

Volatile nature of liquid–liquid phase transition in dense hydrogen

Pavel Levashov, Dmitry Minakov

Joint Institute for High Temperatures RAS, Moscow, Russia

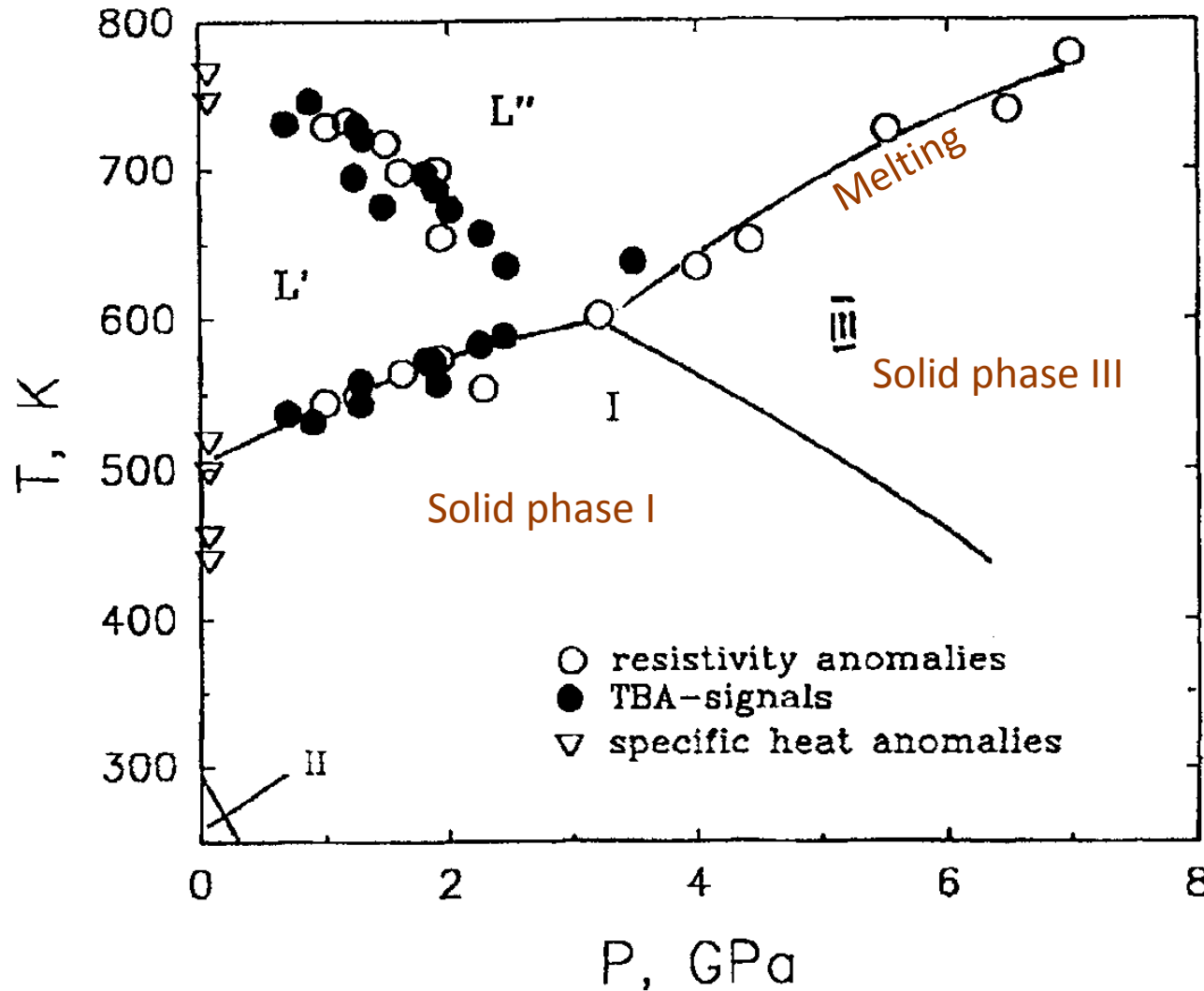


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Motivation

- Plasma phase transition was predicted by G. Norman and A. Starostin in late 60th of the 20th century; still undiscovered experimentally
- Well-known experiments in Sarov (Mochalov M.A.) are debatable even in VNIIEF; our QMD calculations show that temperature in this experiment is much higher than required for liquid-liquid phase transition
- Liquid-liquid phase transitions are known for many years
- Liquid-liquid phase transition in hydrogen is still not confirmed experimentally
- Current experiments are contradictory and can not confirm the 1st-order character of phase transition

