ВНИИА
ПРЕДПРИЯТИЕ ГОСКОРПОРАЦИИ "РОСАТОМ"
ФГУП "ВСЕРОССИЙСКИЙ НАУЧНО-ИССЛЕДОВАТЕЛЬСКИЙ ИНСТИТУТ АВТОМАТИКИ им. Н.Л.Духова"
CENTER OF FUNDAMENTAL AND APPLIED RESEARCH
COMPUTENTIAL MATERIALS SCIENCE

First-principles calculations of uranium properties using pseudopotential and APW methods

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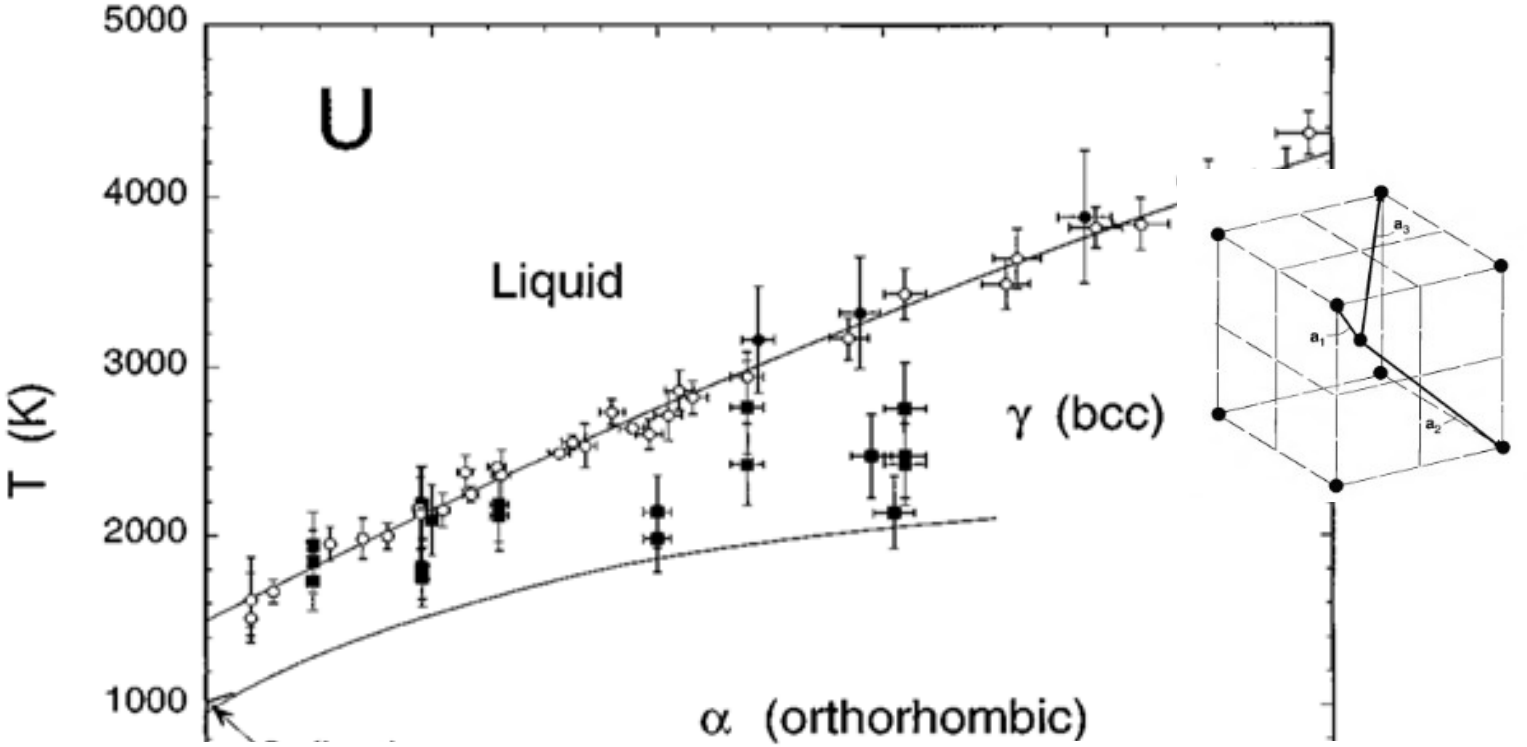
Dukhov Research Institute of Automatics
2017

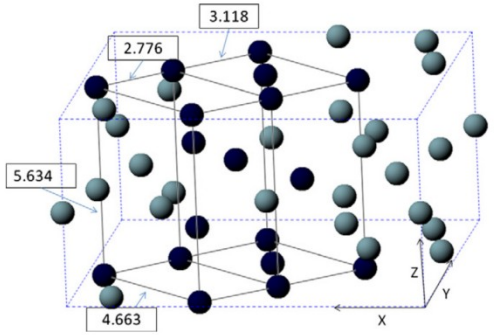
I. Outline

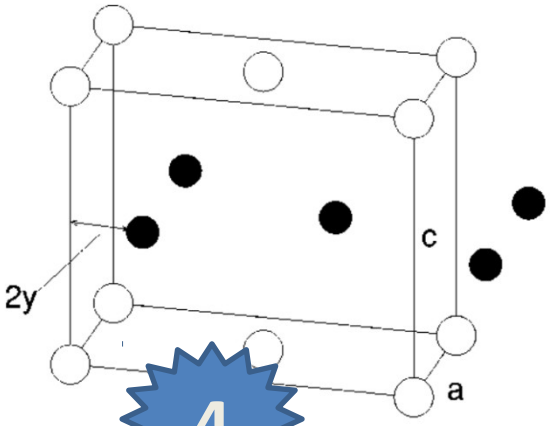
- Motivation
- Methods
- Uranium at T=0K
- Thermal effects in compressed uranium
- Conclusions

