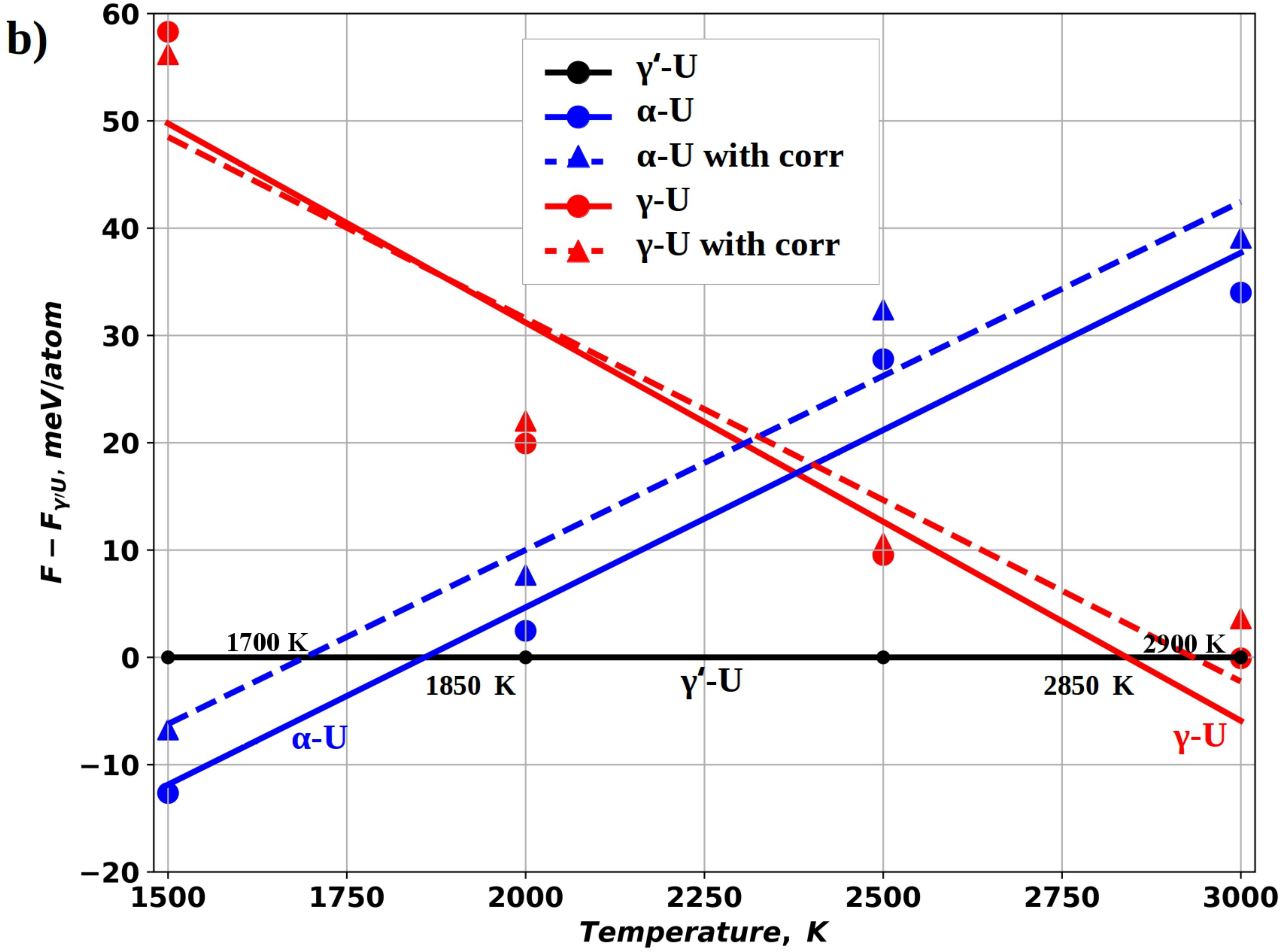
[4] K. P. Migdal et al, AIP Conference Proceedings, 2017

Machine learning interatomic potential predicts forces better than previously published classic potentials

Free energy calculation with TI



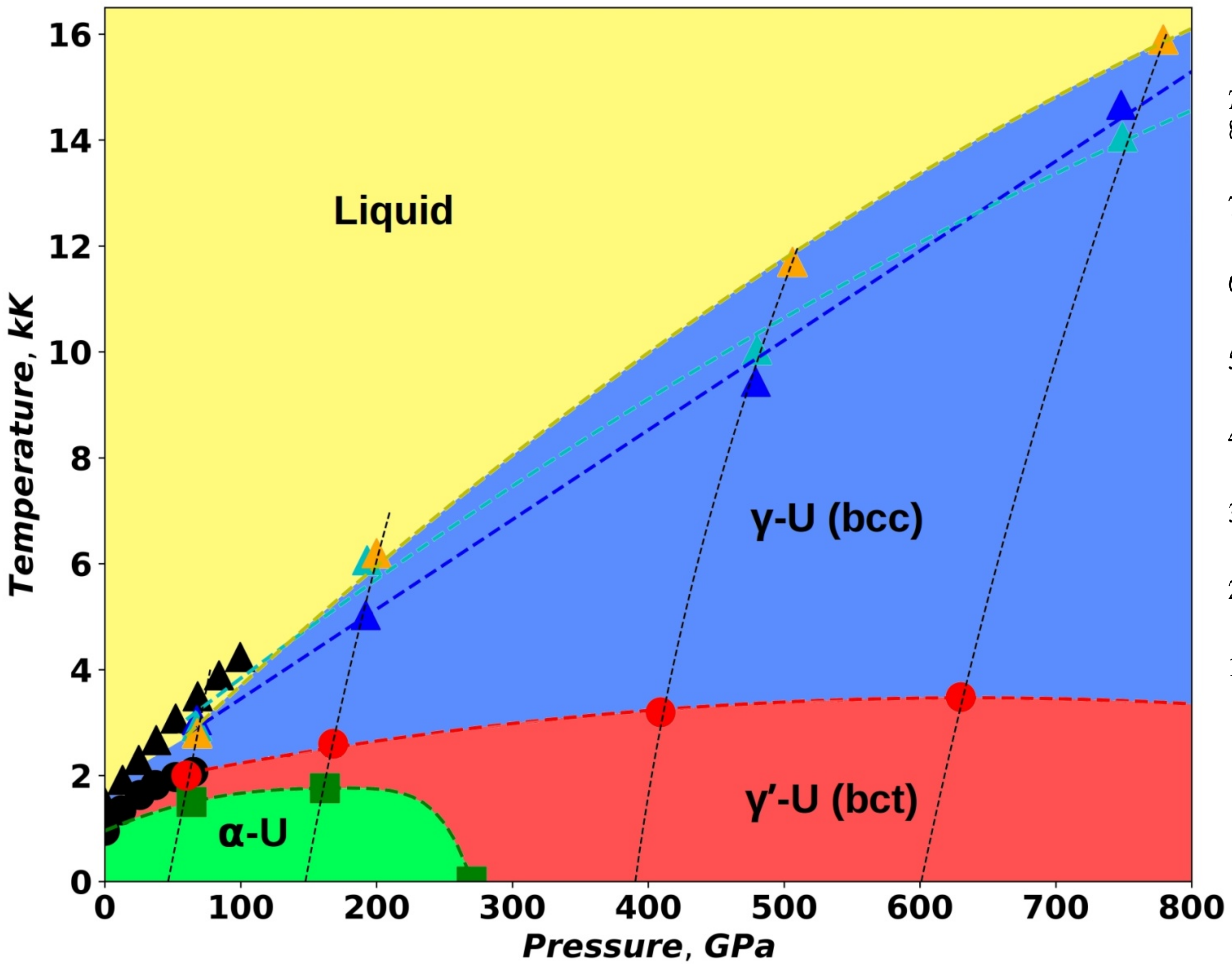
Free energy calculation with TI



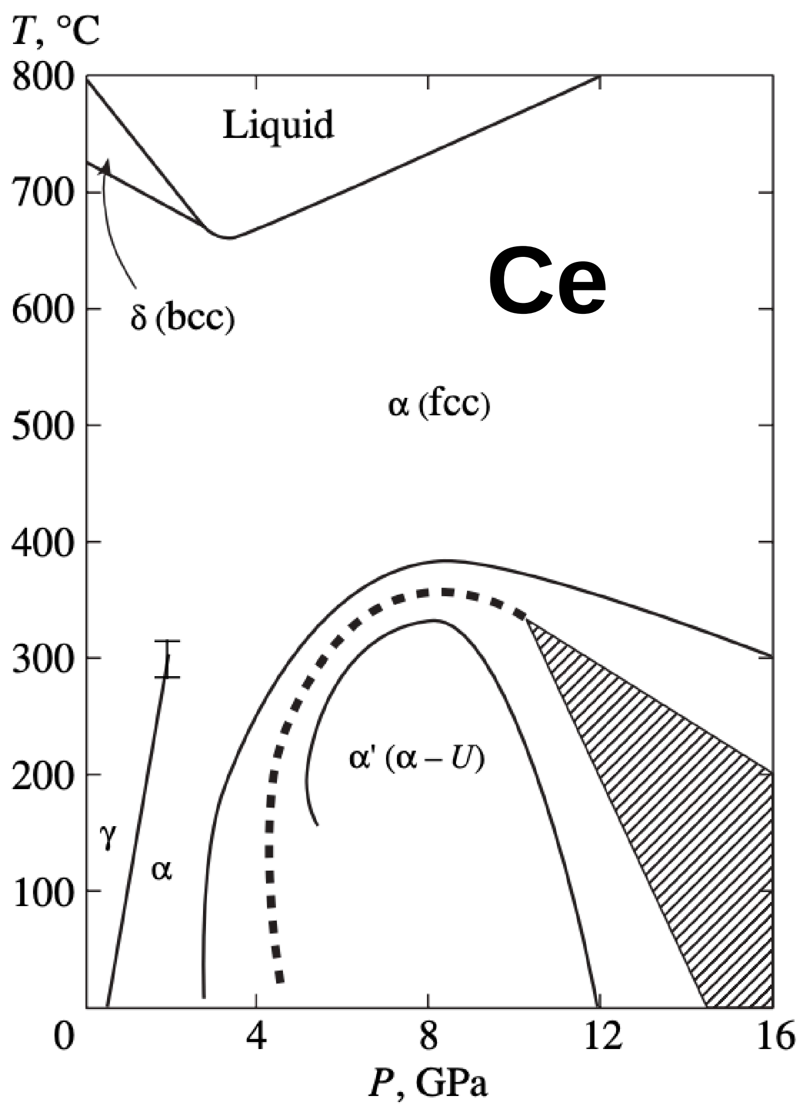
$$\Delta F \simeq \frac{1}{N_{at}}\left[\langle U - U_0\rangle_0 - \frac{1}{2k_bT}\langle[U - U_0 - \langle U - U_0\rangle]^2\rangle_0\right]$$