Phase Diagram of Tin

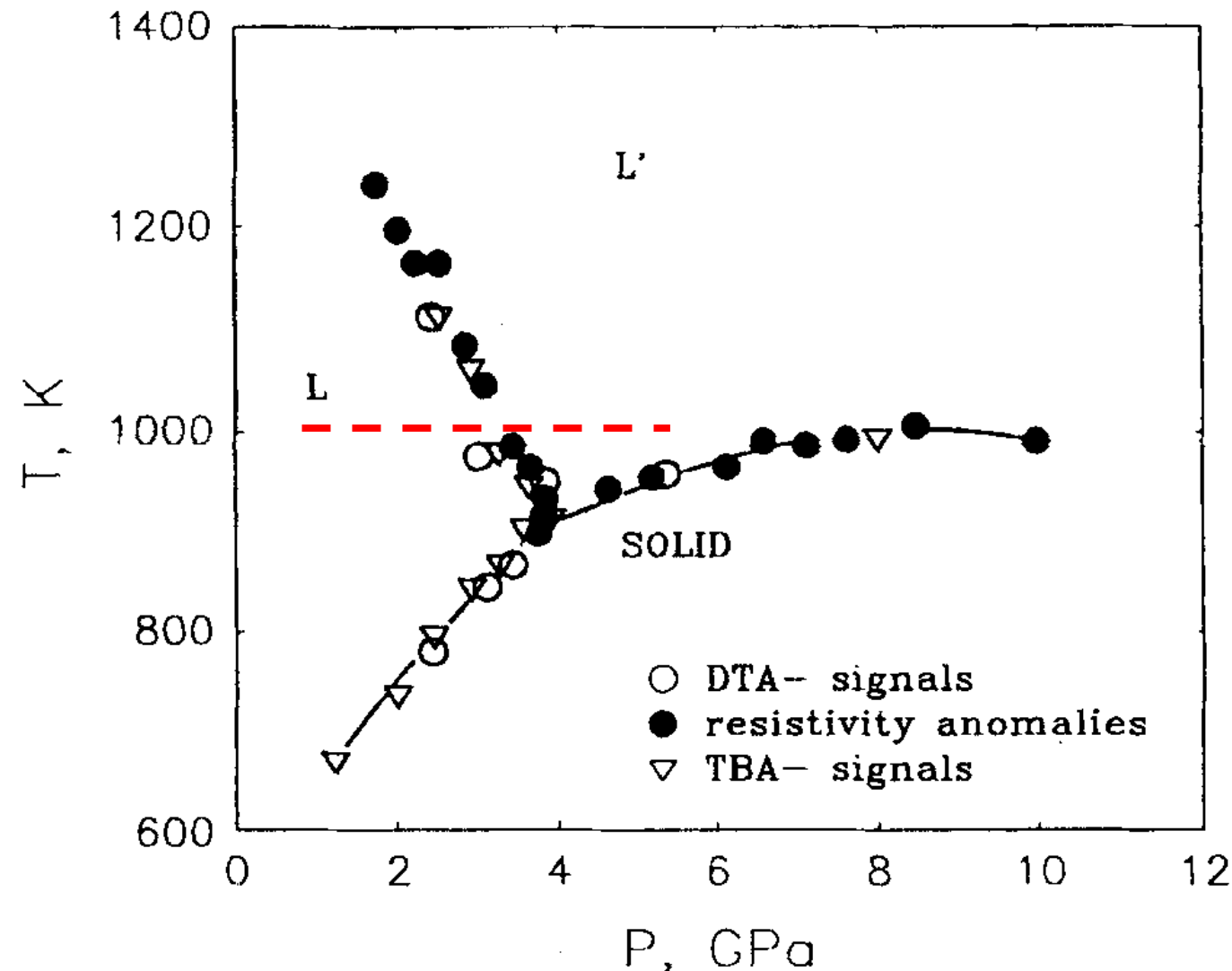


Anomalies in thermobaric analysis (jump in pressure at fixed volume)

Anomalies in resistivity and specific heat

Negative slope

Phase Diagram of Selenium



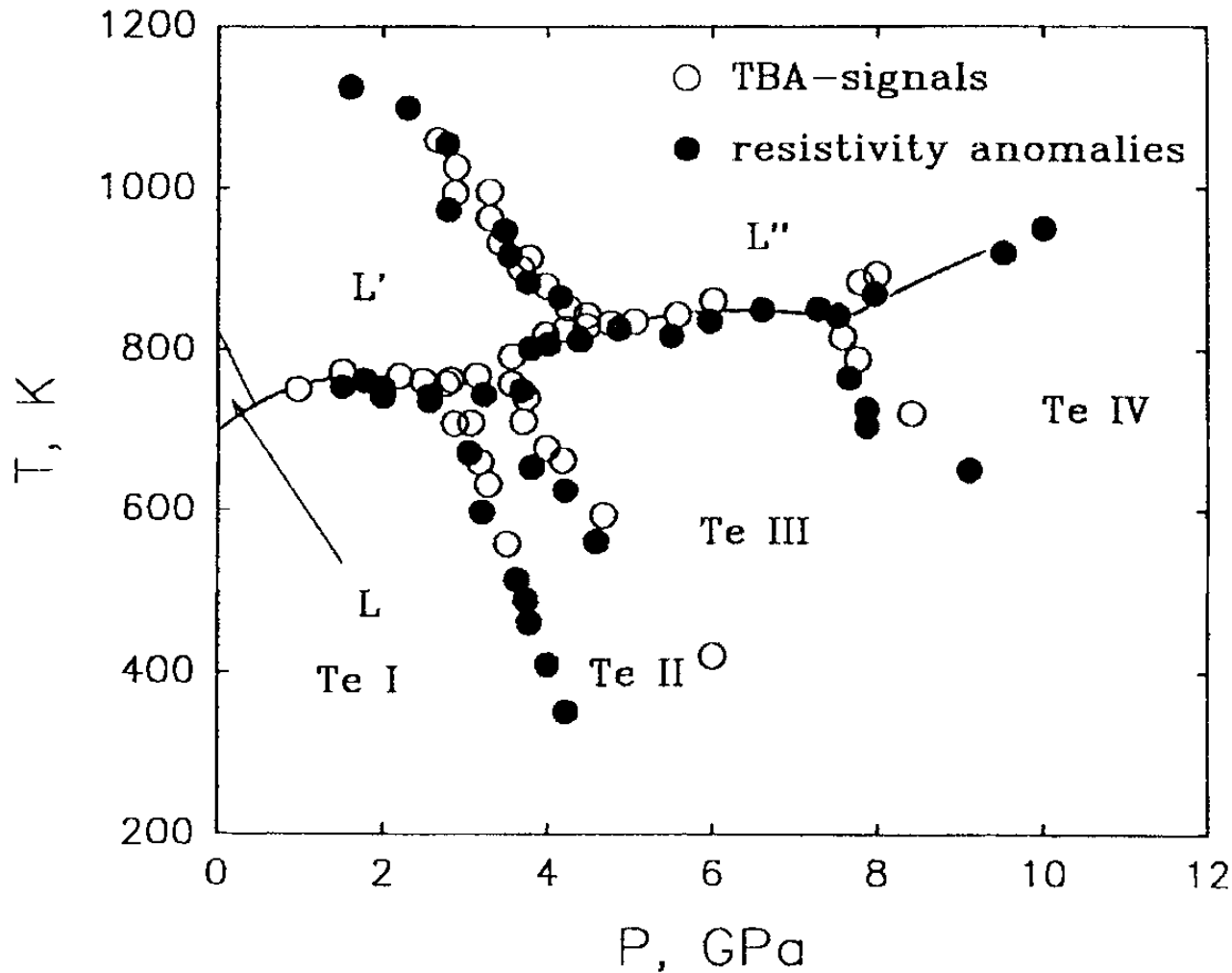
Drop of resistivity (1-3 orders) along L-L' line: metallization