II. Motivation

Uranium polymorph transition at P<100 GPa





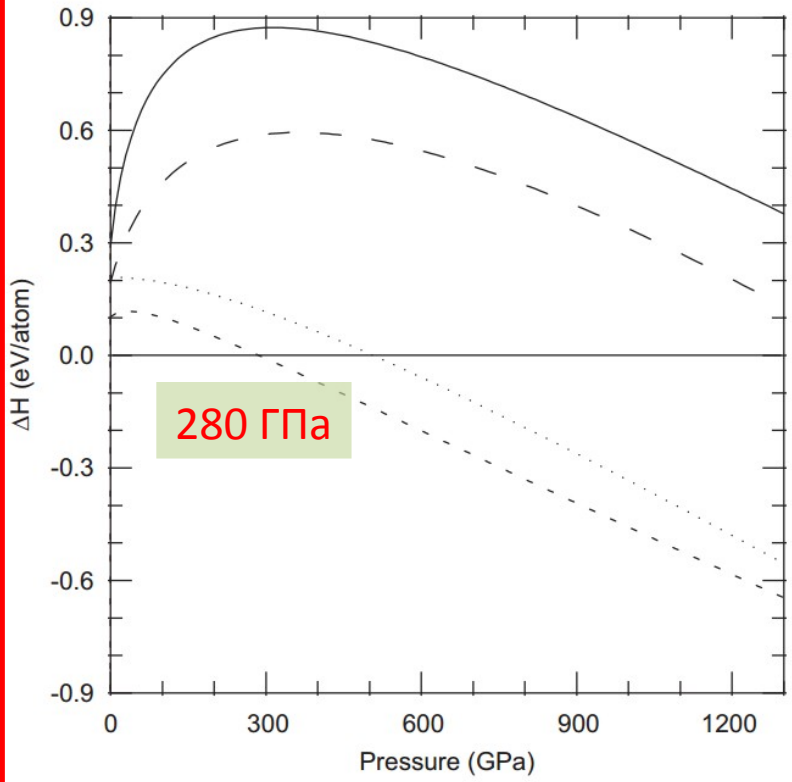


Yoo, C.S. et al, Phys. Rev. B 57, 10359, 2008

Phase diagram of uranium at P>100 GPa

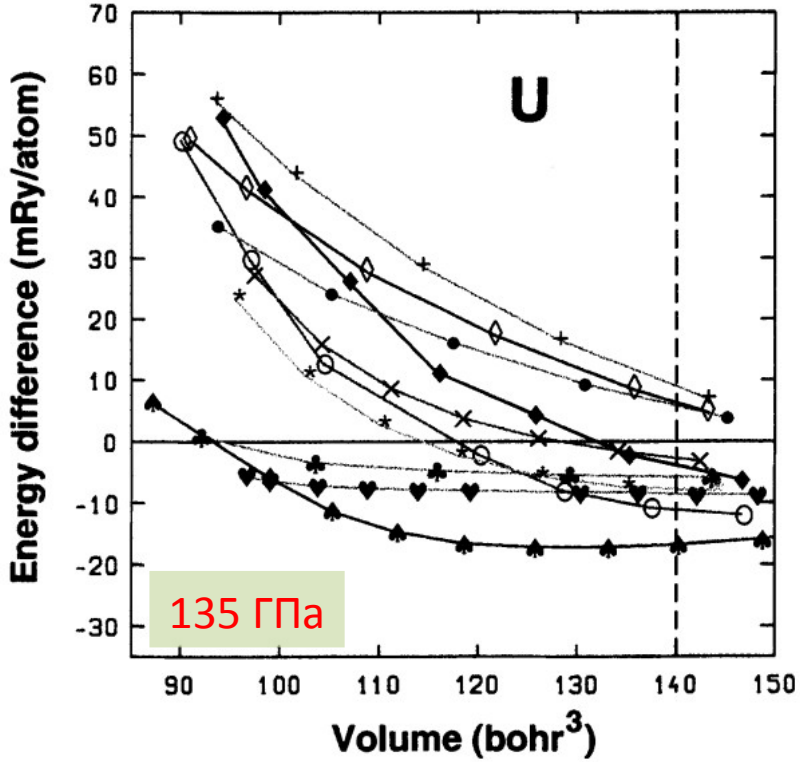
T=0

α-bct phase transition



PAW

S. Adak *et al*, Physica B. 433. 133. 2013

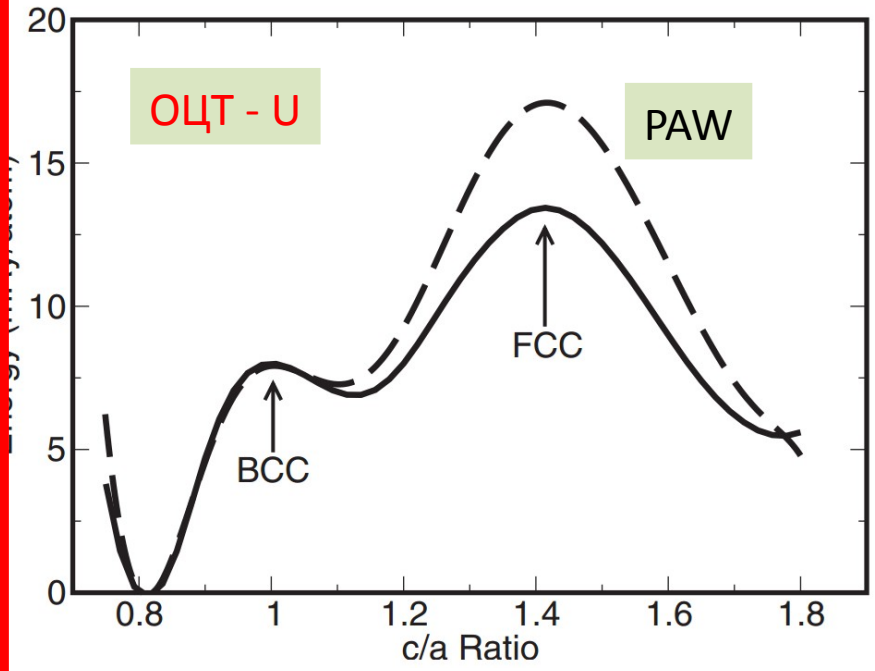


LAPW

M. Penicaud, J.Phys.: Cond. Matt. 14. 3575. 2002

Phase diagram: Stable structure analysis

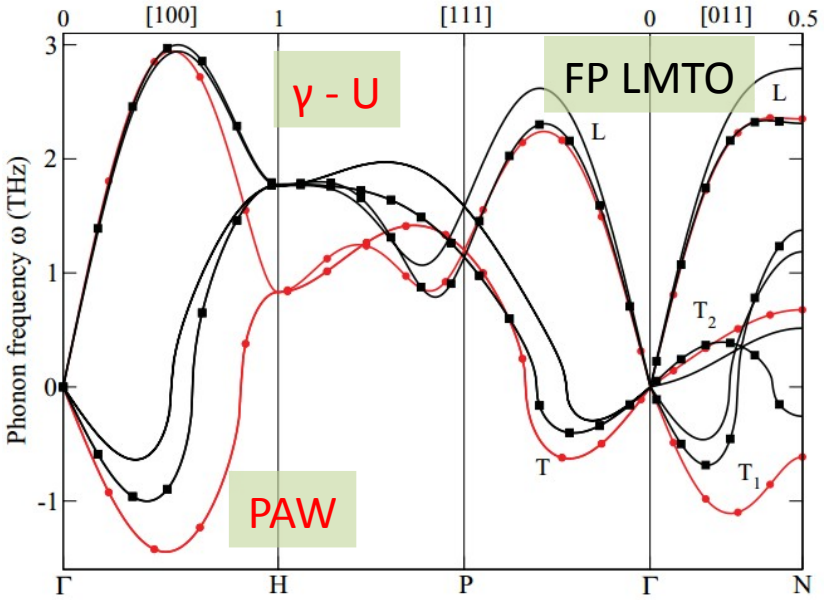
T=0



Equilibrium volume Vexp=20.75 A^3

R.Q. Hood et al, Phys. Rev. B. 78. 024116. 2008

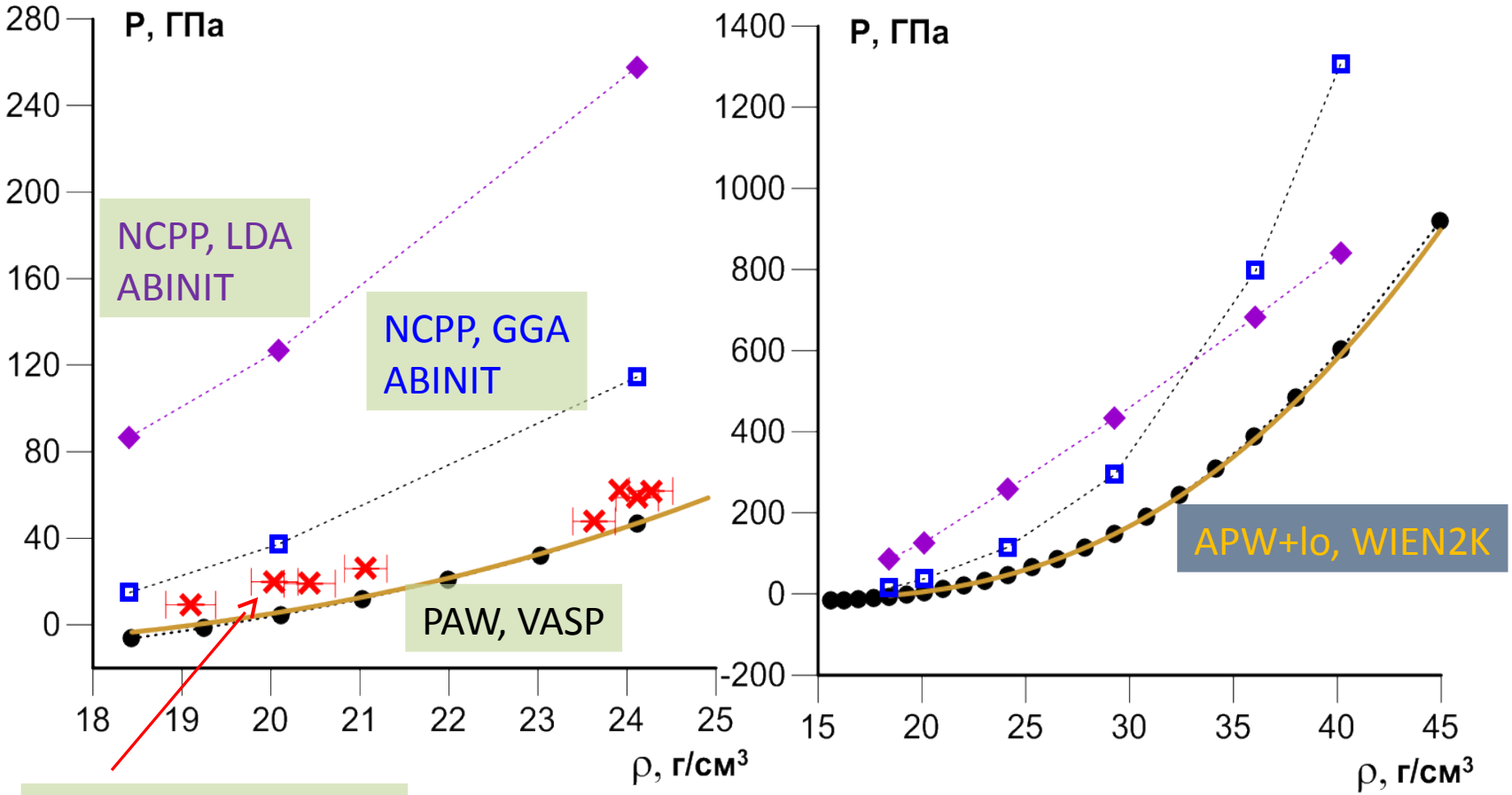
T=500K



SCAILD – an improvement of DFT phonon spectra

P. Soderlind, Phys. Rev. B. 85. 060301. 2012

0K isotherm of γU: test of different approaches



DAC, T=1300-2000K:

Yoo, C.S. et al, Phys. Rev. B 57, 10359, 2008

ftp://ftp.abinit.org/pub/abinitio/Psps/LDA_TM.psps/92/92u.pspnc

ftp://ftp.abinit.org/pub/abinitio/Psps/GGA_FHI/92-U.GGA.fhi

Resume for already published data:

- The difference between data obtained using pseudopotential and full-electron methods are found in some researches;
- The main part of published articles dedicated to uranium at pressure < 100 GPa.