Uranium P-T phase diagram

[Kruglov et al, PRB, 2020]



[Tsiok, O. B. et al, JETP, 2001]



▲ ■ Experimental data: [C.-S. Yoo, Phys. Rev. B, 1998]

▲ ▲ Melting curve: [Migdal et al, High Temperature, 2017]

Plan of presentation

- **USPEX predictions**:
- BS
- U-H
- **Interatomic (machine learning) potentials:**
- Molecular crystals
- Al and U
- **T-USPEX predictions:**
- Al
- MgSiO3
- WB, WC
- **Conclusions**

T-USPEX scheme

Crystal Structure

↓

Relaxation at 0 K

↓

MD at finite T

↓

Pressure corrections

↓

MD at finite T with pressure corrections

Free Energy

Database for FE corrections

↓

Thermodynamic Integration

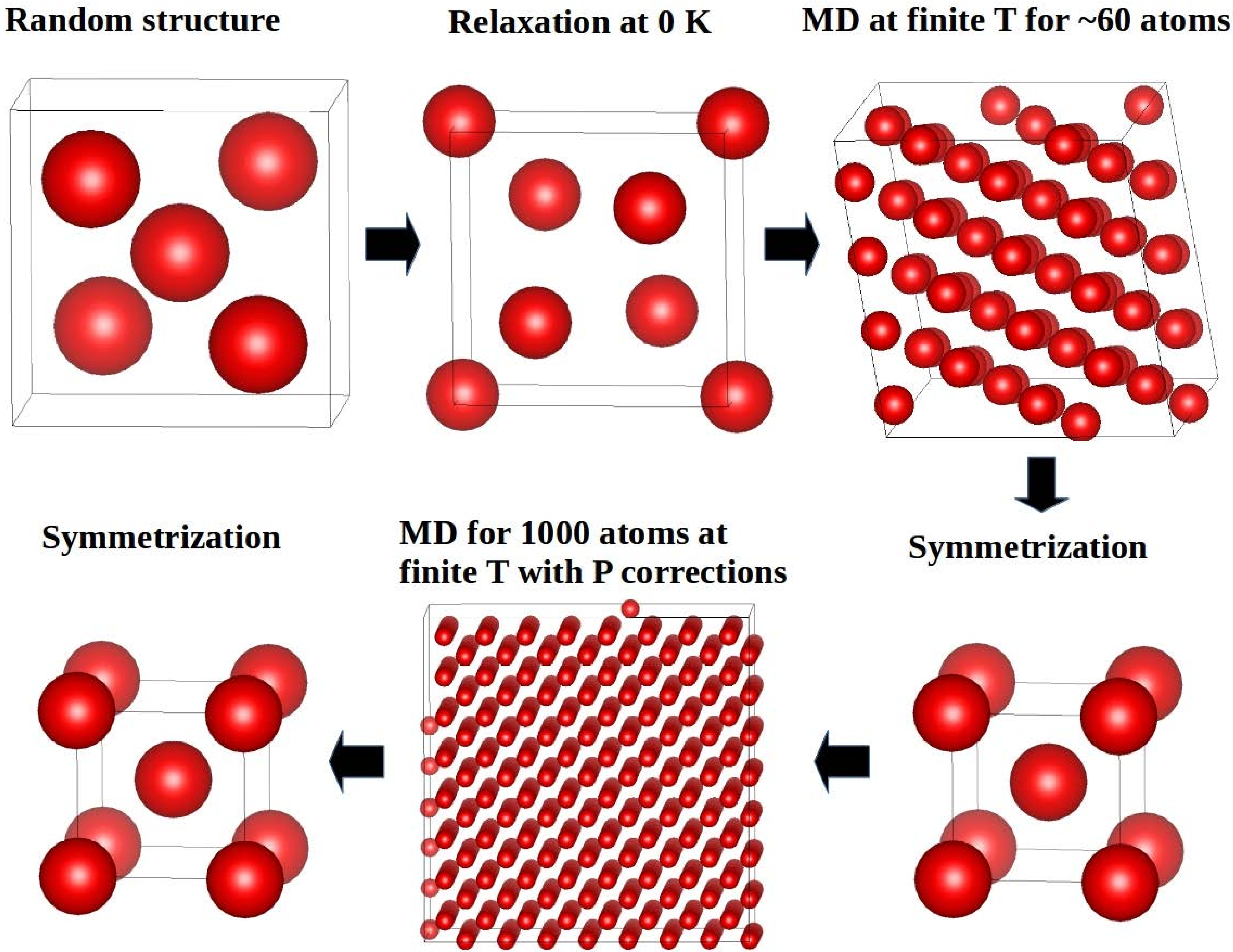
↓

FE with all corrections

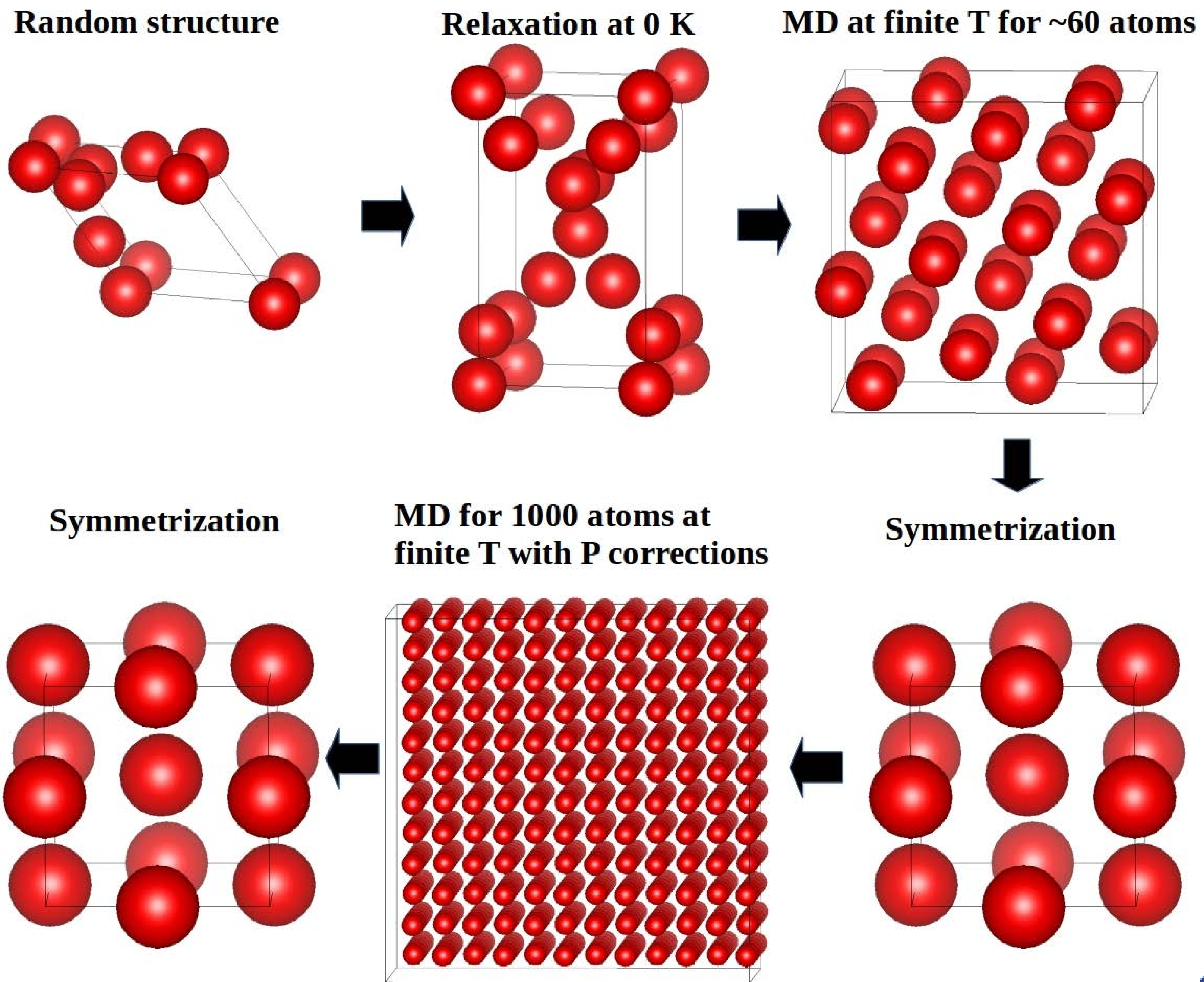
↓

Final structure + its FE

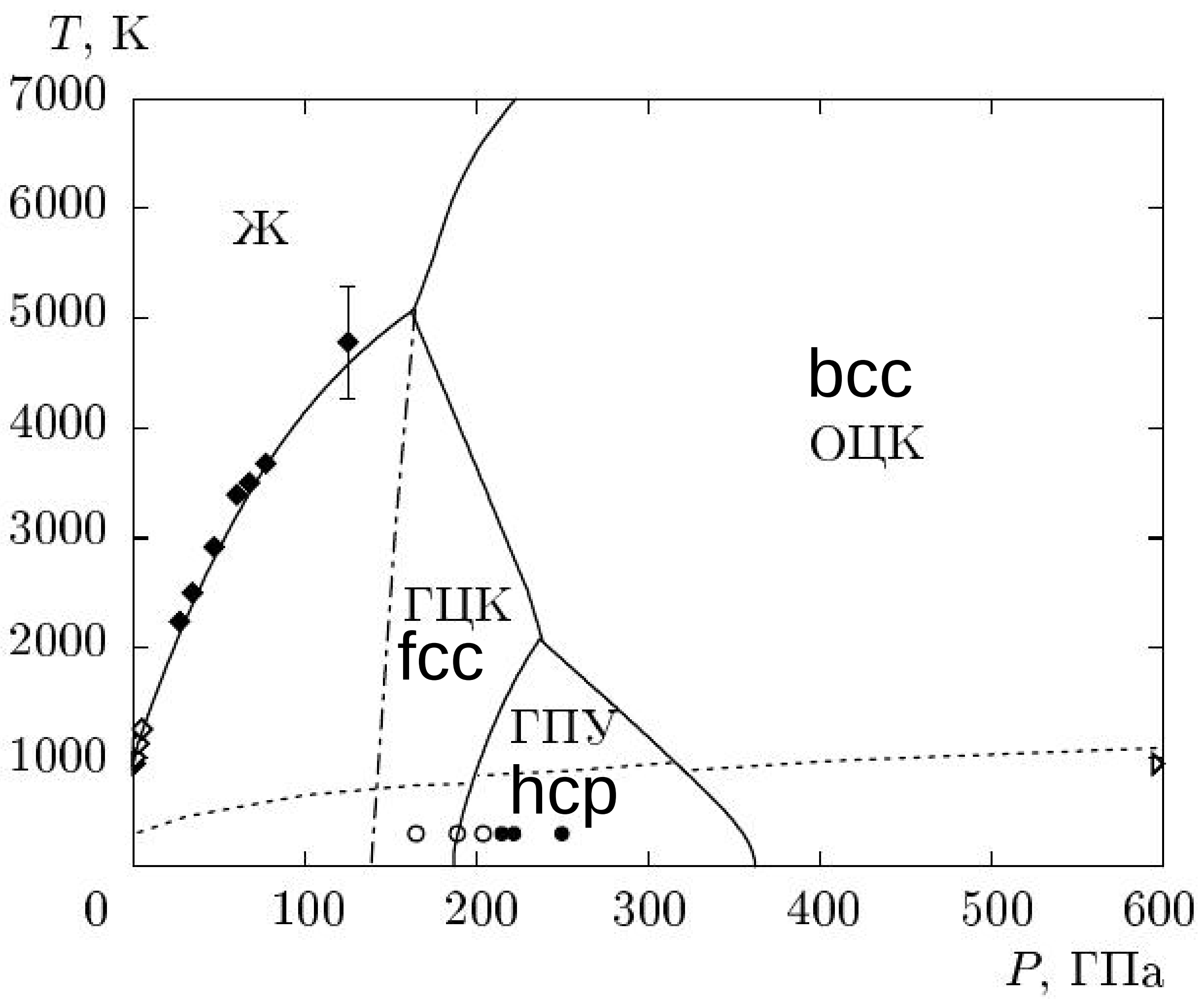
Structure relaxation at finite T



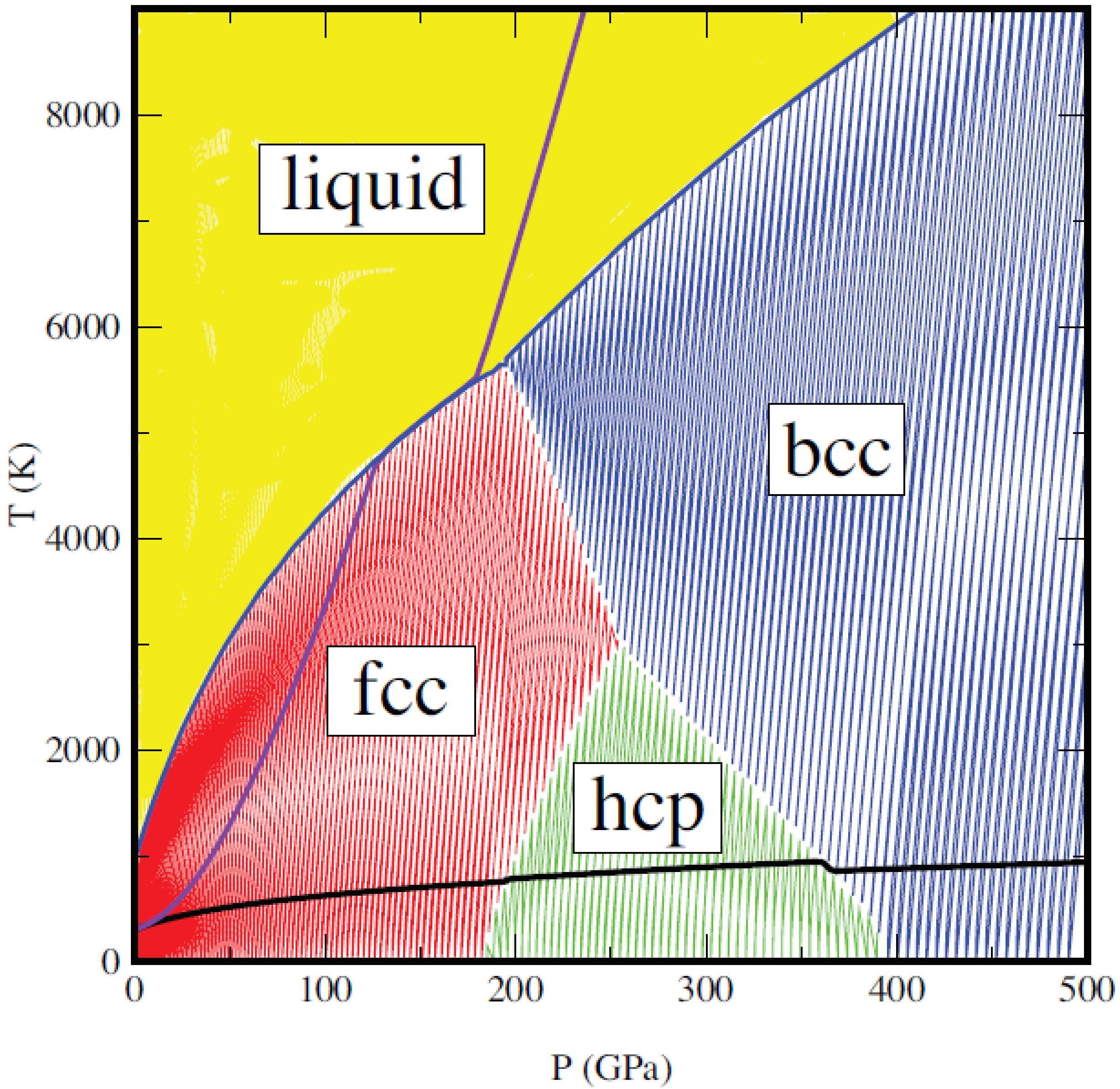
Structure relaxation at finite T



Aluminum



[Kudasov et al, JETP, 2013]



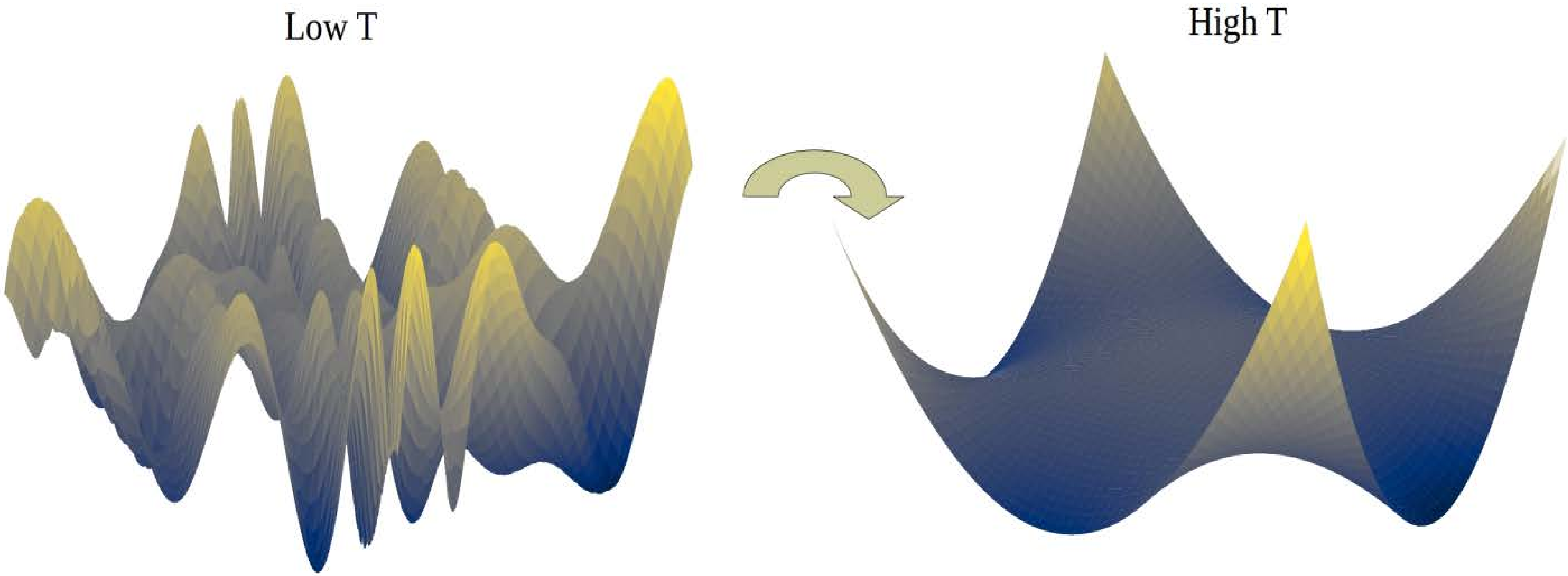
[Sjostrom et al, 2016, PRB]