Decrease of volume in L-L' transition

Liquid Se has a chain-like structure with ring fragments (up to 10^4 molecules)

DFT and QMD simulations do not reveal phase transition and

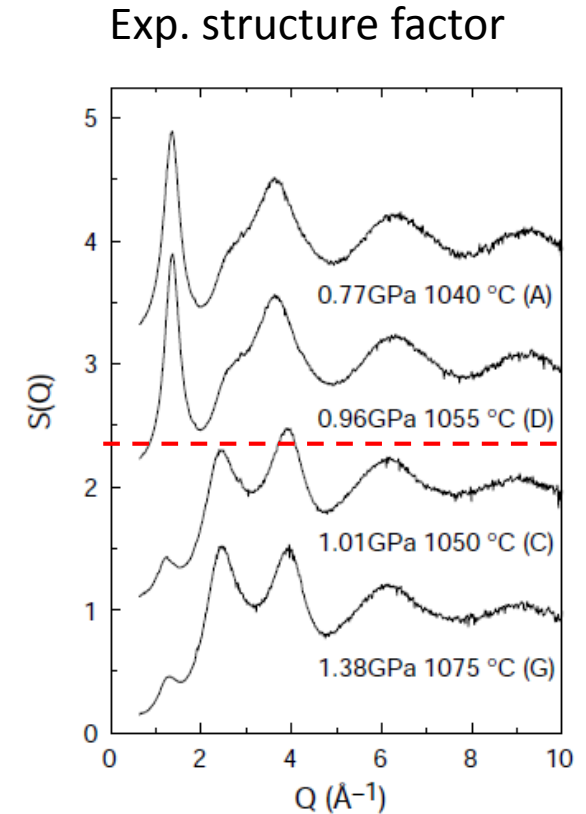
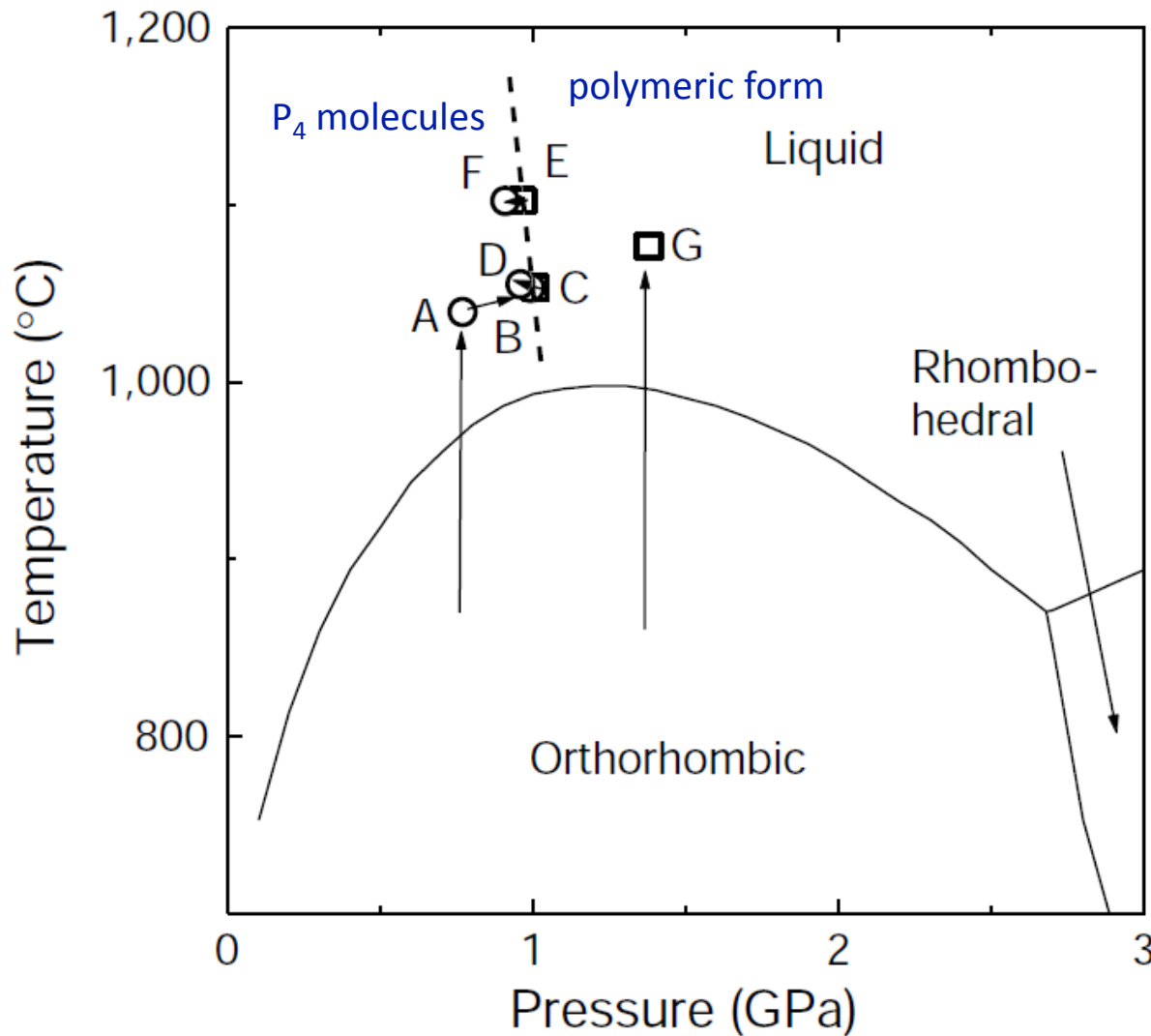
Phase Diagram of Tellurium