1) To check pseudopotential DFT calculations using full electron methods.

2) To investigate lattice parameters of stable uranium at the pressures up to 1 TPa.

3) To estimate an accuracy of free energy at non-zero temperatures which was calculated with hot electrons contribution for uranium.

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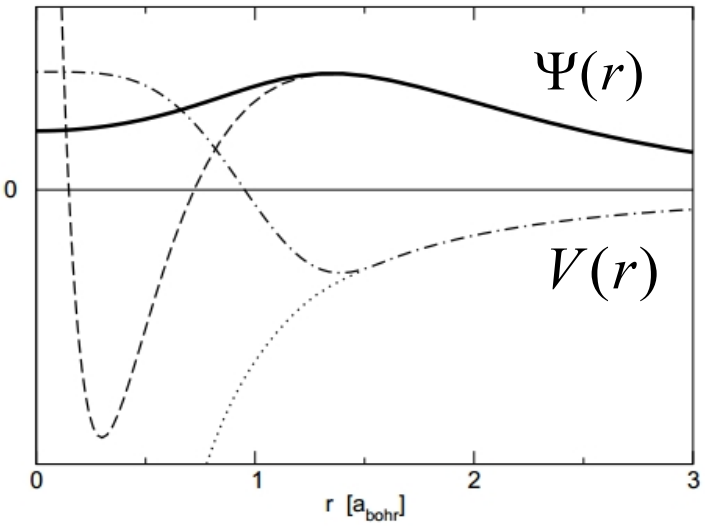
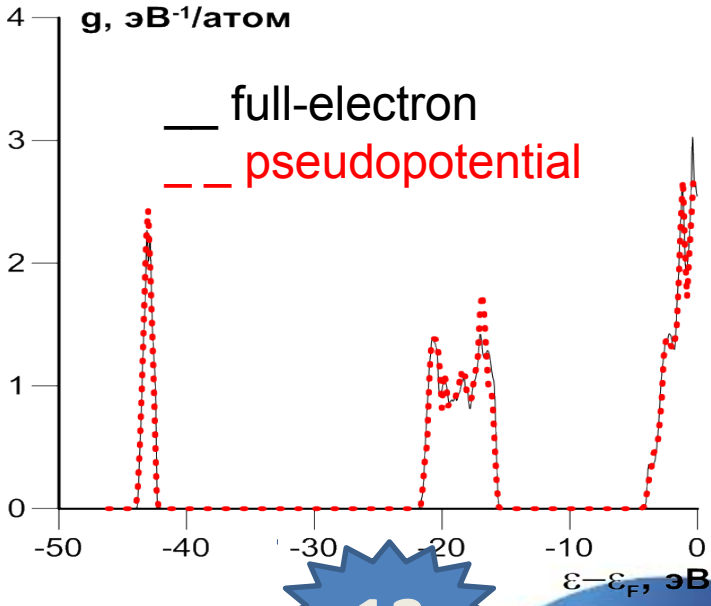
III. Calculation methods

Main approaches in DFT

- Pseudopotentials
- (NCPP, USPP, **PAW**)



- Full-electron methods
- (APW,LMTO,LAPW,
- GTO,**APW+lo**)



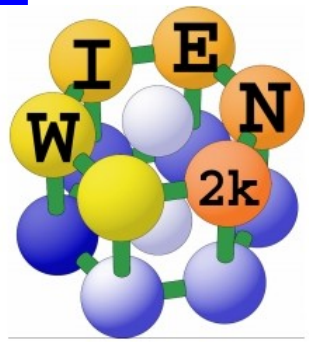
* P.E. Bloechl, arXiv:1104v1

Parameters of pseudopotential calculation

Electron basis	PAW
xc-functional	PBE
Used package	VASP
Number of atoms in the cell (α/ОЦТ/γ)	4/2/1
Valence bands	$6s^2 6p^6 6d^1 7s^2 5f^3$
Core electrons radius, a_B	2.2
Cutoff energy	500 eV
Monkhorst-Pack grid	11×11×11

* G. Kresse *et al*, Comput. Mater. Sci. 6. 15. 1996
* G. Kresse *et al*, Phys. Rev. B. 59. 1758. 1999.

Parameters of full-electron calculation

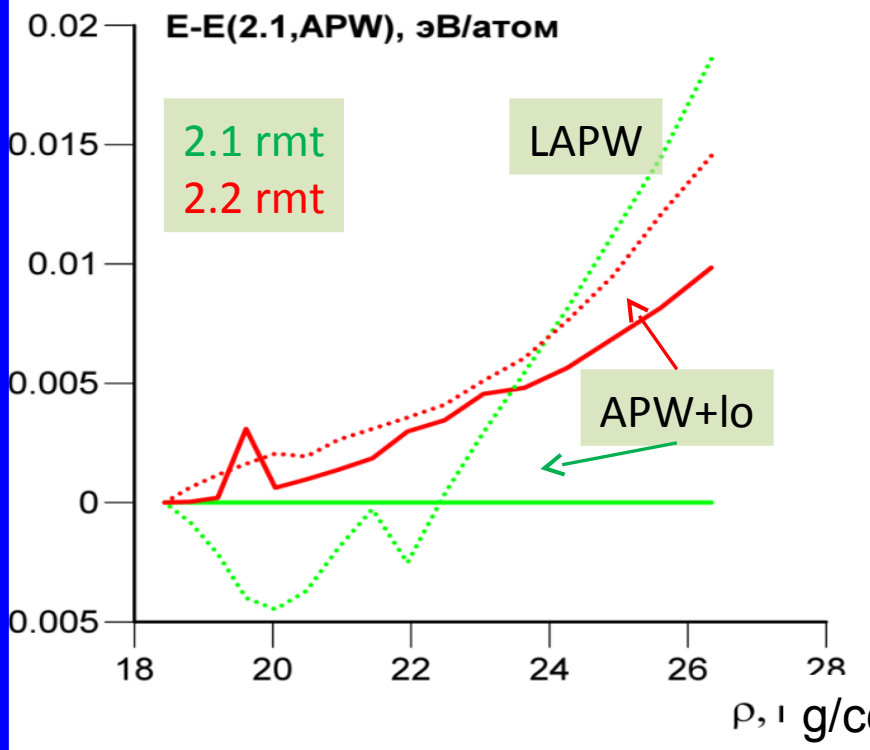


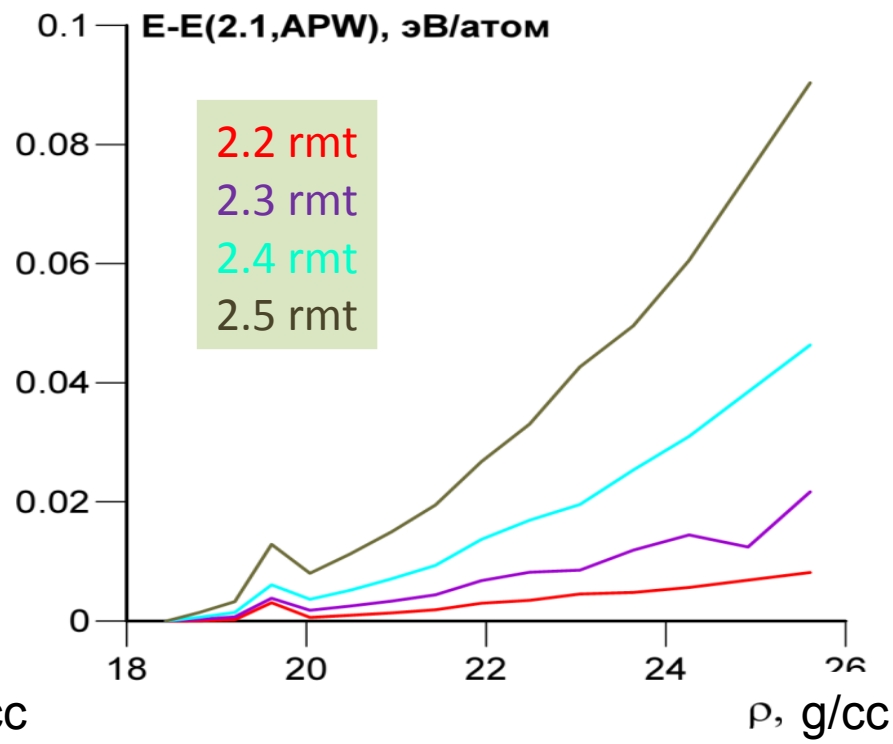
WIEN2k

Electron basis	APW+lo
xc-functional	PBE
Used package	Wien2K
Number of atoms in the cell (α/ОЦТ/γ)	4/2/1
Valence bands	$5d^{10}6s^{2}6p^{6}6d^{1}7s^{2}5f^{3}$
Core electrons radius, a_B	2.1 (1.9, ρ > 26 g/cc)
Cutoff energy	11
Monkhorst-Pack grid	20×20×20