Aluminum: T-USPEX results

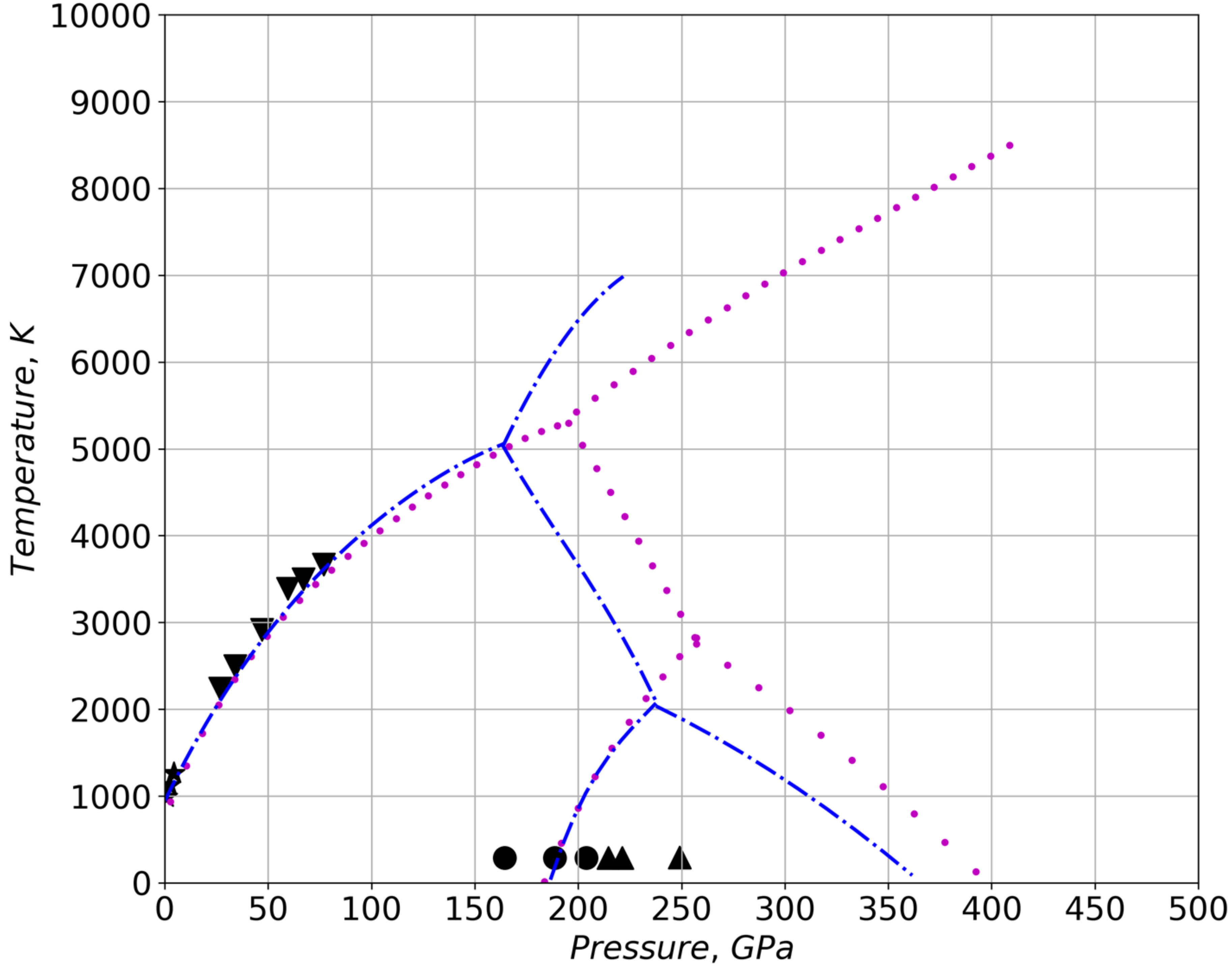
0 GPa 300 K:

SG	N atoms	TI	FE corr 1	FE corr 2	pV	E_{Eins}	G
225	4	-3.8327	0.0025	0.0000	0.0000	-0.0171	-3.8473
225	4	-3.8159	-0.0144	0.0000	0.0000	-0.0171	-3.8474
225	4	-3.8390	0.0086	0.0000	0.0000	-0.0171	-3.8475
225	4	-3.8090	-0.0211	0.0000	0.0000	-0.0171	-3.8473
225	4	-3.8095	-0.0205	0.0000	0.0000	-0.0171	-3.8472
225	4	-3.8286	-0.0014	0.0000	0.0000	-0.0171	-3.8471
225	4	-3.8237	-0.0066	0.0000	0.0000	-0.0171	-3.8474
225	4	-3.8224	-0.0080	0.0000	0.0000	-0.0171	-3.8476
225	4	-3.8060	-0.0244	0.0000	0.0000	-0.0171	-3.8475
225	4	-3.8279	-0.0025	0.0000	0.0000	-0.0171	-3.8475
225	4	-3.8091	-0.0209	0.0000	0.0000	-0.0171	-3.8472
225	4	-3.8199	-0.0105	0.0000	0.0000	-0.0171	-3.8475
225	4	-3.8101	-0.0203	0.0000	0.0000	-0.0171	-3.8475
225	4	-3.8307	0.0005	0.0000	0.0000	-0.0171	-3.8474
139	14	-3.7393	0.0075	0.0000	0.0000	-0.0171	-3.7490
225	4	-3.8293	-0.0010	0.0000	0.0000	-0.0171	-3.8475