Negative slope of L'-L'' line

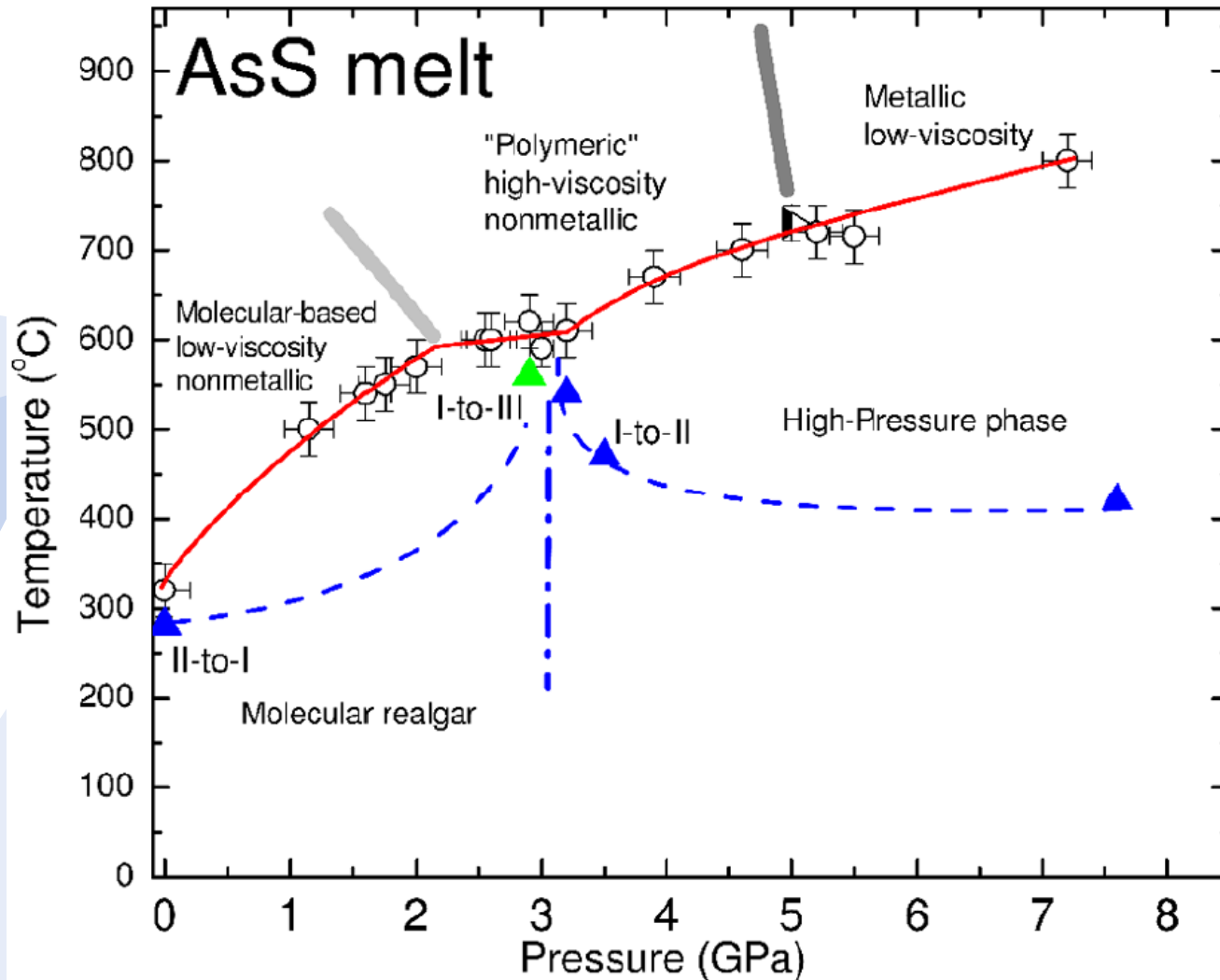
Decrease of volume and electrical conductivity along L'-L'' line

Liquid-Liquid Phase Transition in P



Reversible transition to a polymeric structure at $P > 1$ Gpa
Transition occurs within a few minutes!