* G.K.H. Madsen *et al*, PRB, **64**, 195134 (2001)

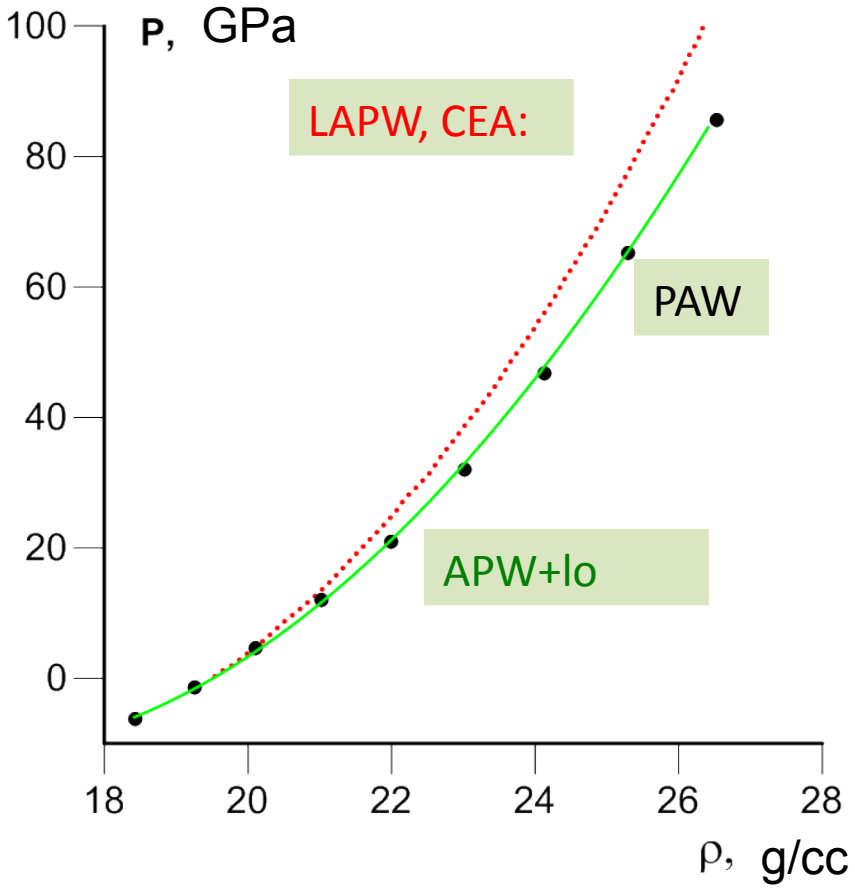
Tests of APW+lo and LAPW approaches





IV. Results

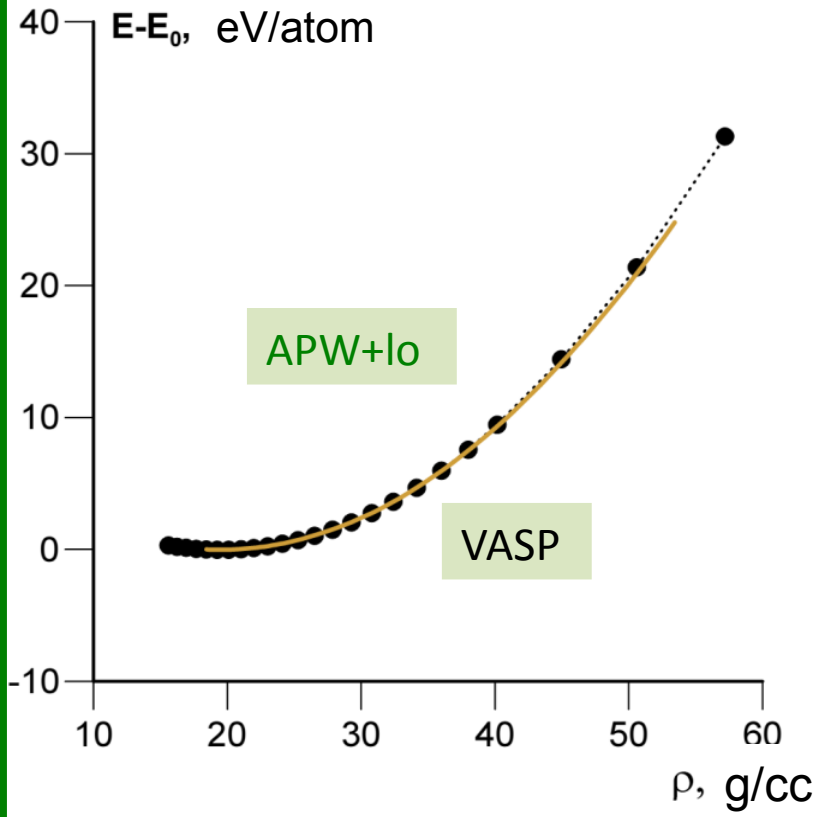
0 K isotherm of γU at P<100 GPa

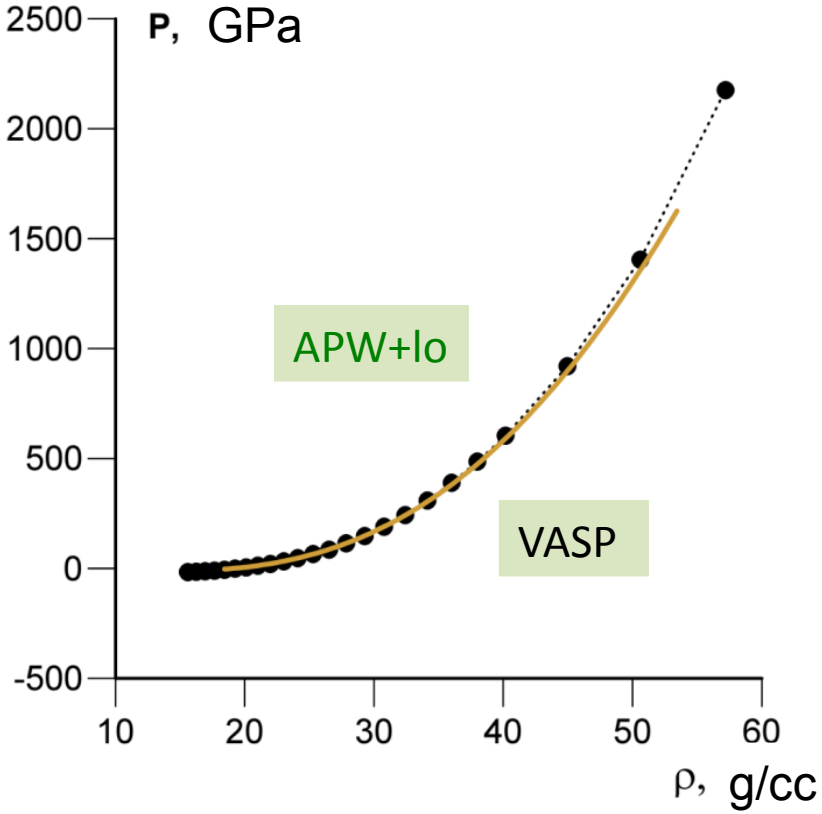


M. Penicaud, J.Phys.: Cond. Matt. 14. 3575. 2002

IV

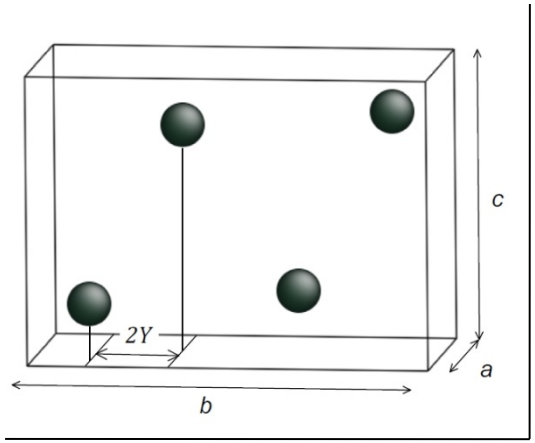
0 K isotherm of γU at P ~ 1 TPa





IV

Lattice parameters of stable αU at T=0 K



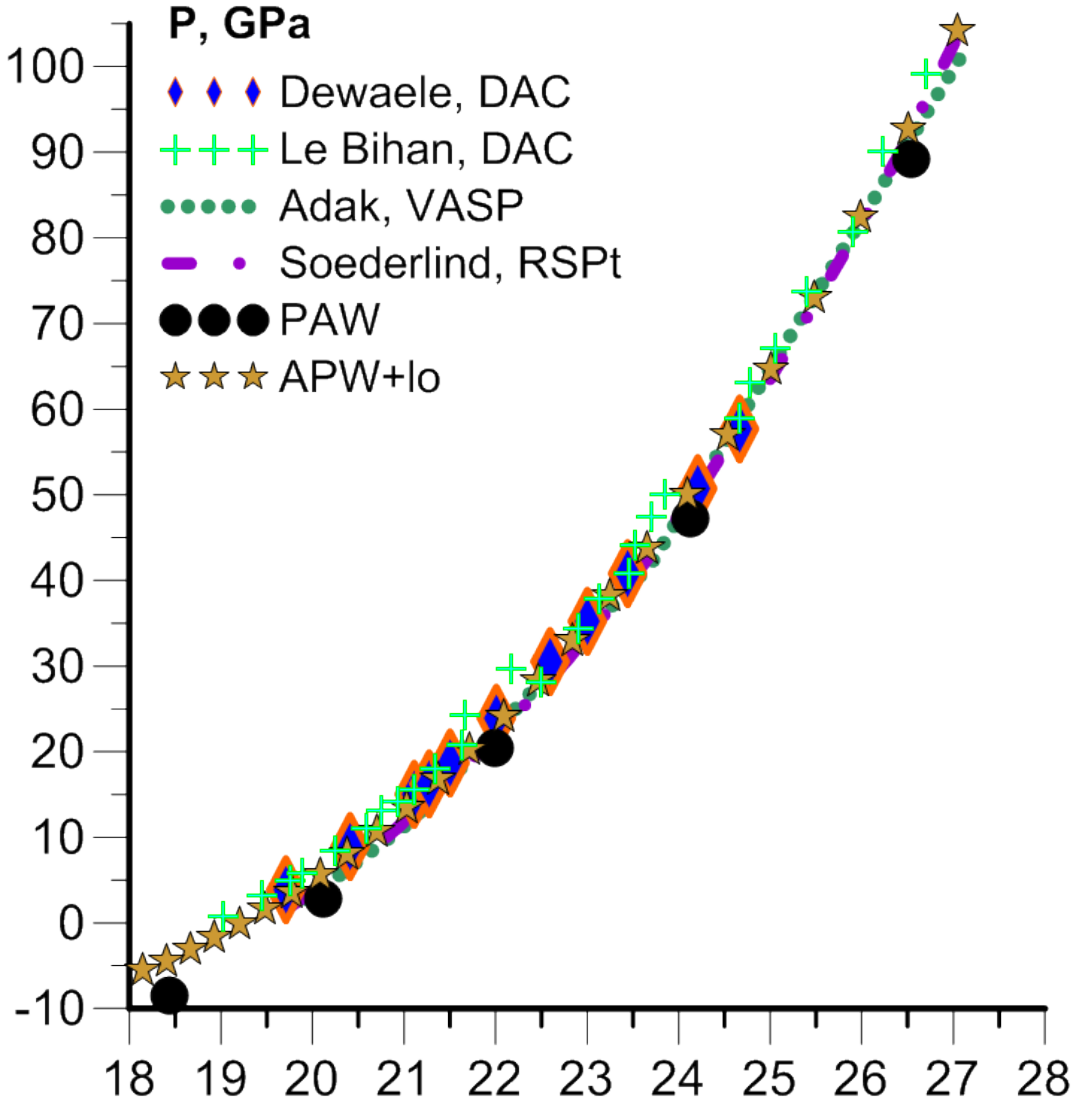
VASP:

Density, g/cc	a, Å	b, Å	c, Å	$2Y$
18.4	2.8735	6.0268	4.9515	0.1961
20.1	2.7387	5.8691	4.8954	0.1977