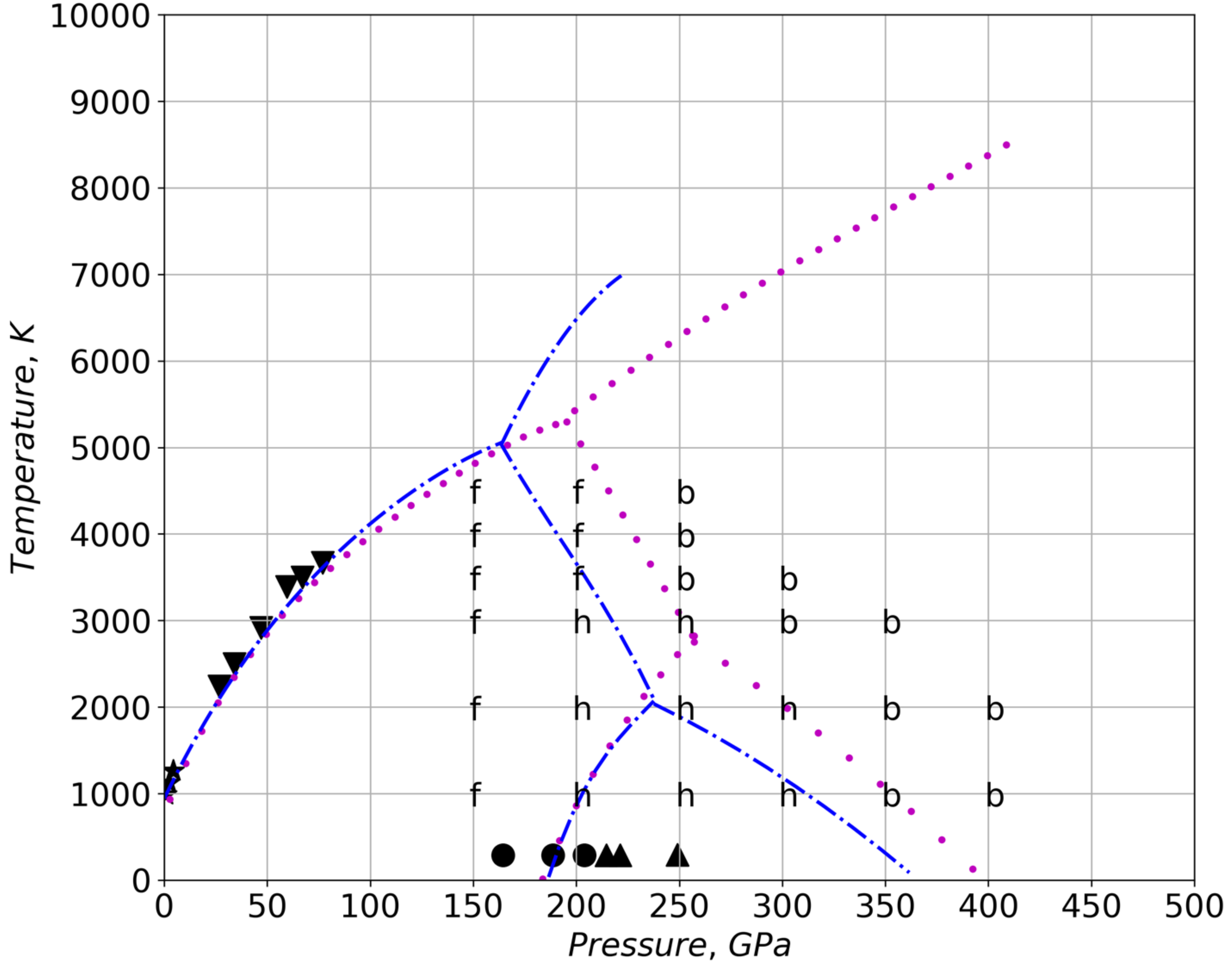
Free energy surface



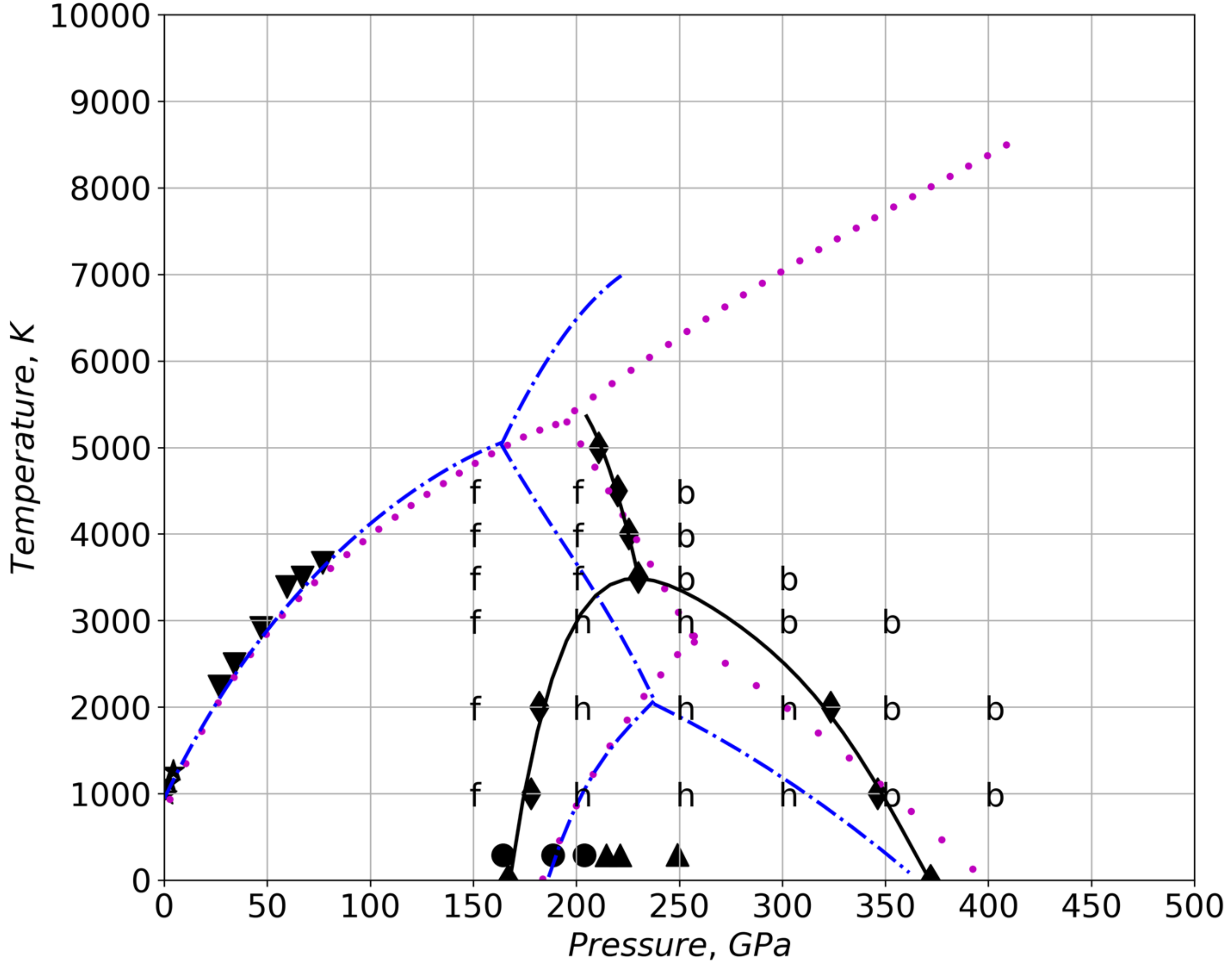
Al: P-T phase diagram



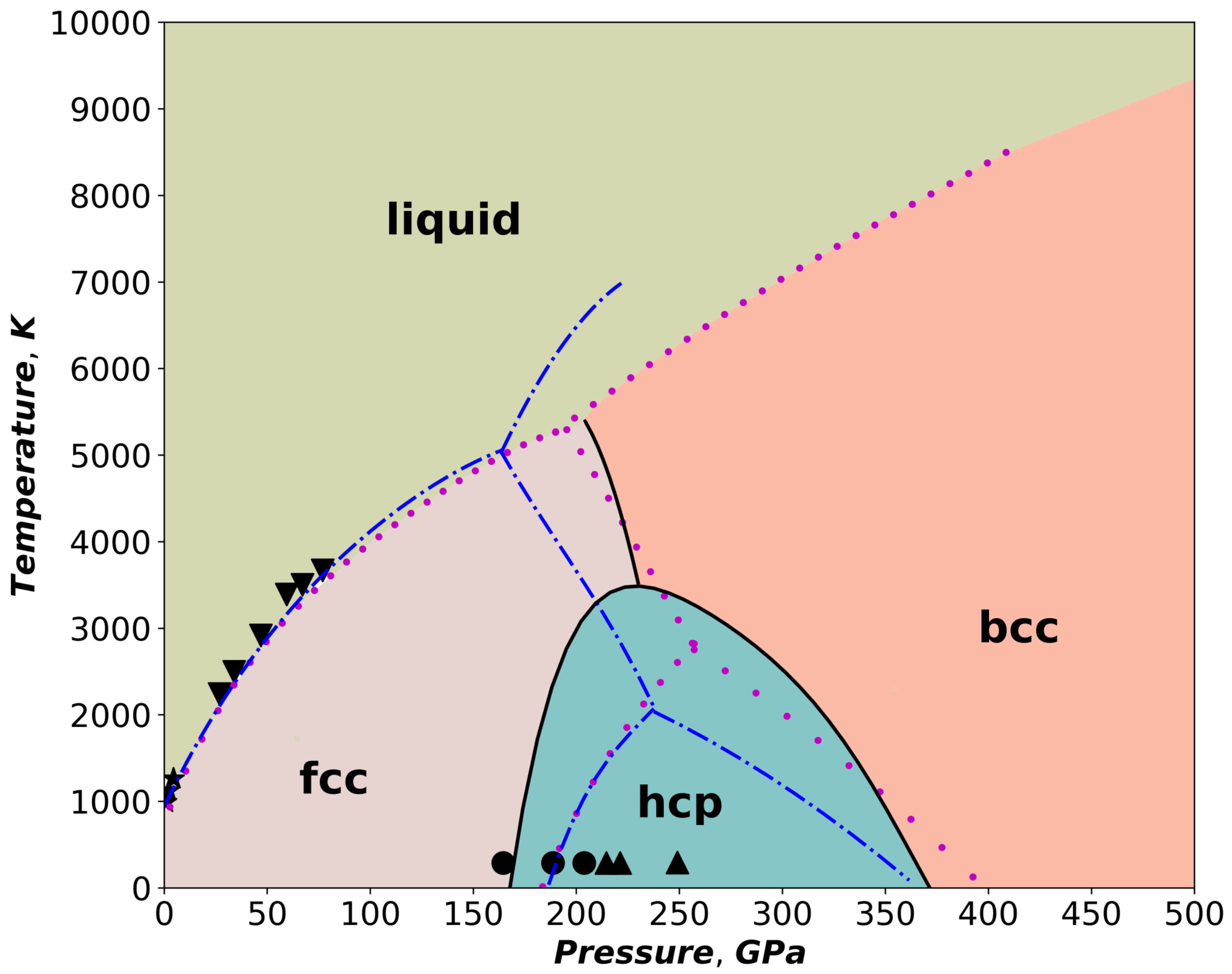
Al: P-T phase diagram



Al: P-T phase diagram

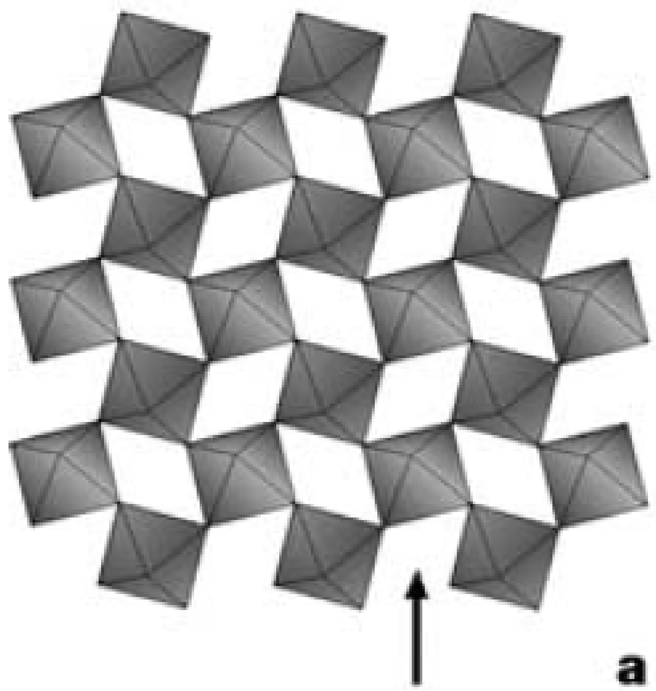


Al: P-T phase diagram



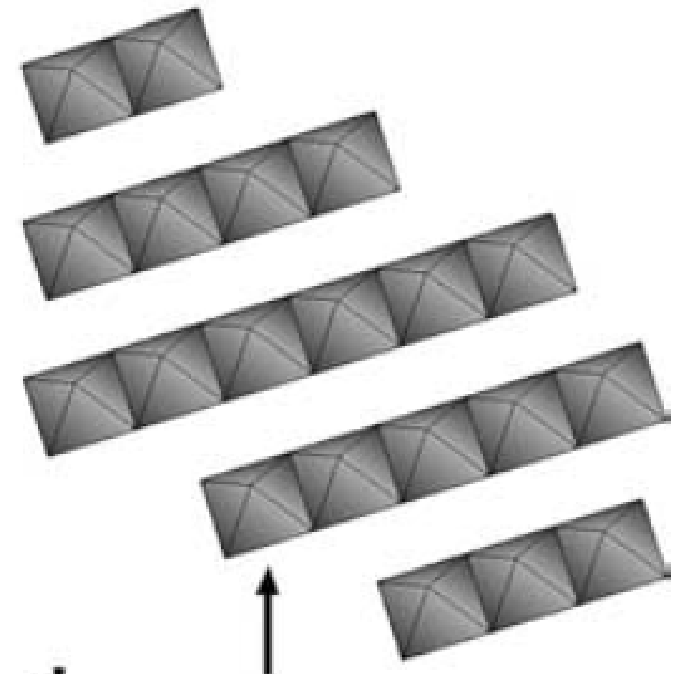
MgSiO3

Pv



a

pPv

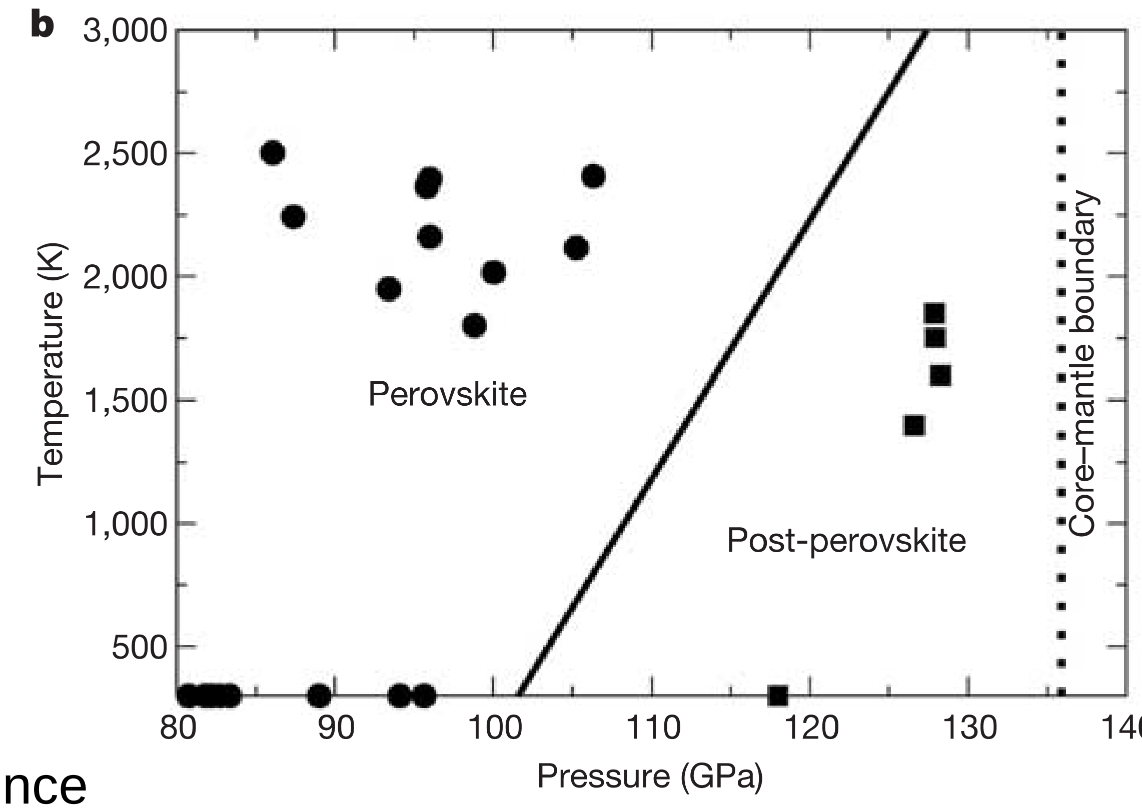


d

Table 1 **Structures of post-perovskite and perovskite at 120 GPa**							
	Post-perovskite*				Perovskite†		
Mg	0	0.2532	1/4	**Mg**	0.5246	0.5768	1/4
Si	0	0	0	**Si**	1/4	0	1/4
O1	0	0.9276	1/4	**O1**	0.1164	0.4669	1/4
O2	0	0.6356	0.4413	**O2**	0.1829	0.1926	0.5575