Liquid-Liquid transitions in AsS

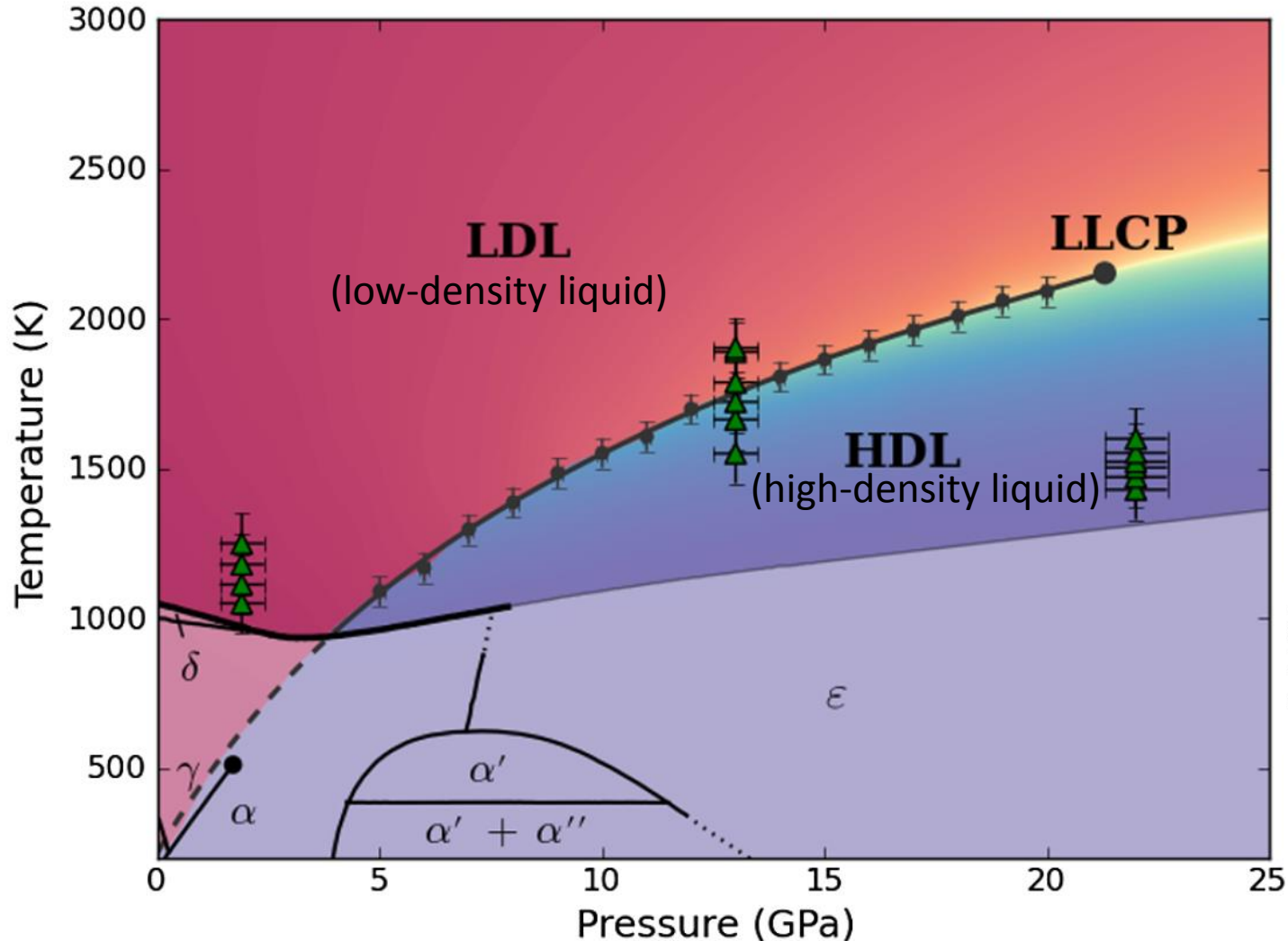


X-ray diffraction and resistivity measurements

Polymeric high-viscosity phase is observed

This polymeric phase transforms into glass at rapid cooling

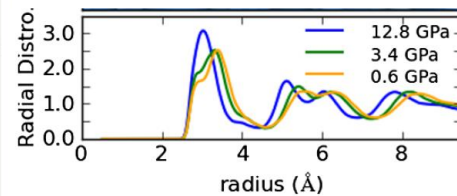
Liquid-liquid transition in Ce



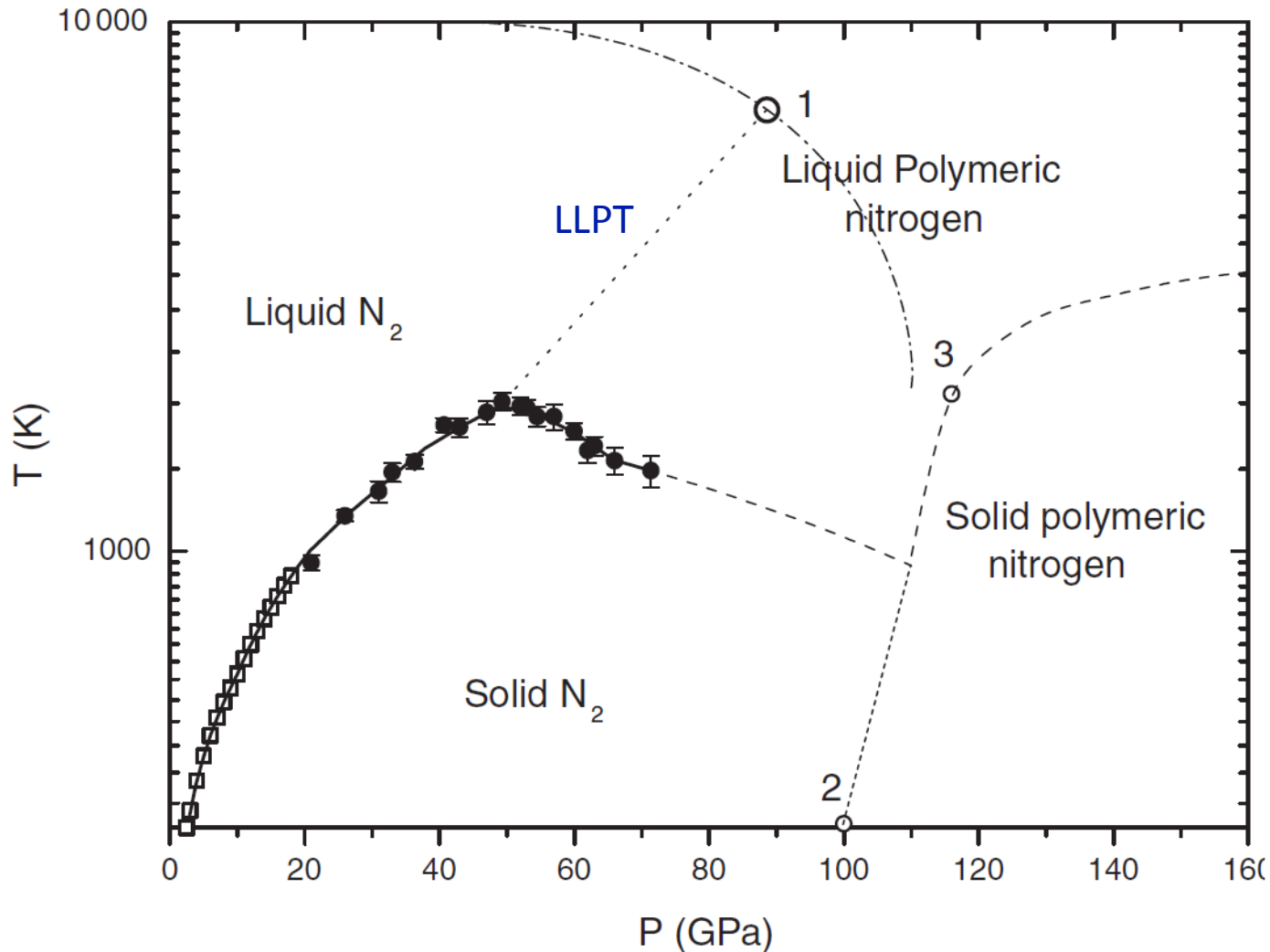
X-ray diffraction

Delocalization of f-electrons (3-valent to 4-valent)