24.1	2.5806	5.3978	4.7098	0.2021
29.3	2.4467	4.9111	4.4941	0.2093
36.0	2.3050	4.5397	4.1960	0.2270
40.1	2.2402	4.3703	4.0212	0.2419

E(WIEN2K)-E(VASP):

Density, g/cc	Deformation vector	Energy lowering, meV/atom
18.4	$(11\bar{1})$	-1.1
20.1	$(1\bar{1}\bar{1})$	-20.9
24.1	$(10\bar{1})$	-16.4
29.3	$(1\bar{1}1)$	-2.7
36.0	$(01\bar{1})$	-5.1
40.1	$(01\bar{1})$	-1.5

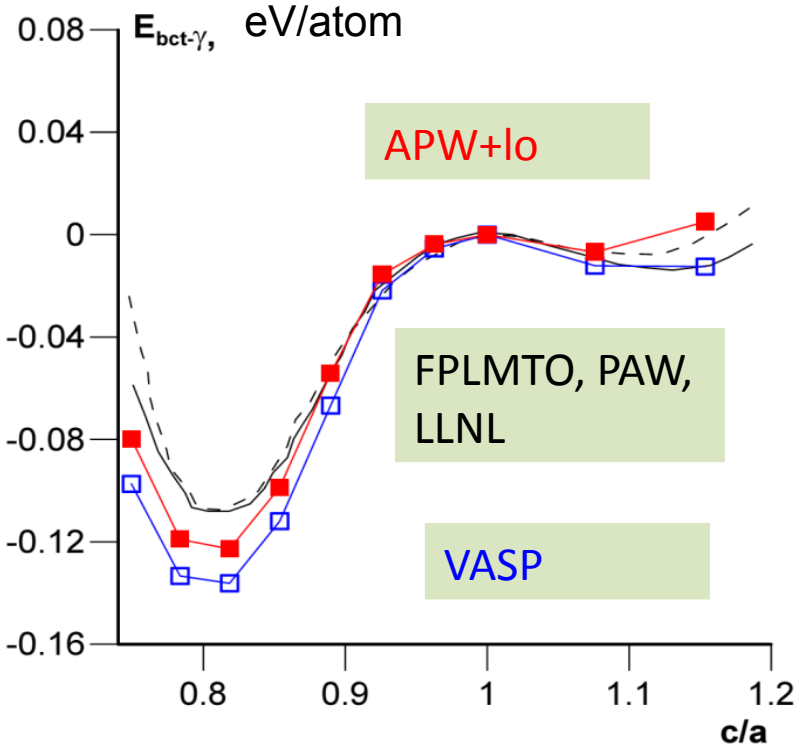
0 K isotherm of αU

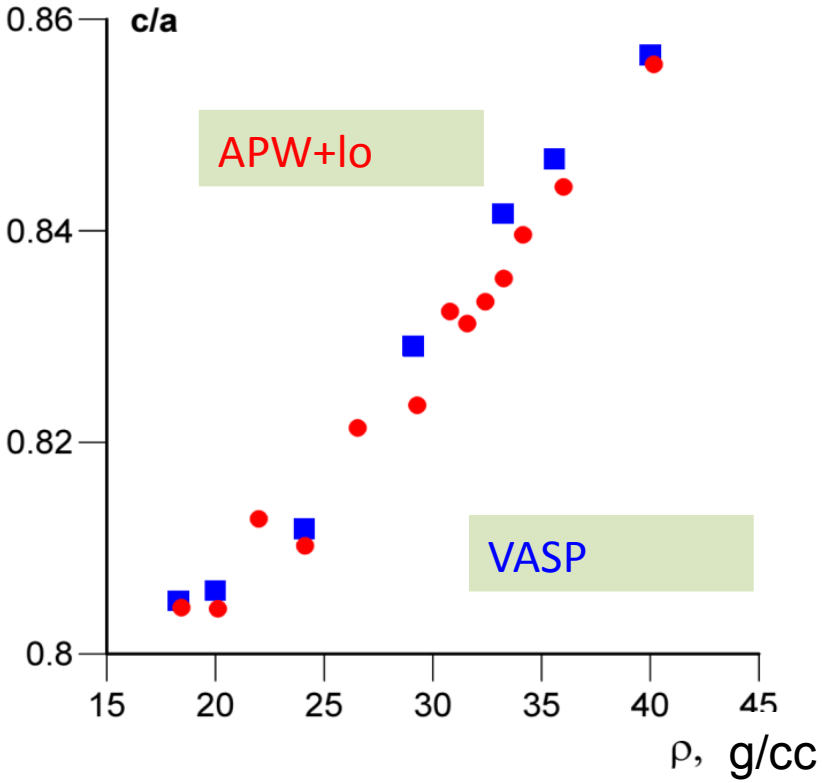


S. Adak *et al*, Physica B. 433. 133.
T. Le Bihan *et al.* PRB, 67, 134102. 2003.
A. Dewaele. PRB. 88. 134202, 2013
P. Soderlind. PRB, 66, 235112, 2002

