Thermodynamic properties of liquid metals measured by picoseconds acoustics

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context

Liquid metals @ HP
- geological fluids (planetary interiors)
- liquid state (liquid-liquid phase transitions)

Sound velocity
- equation of state ρ(P,T) and thermoelastic properties
- high sensitivity to the variations of the interaction potential
  → phase transitions

$$\varepsilon_{kl} = s_{klmn}\sigma_{mn} \qquad \beta = -\frac{1}{V}\frac{\partial V}{\partial P} = s_{iihh}$$

$$C_{ijkl} = \frac{\partial^2 G}{\partial \varepsilon_{ij}\partial \varepsilon_{kl}}$$

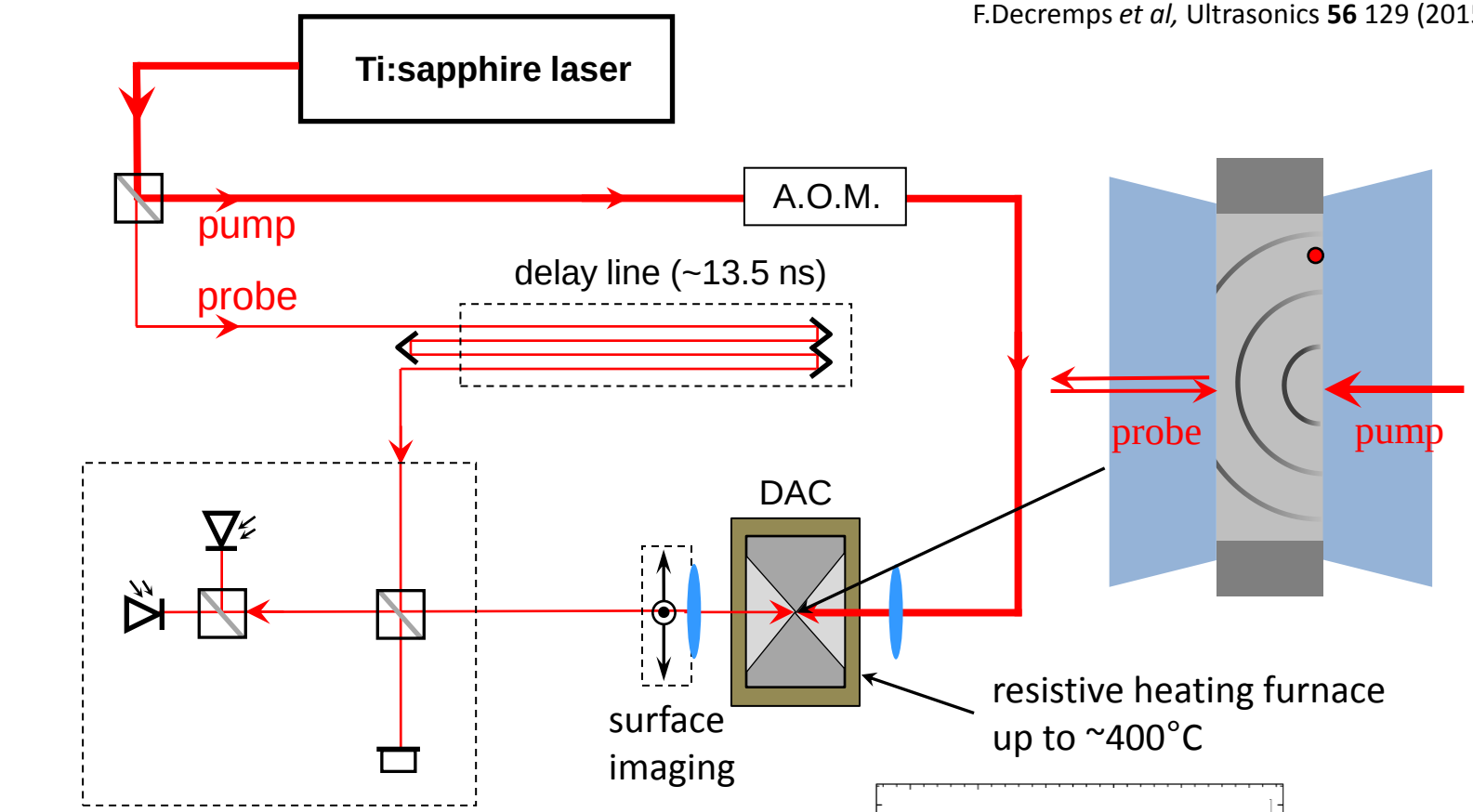
difficulties with classical techniques : ultrasonics, Brillouin scattering …
→ combine diamond anvil cell (DAC) + picosecond acoustics