Simulated structure of high-density Ce liquid (MD, EAM), amorphous liquid (split of RDF 2nd peak)

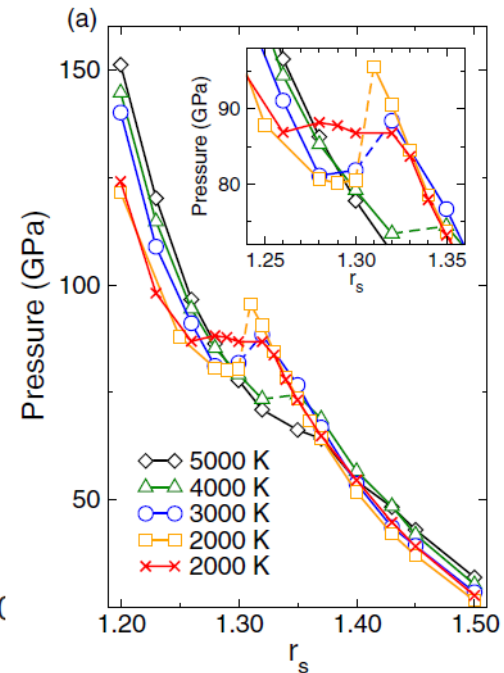


Liquid-Liquid Phase Transition in N



Pronounced maximum on the melting curve revealed in laser-heated DAC

Ab initio simulations confirm the existence of nitrogen polymeric phase



Mukherjee G.D. and Boehler R. PRL **99**, 225701 (2007)

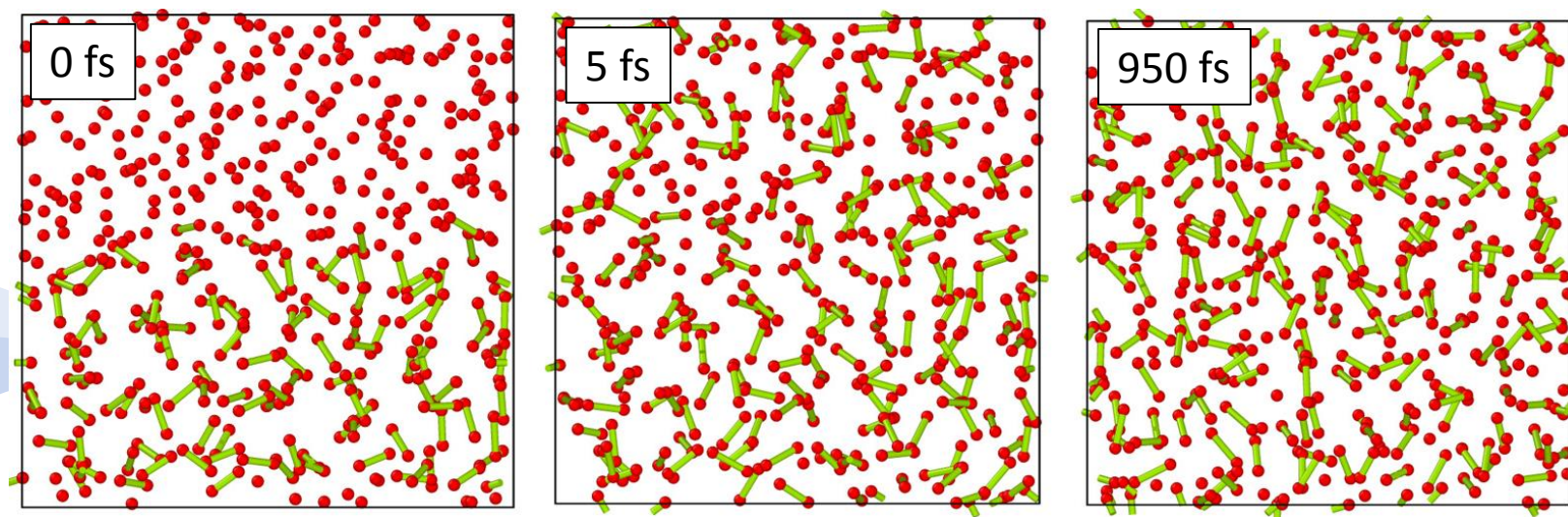
Boates B. and Bonev S. PRL **102**, 015701 (2009)