IV

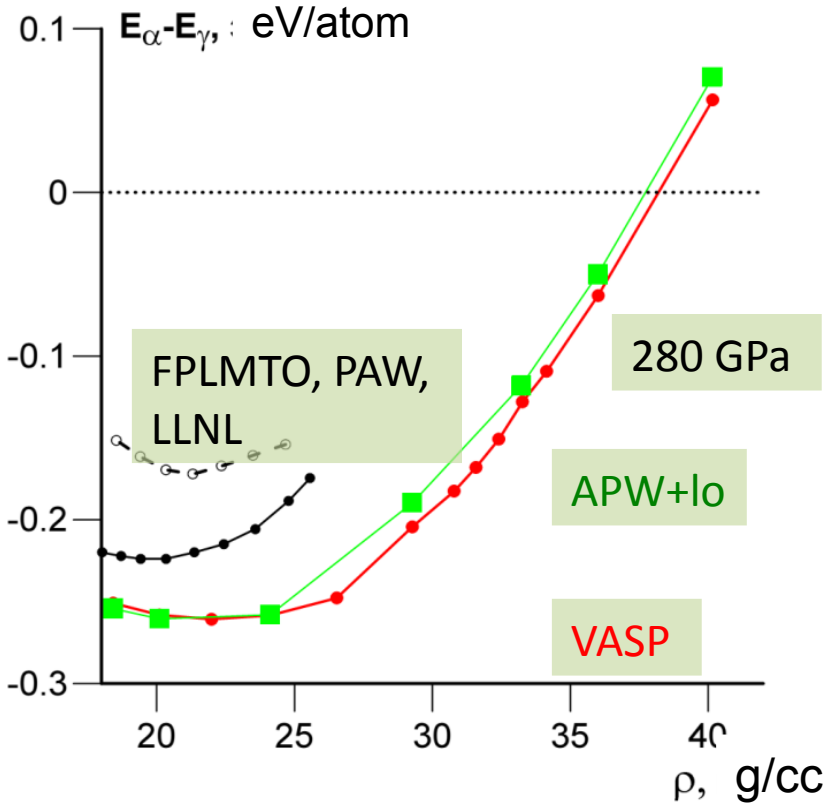
Lattice parameters of stable *bct* U at T=0 K