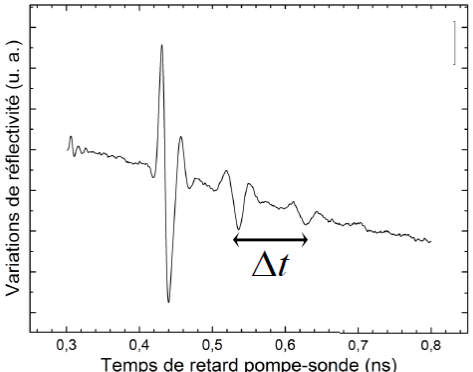
F. Decremps *et al*, PRL **100**, 3550 (2008)
F.Decremps *et al,* RSI **80**, 073902 (2009)

<u>Review article :</u> F.Decremps *et al,* Ultrasonics **56** 129 (2015)

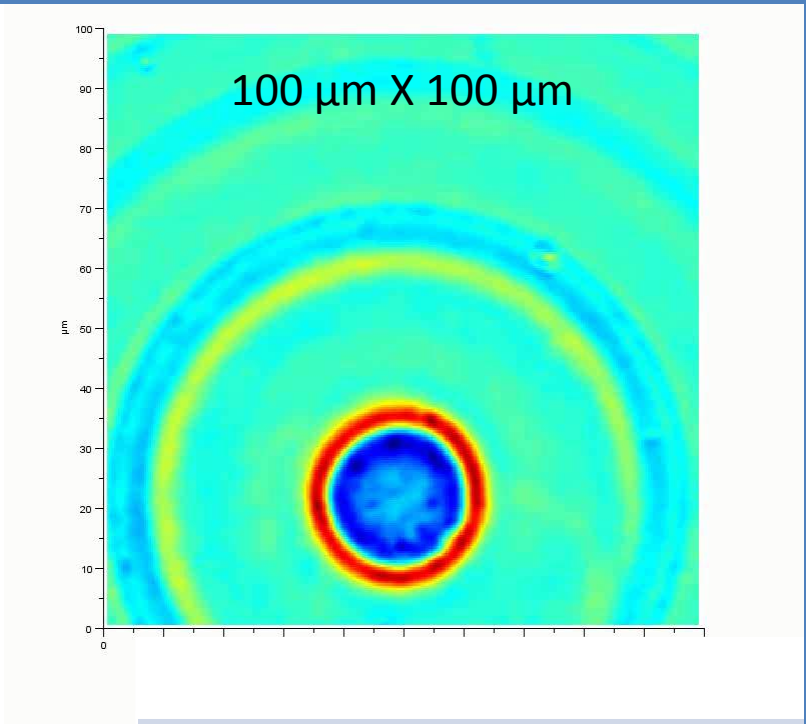
picosecond acoustics combined with DAC

F. Decremps *et al*, PRL **100**, 3550 (2008)
F.Decremps *et al,* Ultrasonics **56** 129 (2015)



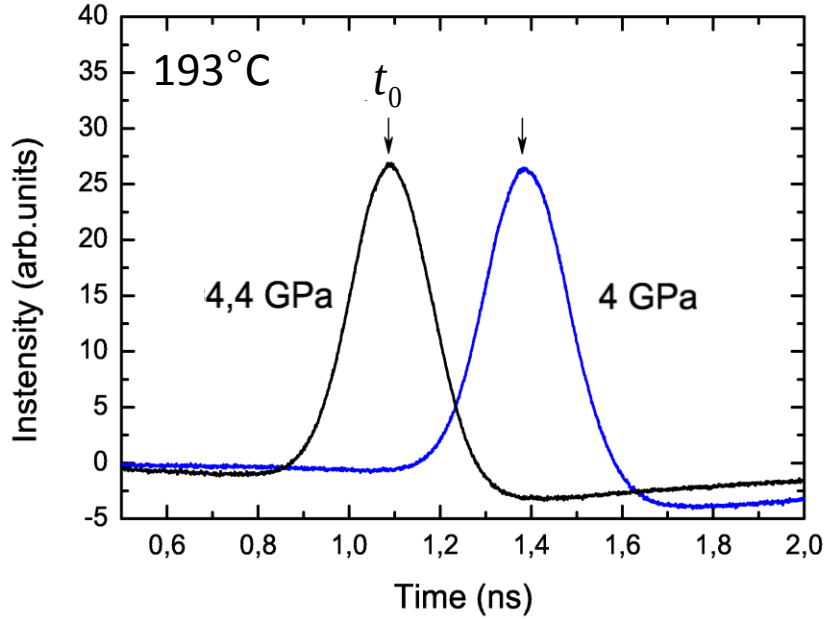


Surface imaging method



Temporal method

(pump / probe spatially coincident)



Careful analysis of R(t) → velocity v, thickness e_0	t_0 accurately determined 1 scan ~ 10 s (very fast)
1 scan ~ 4h (time consuming)	e_0 is needed to obtain v