Simulations of Liquid-Liquid transition

- Supercooled liquid silicon
Sastry S., Angell C.A. *Nature Materials* **2**, 739 (2003) (MD, Stillinger-Weber)
Vasisht V.V. *et al.* *Nature Physics* **7**, 549 (2011) (MD, Stillinger-Weber)
Ganesh P. and Widom M. *PRL* **102**, 075701 (2009) (QMD, 300 particles)
- Supercooled liquid water
Poole P.H. *et al.* *Nature* **360**, 324 (1992)
Xu L. *et al.* *PNAS* **102**, 16558 (2005)
- Supercooled liquid silica (quartz)
Saika-Voivod I. *et al.* *PRE* **63**, 011202 (2000)
- Hydrogen (deuterium)
Lorenzen W. *et al.* *PRB* **82**, 195107 (2010)
Morales M.A. *et al.* *PNAS* **107**, 12799 (2010)

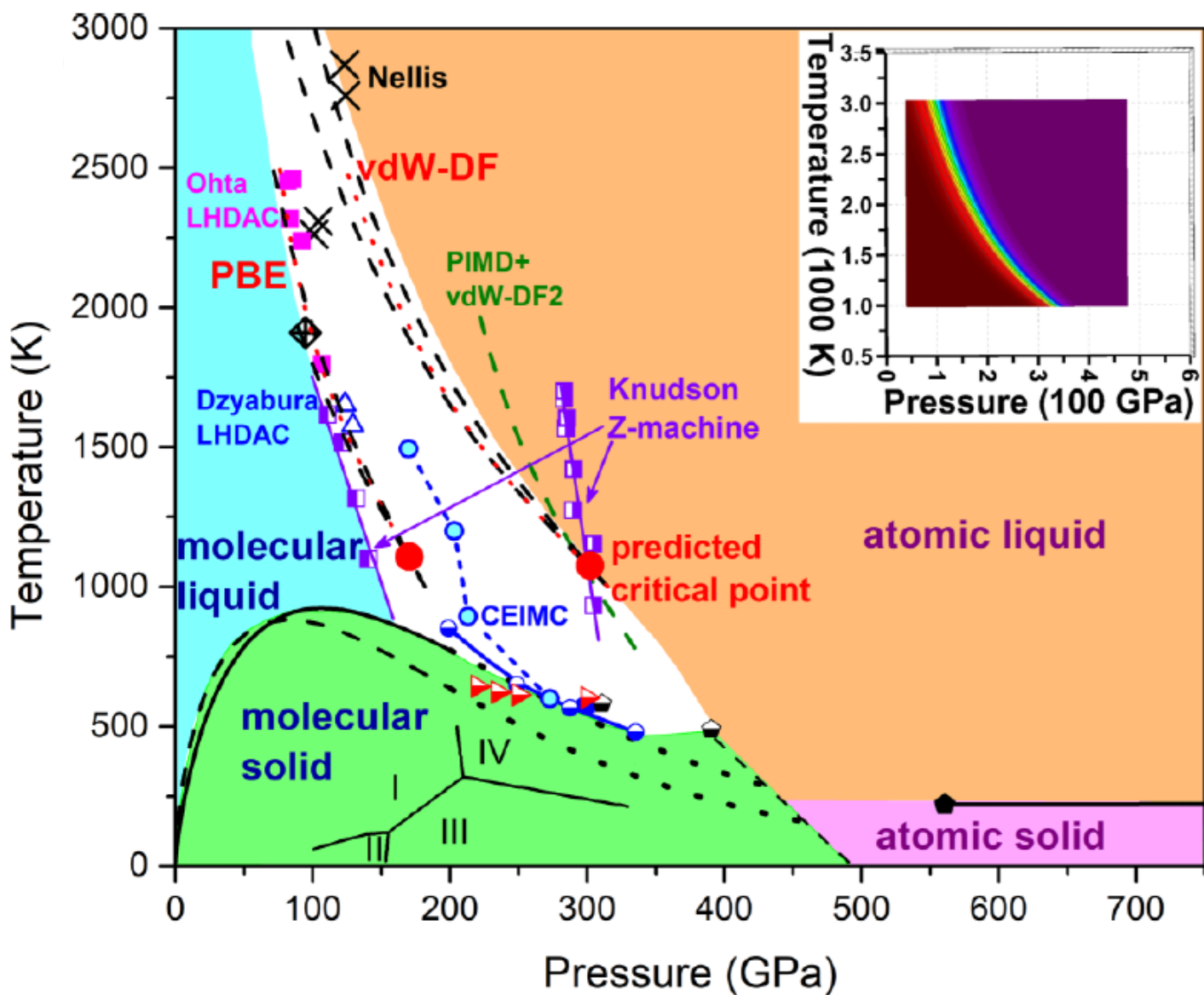
Hydrogen (deuterium), mixing H & H₂

$P = 125$ GPa, $T = 1500$ K, QMD simulation, PBE



- Phase boundary is volatile if subjected to thermal perturbation
- No phase separation due to the negative slope of phase boundary on the P-T space
- The interfacial H₂/H free energy is negative
- Critical nucleus of the new phase is infinitely small, volumetric spontaneous dissociation