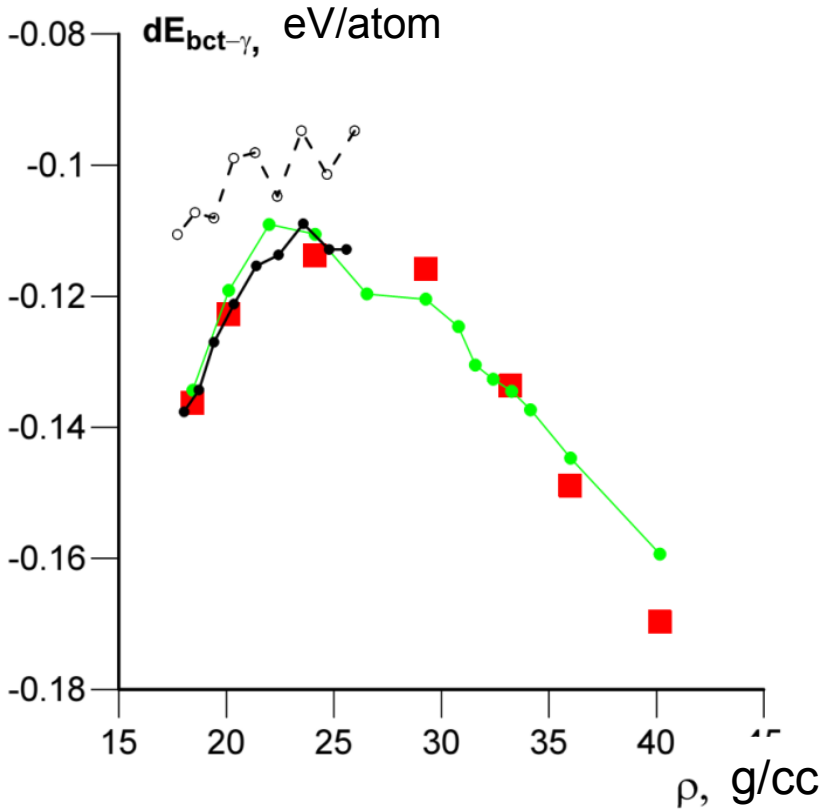




R.Q. Hood et al, Phys. Rev. B. 78. 024116. 2008

α-bct polymorph transition

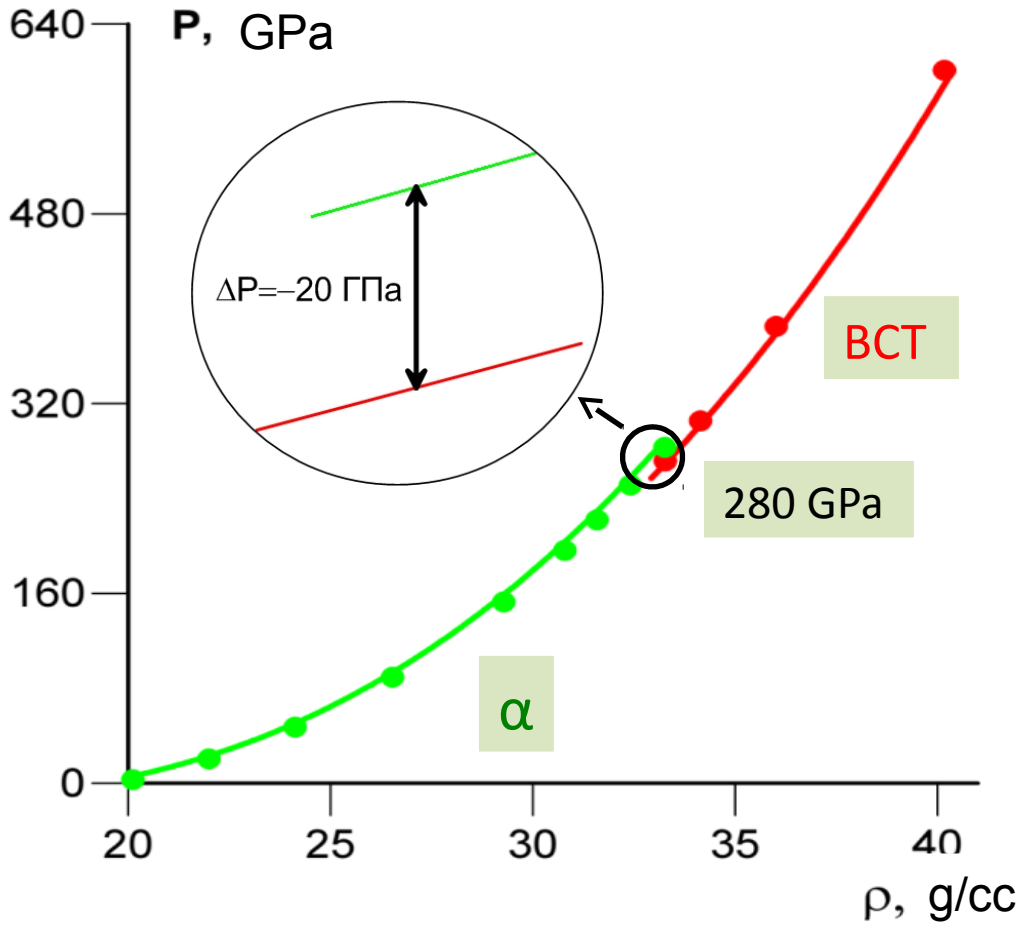


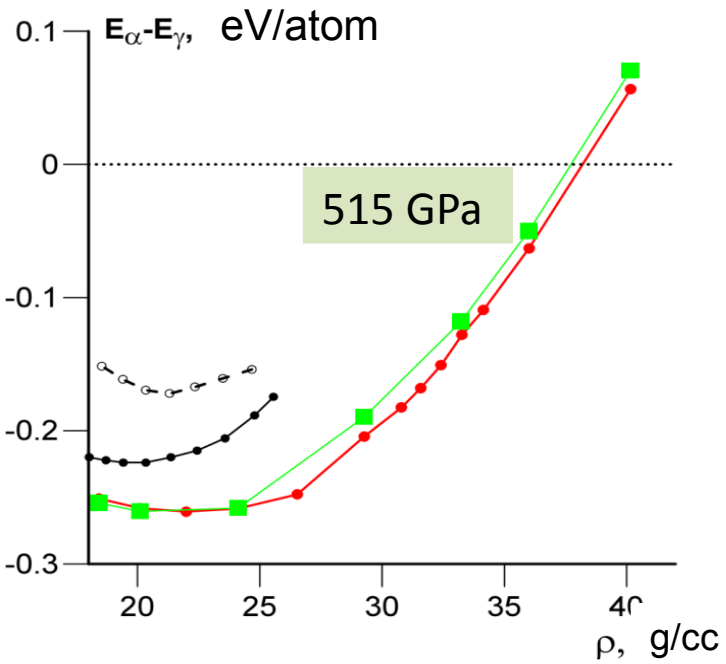


Bct U becomes stable up to at least 1 TPa

R.Q. Hood et al, Phys. Rev. B. 78. 024116. 2008

Total 0K isotherm of U at P<1 TPa

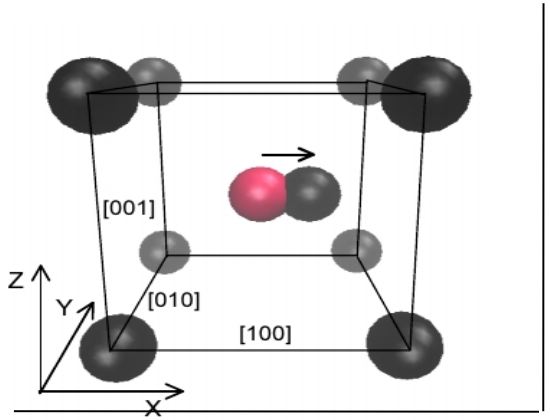




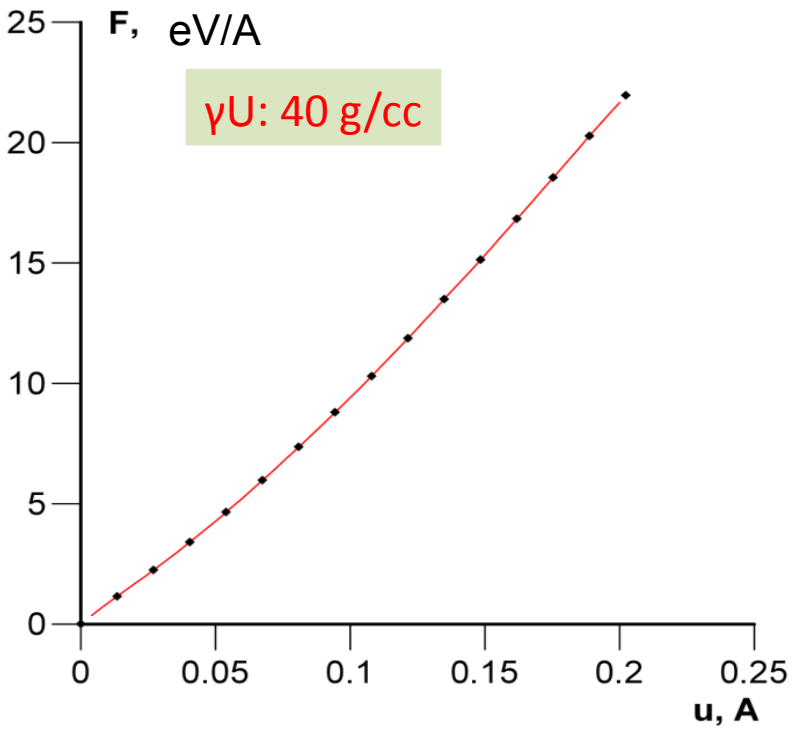
R.Q. Hood et al, Phys. Rev. B. 78. 024116. 2008

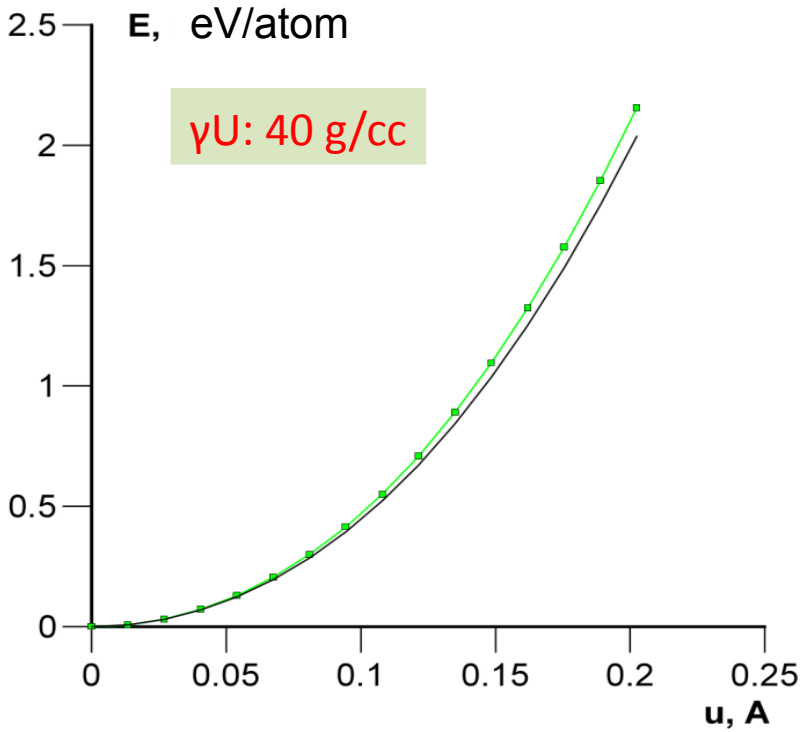
IV

Accordance of forces and energies

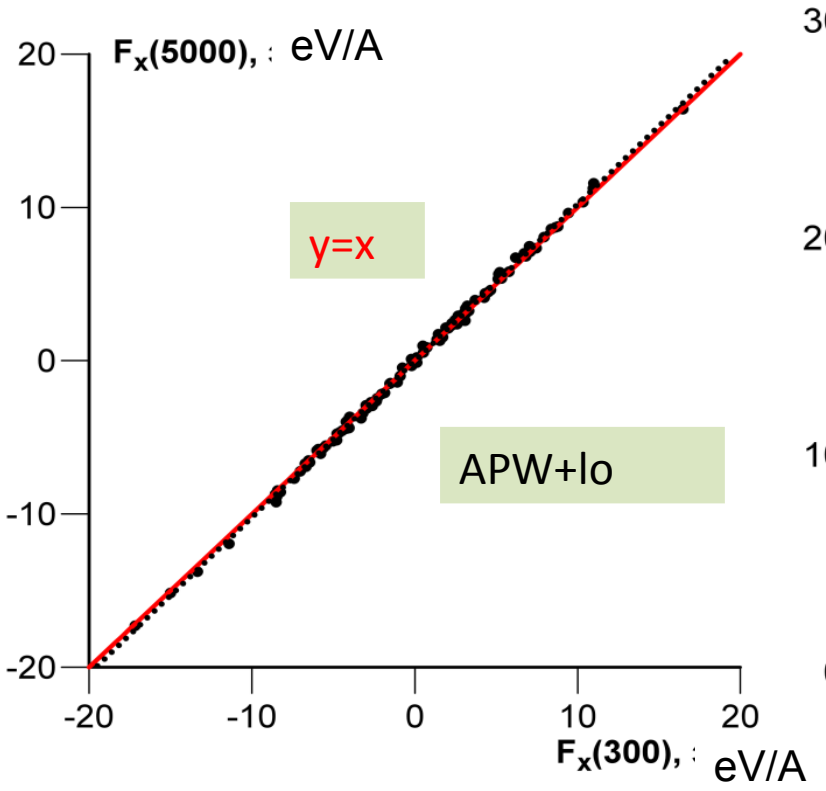


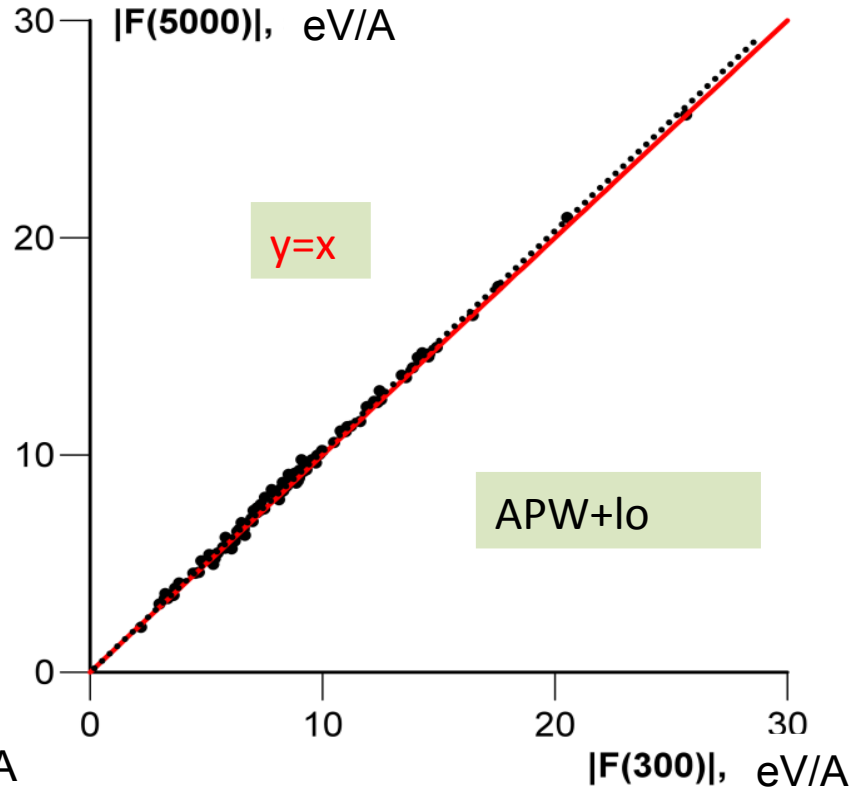
$$E_A^{(a)} - E_B^{(a)} = -\int\limits_{A\to B} \vec{F}^{(a)} d\vec{\tau}_{A\to B}$$