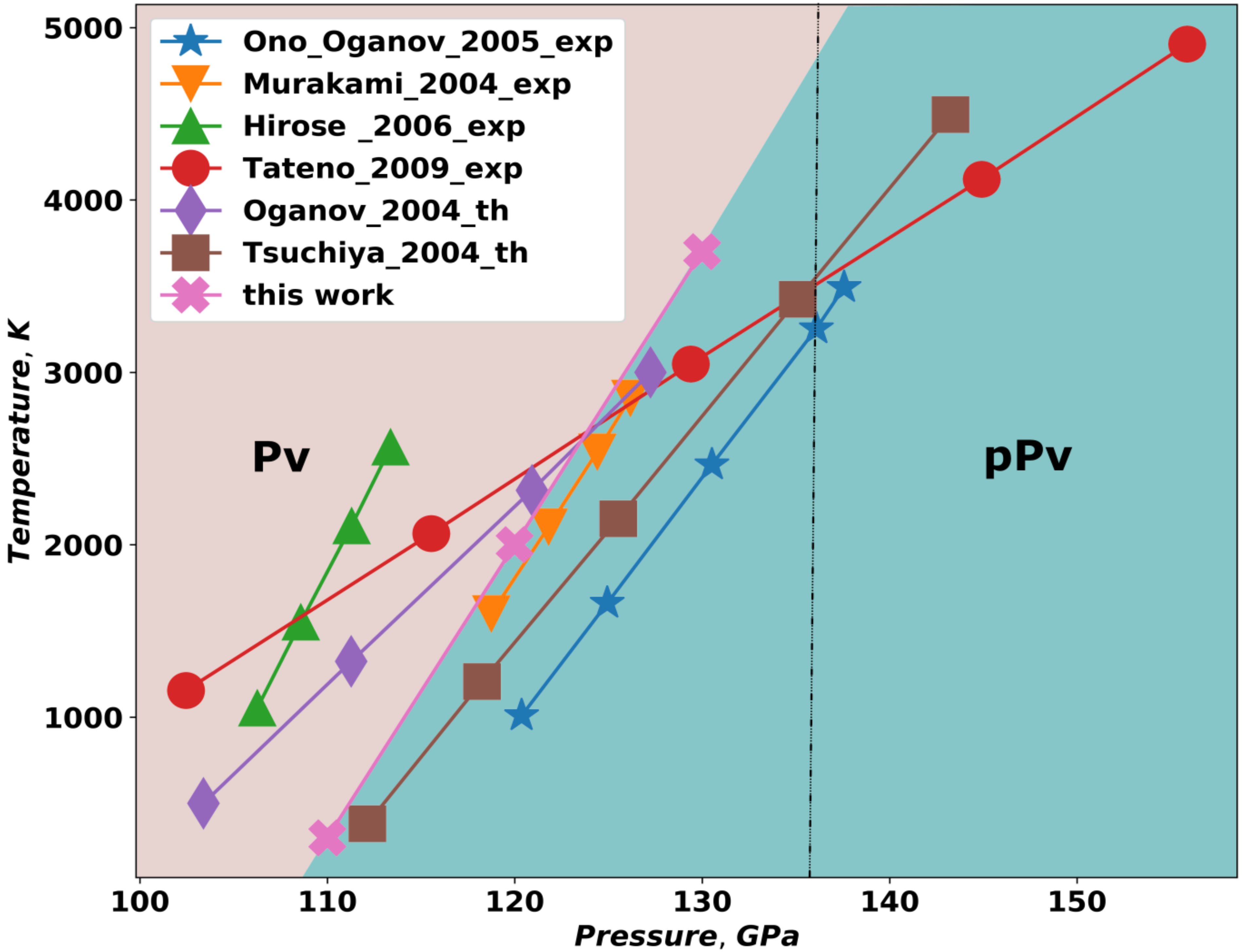
Table shows GGA results.
*Space group *Cmcm*: $a = 2.474$ Å, $b = 8.121$ Å, $c = 6.138$ Å; distances (in Å): Mg–O1 = 1.880 (× 2), Mg–O2 = 1.955(× 4), 2.099(× 2); Si–O1 = 1.643 (× 2), Si–O2 = 1.695 (× 4).
†Space group *Pbnm*: $a = 4.318$ Å, $b = 4.595$ Å, $c = 6.305$ Å; distances (in Å): Mg–O1 = 1.833(× 1), 1.893(× 1), Mg–O2 = 1.864(× 2), 2.047(× 2), 2.201(× 2); Si–O1 = 1.661(× 2), Si–O2 = 1.659(× 2), 1.670(× 2).