Phase diagram of hydrogen (QMD)



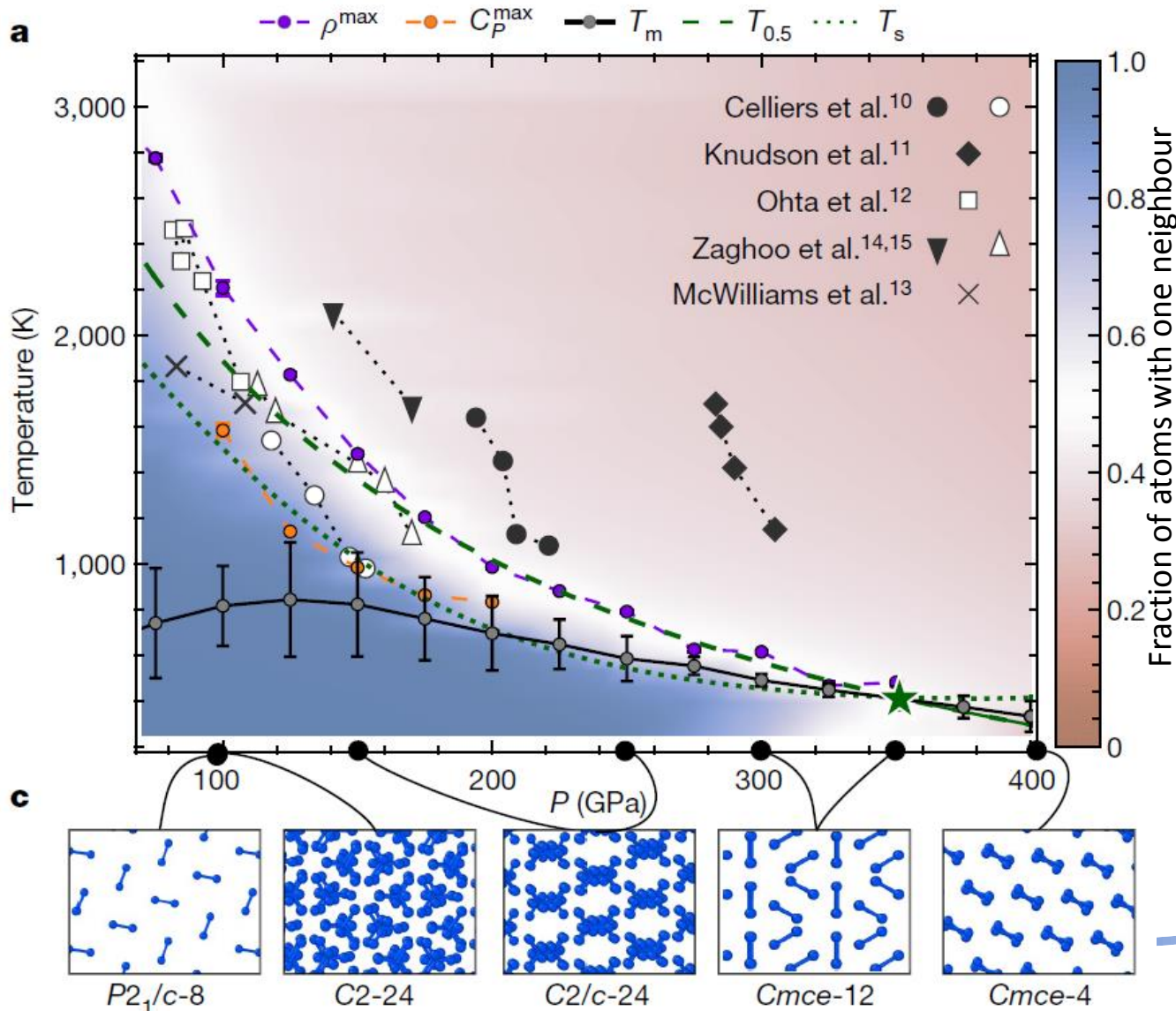
QMD with 500 and more atoms

LLPT is predicted at $T < T_c$ (~1250 K), at higher temperatures it is a crossover

There is an uncertainty because of xc-functionals (white region)

LLPT is very close to the melting region

Machine-learning MD Potential: smooth transition in hydrogen



Neural network as an MD potential (learning using QMD configurations)

1728 atoms

All crystal phases of hydrogen are reproduced

Order parameter is smooth, other parameters (density, C_p , RDF, DOS) show no discontinuities

Sharp maxima of density and C_p are observed below the melting curve

Conclusions

- Liquid-liquid phase transition in hydrogen (deuterium) has nothing to do with plasma phase transition
- Phase separation between molecular and atomic phases of hydrogen is impossible because the interfacial H_2/H free energy is negative
- All experimentally confirmed liquid-liquid phase transitions deal with either amorphous or polymeric phase
- Numerical predictions of liquid-liquid phase transition in hydrogen are strongly dependent on the number of particles and calculation parameters
- Liquid-liquid phase transition in hydrogen, if exists, may be found in supercooled liquid (below the melting line)