Thermal effects in γ-U at T<5000 K





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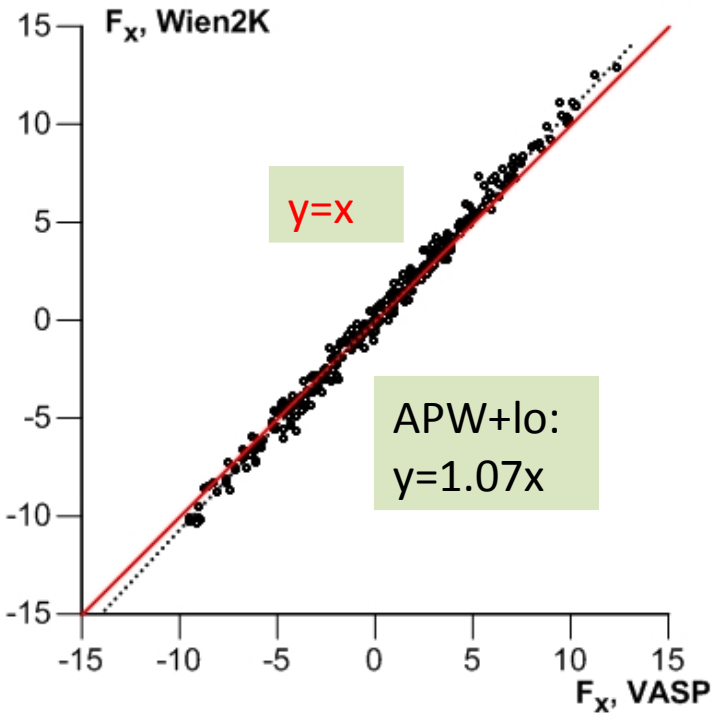
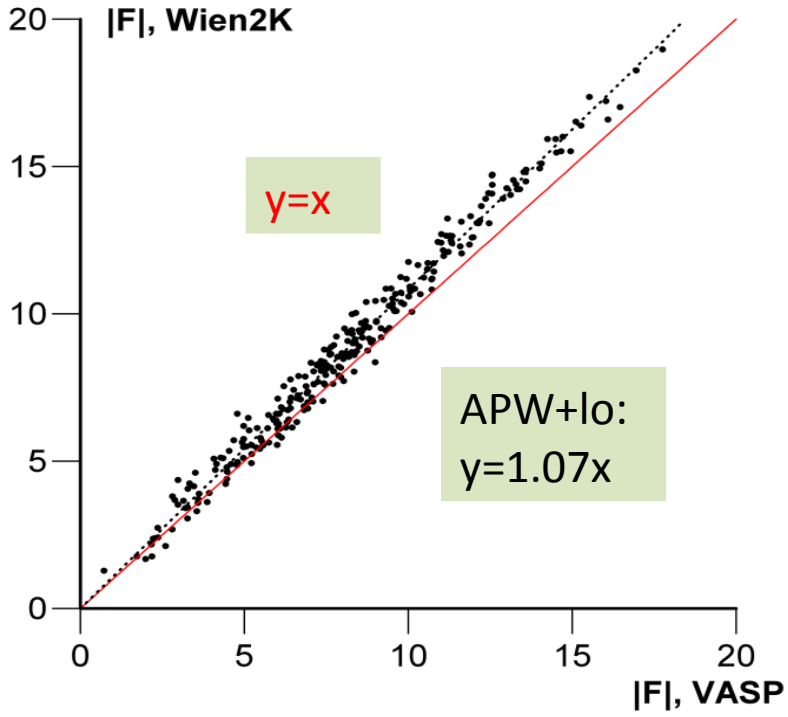
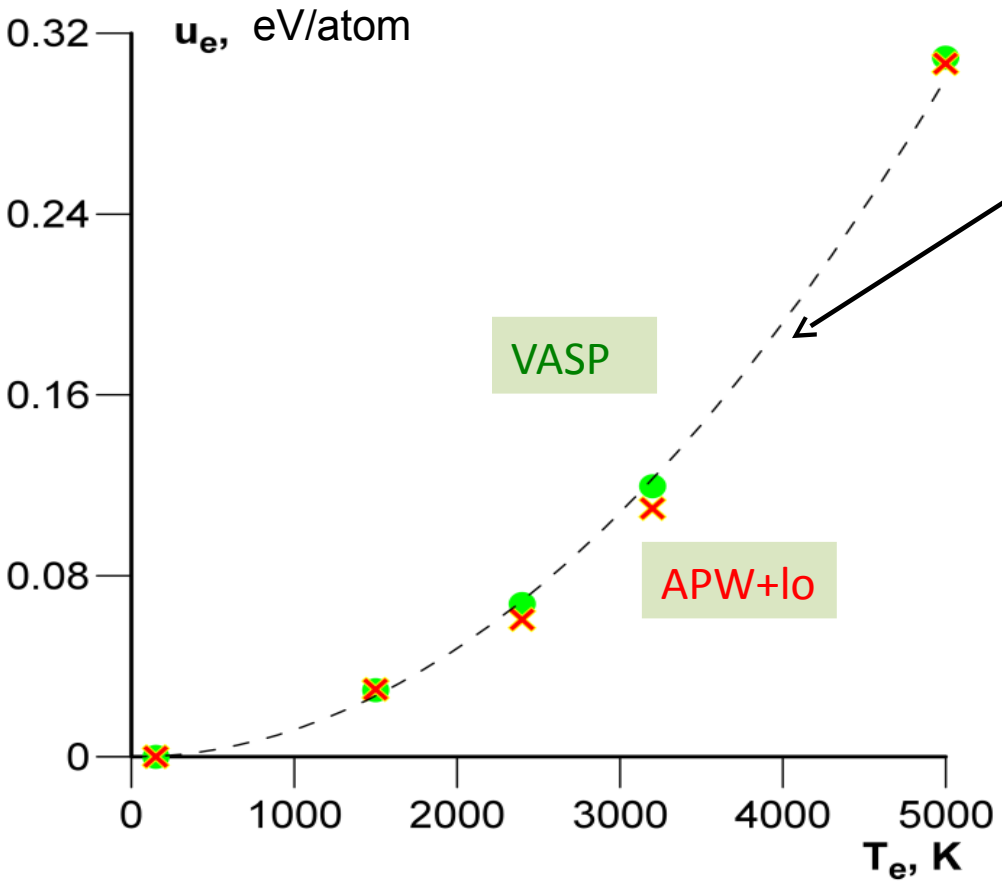




Hot electrons contribution at T<5000 K



$$u_e = 1/2\, G_e T_e^2$$

$$G_e = 390 J / m^3 / K^2$$

IV

Accuracy of free energy calculation at T <5000K

$$F - F_0 \approx \langle U - U_0 \rangle_i - \frac{1}{2k_B T} \left\langle \left(U - U_0 - \langle U - U_0 \rangle_i \right)^2 \right\rangle_i$$

$$F_{FE}^{(c)} - F_{psp}^{(c)} \approx \left\langle U_{FE}^{(c)} - U_{FE}^{(c)} \right\rangle_i - \frac{1}{2k_B T} \left\langle \left(U_{FE}^{(c)} - U_{FE}^{(c)} - \left\langle U_{FE}^{(c)} - U_{FE}^{(c)} \right\rangle_i \right)^2 \right\rangle_i$$

T, K	ΔE_1, meV/atom	ΔE_{54}, meV/atom
1500	6(-0.05)	17(-0.05)
5000	-5(-0.015)	11(-0.015)

Conclusions

- Using DFT we obtained quantitative description of uranium phase diagram at compressions P < 1 TPa for known candidates between lattice types:

  α-bct polymorph transition at 280 GPa, bct-U is stable at P<1 TPa

- The results of pseudopotential calculation are in good agreement with the presented data of full-electron approach:

  0 K isotherms, total energies for different lattices, Bain path, forces, electron thermal energies

Thank you for your kind attention!