b

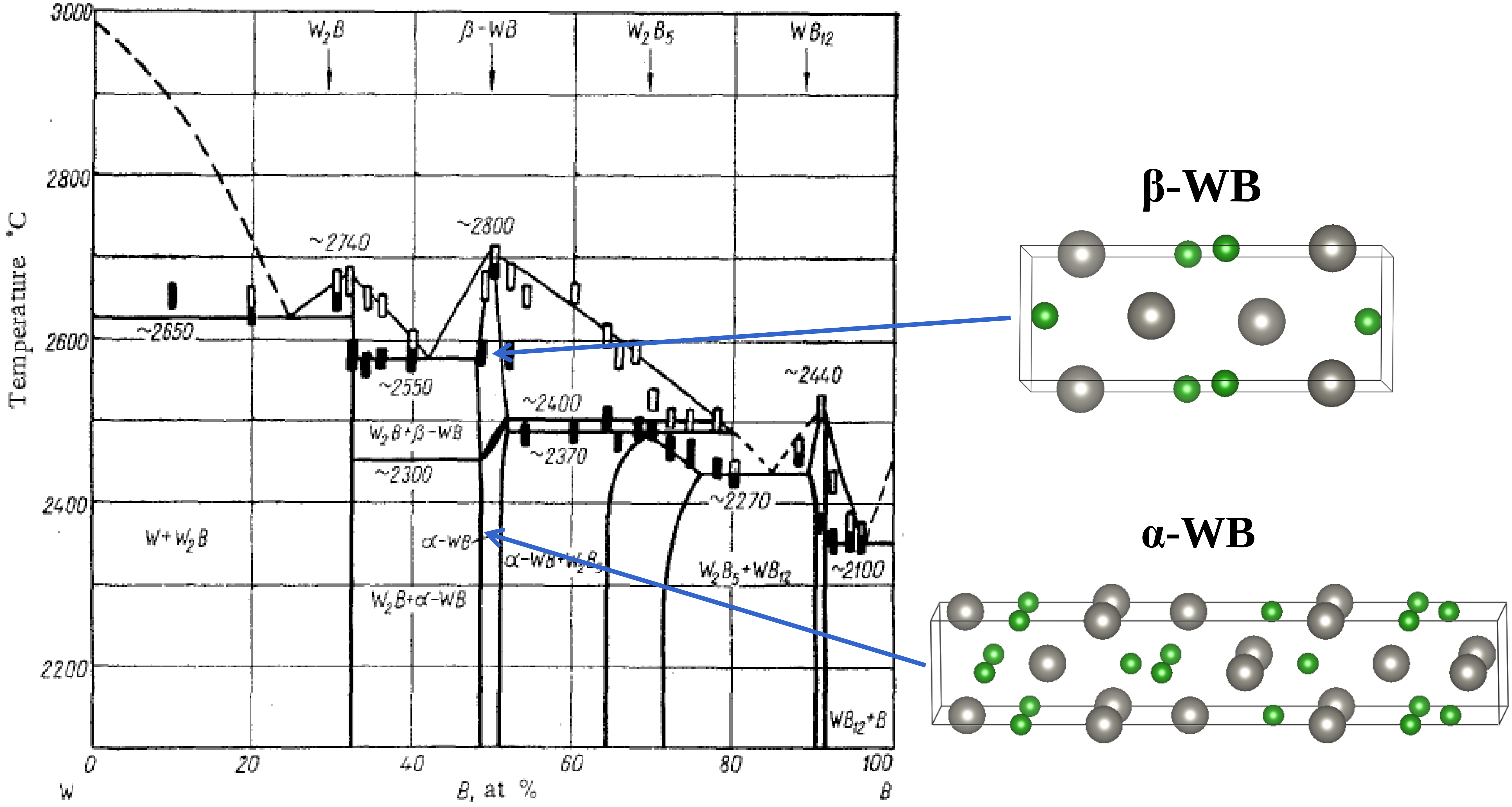


S. Ono, A.R. Oganov / Earth and Planetary Science Letters 236 (2005) 914–932

MgSiO3: T-USPEX results



WB

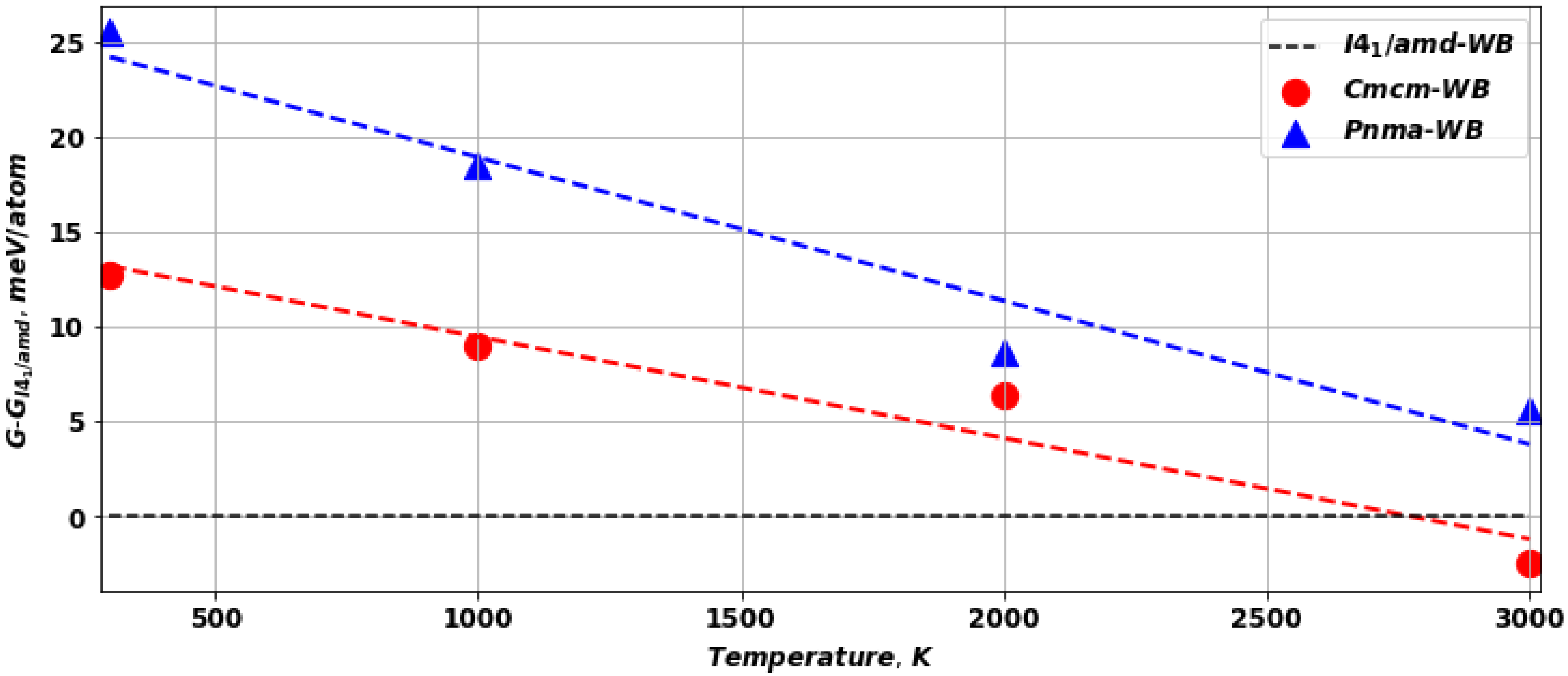


Portnoi, K. I., et al. "Phase diagram of the system tungsten-boron." Soviet Powder Metallurgy and Metal Ceramics 6.5 (1967): 398-402.

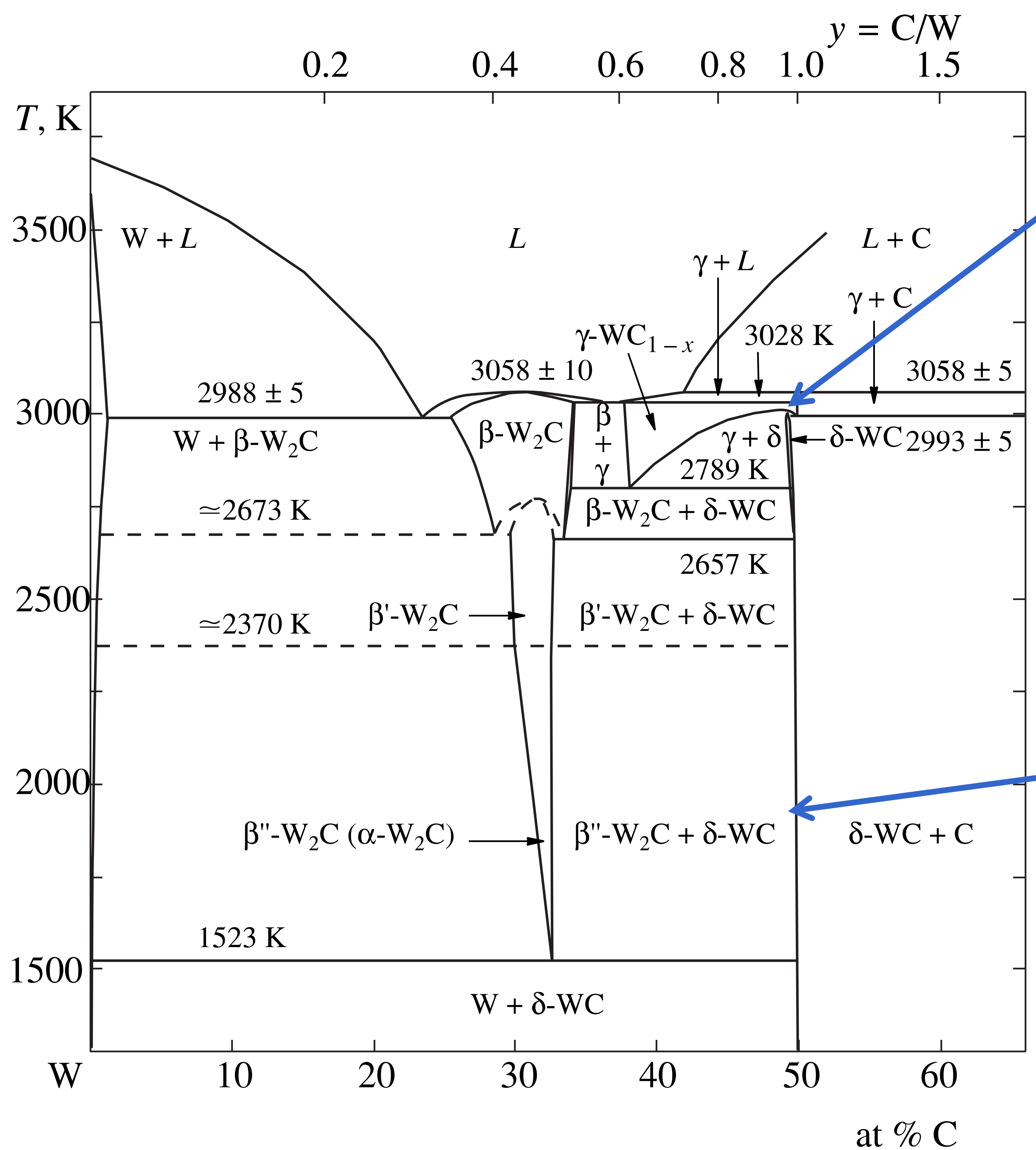
WB: T-USPEX results

0 GPa 2000 K:

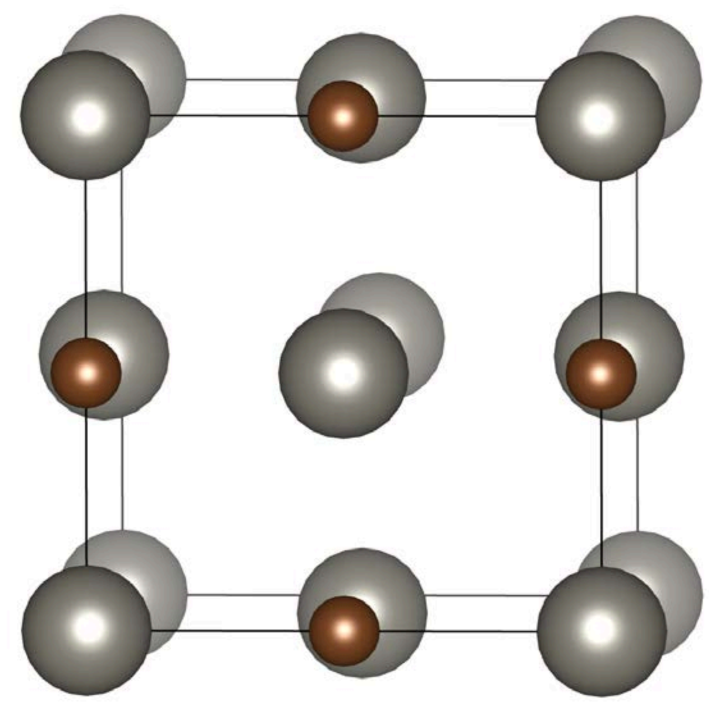
SG	N atoms	TI	FE corr 1	FE corr 2	pV	E_{Eins}	G
225	8	-10.1914	0.0508	0.0000	0.0000	-0.6136	-10.7543
63	8	-10.3158	-0.0236	0.0001	0.0000	-0.6136	-10.9531
63	8	-10.3208	-0.0272	0.0001	0.0000	-0.6136	-10.9617
63	8	-10.3503	0.0011	0.0000	0.0000	-0.6136	-10.9629
141	16	-10.3339	-0.0162	0.0000	0.0000	-0.6136	-10.9638
62	8	-10.3307	-0.0117	0.0001	0.0000	-0.6136	-10.9561



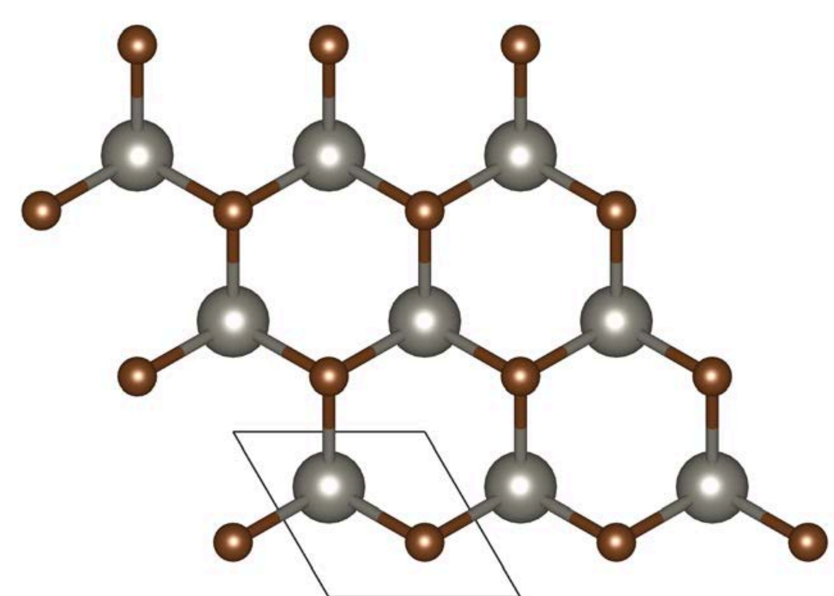
WC


y = C/W
0.2
0.4
0.6
0.8
1.0
1.5
T, K
3500
3000
2500
2000
1500
W + L
L
γ + L
L + C
γ + C
γ-WC1 – x
3028 K
3058 ± 10
3058 ± 5
2988 ± 5
W + β-W2C
β-W2C
β
+
γ
γ + δ
δ-WC
2993 ± 5
2789 K
≃2673 K
β-W2C + δ-WC
2657 K
≃2370 K
β'-W2C
β'-W2C + δ-WC
β''-W2C (α-W2C)
β''-W2C + δ-WC
δ-WC + C
1523 K
W + δ-WC
W
10
20
30
40
50
60
at % C

γ(β)-WC



δ(α)-WC



WC: T-USPEX results

0 GPa 300 K:

SG	N atoms	TI	FE corr 1	FE corr 2	pV	E_{Eins}	G
194	8	-11.0177	0.1629	0.0051	0.0000	-0.0430	-10.9029
1	24	-10.6732	0.1181	0.0013	0.0000	-0.0430	-10.5993
129	4	-10.8590	0.0027	0.0047	0.0000	-0.0430	-10.9039
129	4	-10.8598	0.0082	0.0049	0.0000	-0.0430	-10.8995
129	4	-10.8560	-0.0084	0.0016	0.0000	-0.0430	-10.9089
129	4	-10.8621	0.0050	0.0017	0.0000	-0.0430	-10.9017
189	6	-10.9173	0.0259	0.0034	0.0000	-0.0430	-10.9378
8	12	-10.7019	0.0206	0.0083	0.0000	-0.0430	-10.7326
127	12	-10.7378	0.1397	0.0084	0.0000	-0.0430	-10.6495
187	2	-11.2524	0.0377	0.0007	0.0000	-0.0430	-11.2585
12	8	-10.6560	-0.0398	0.0075	0.0000	-0.0430	-10.7463
129	4	-10.8626	0.0122	0.0077	0.0000	-0.0430	-10.9011
187	2	-11.0304	-0.1790	0.0007	0.0000	-0.0430	-11.2531
8	8	-10.8290	0.2177	0.0043	0.0000	-0.0430	-10.6585
31	12	-10.6269	0.0452	0.0016	0.0000	-0.0430	-10.6263
194	4	-10.9100	0.0181	0.0084	0.0000	-0.0430	-10.9433

WC: T-USPEX results

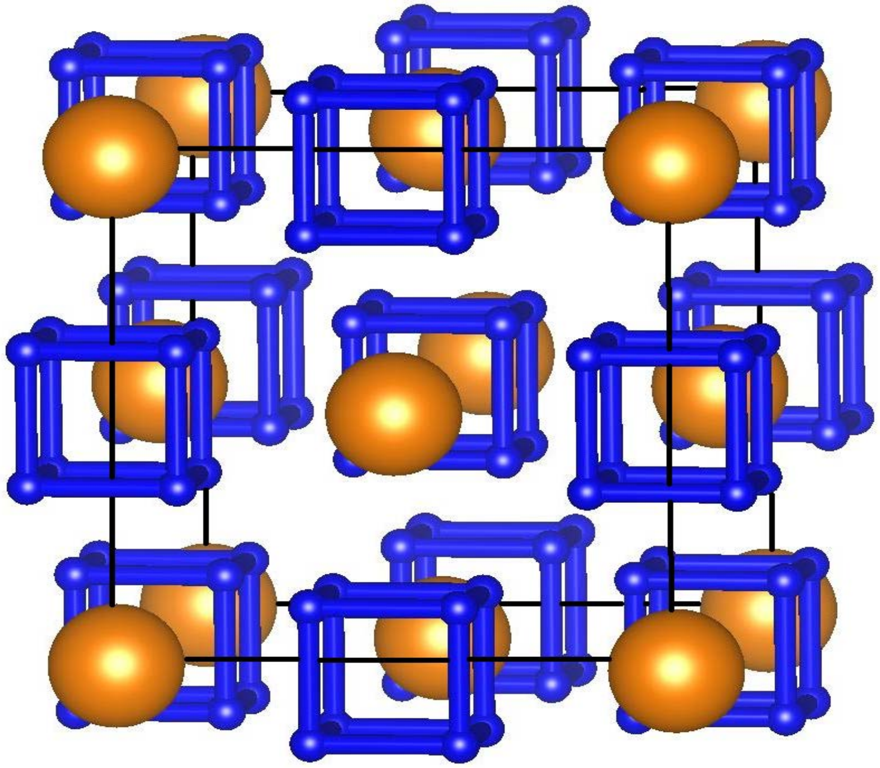
0 GPa 2000 K:

SG	N atoms	TI	FE corr 1	FE corr 2	pV	E_{Eins}	G
225	8	-11.0559	0.0061	0.0003	0.0000	-0.6142	-11.6642
225	8	-11.1011	0.0480	0.0002	0.0000	-0.6142	-11.6675
194	8	-10.9731	-0.0615	0.0001	0.0000	-0.6142	-11.6489
225	8	-11.1474	0.0958	0.0002	0.0000	-0.6142	-11.6659
225	8	-11.0192	-0.0358	0.0002	0.0000	-0.6142	-11.6694
225	8	-11.0932	0.0399	0.0002	0.0000	-0.6142	-11.6678

UH8: T-USPEX results

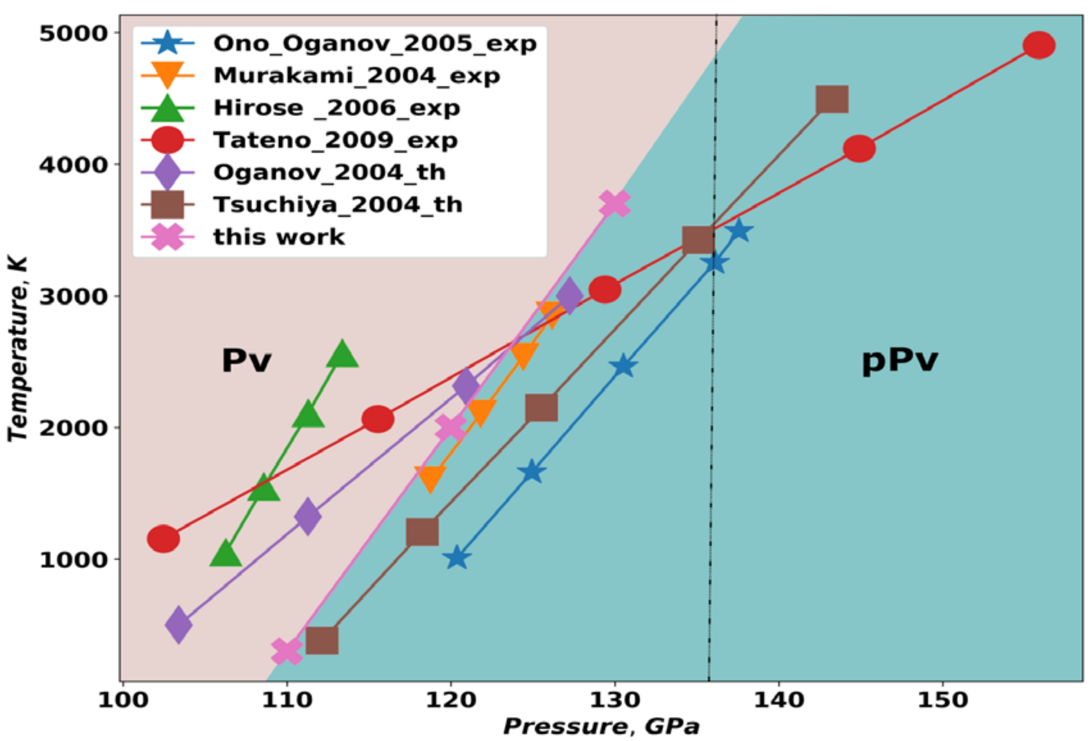
50 GPa 300 K:

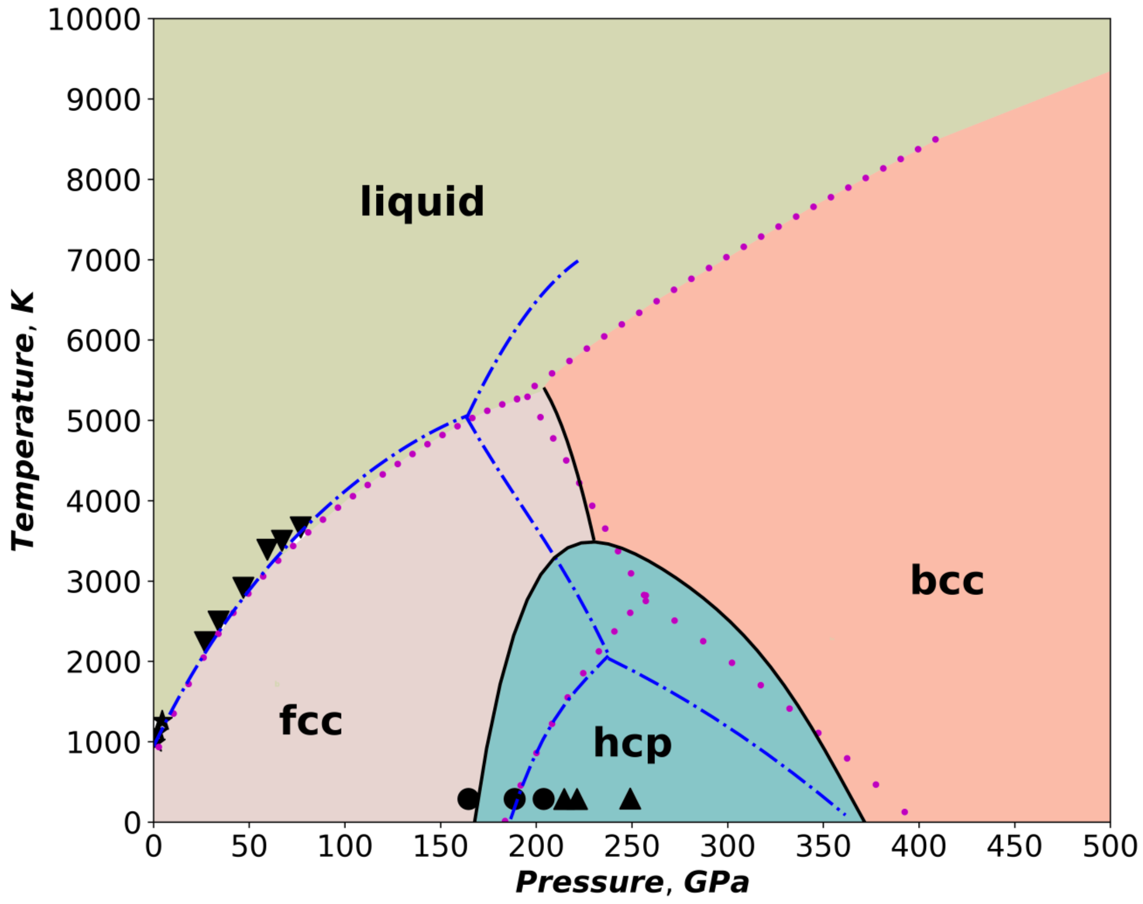
SG	N atoms	TI	FE corr 1	FE corr 2	pV	E_{Eins}	G
225	36	-4.0101	-0.0000	0.0001	1.1994	-0.0456	-2.8564
225	36	-4.0129	-0.0030	0.0005	1.2022	-0.0456	-2.8597



Conclusions

T- USPEX Computational Materials Discovery





[Kruglov et al, submitted, 2020]