→ 2 complementary methods to explore P range

Liquid mercury : thermodynamic data extensively studied

F.Decremps *et al,* RSI **80**, 073902 (2009)
S.Ayrinhac *et al,* J.Chem.Phys. **105** 041906 (2014)

liquid gallium : a complex liquid

- very low melting point (30°C)

- not « simple » liquid : water-like system

- liquid-liquid phase transition (LLPT)

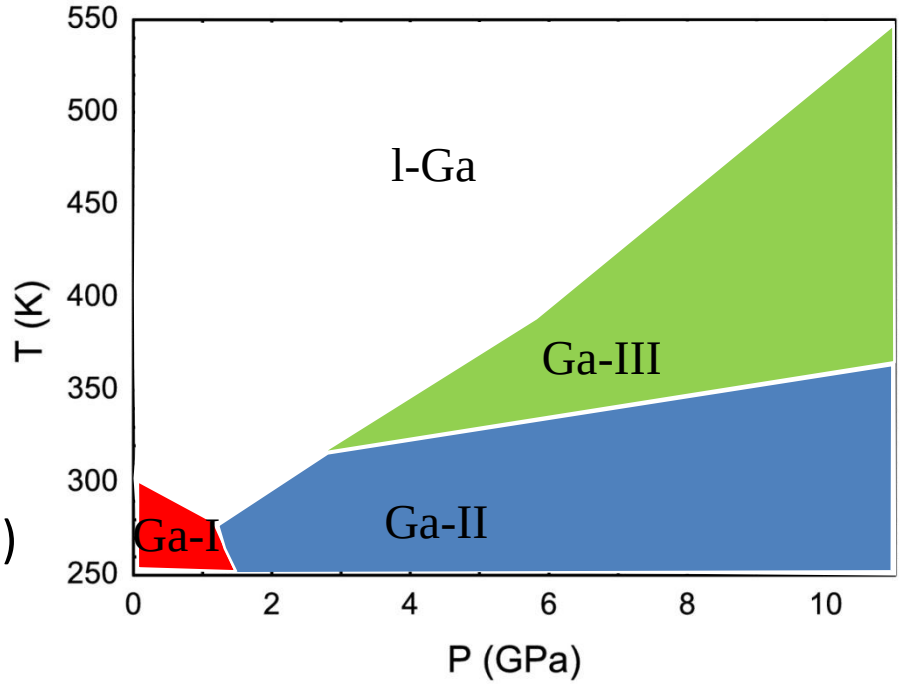
~ 200/250 K, in supercooled liquid

simulations

D.Jara *et al* JCP **130**, 221101 (2009)

experiments

C.Tien *et al* PRB **74,** 024116 (2006)



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D.Jara *et al* JCP **130**, 221101 (2009)

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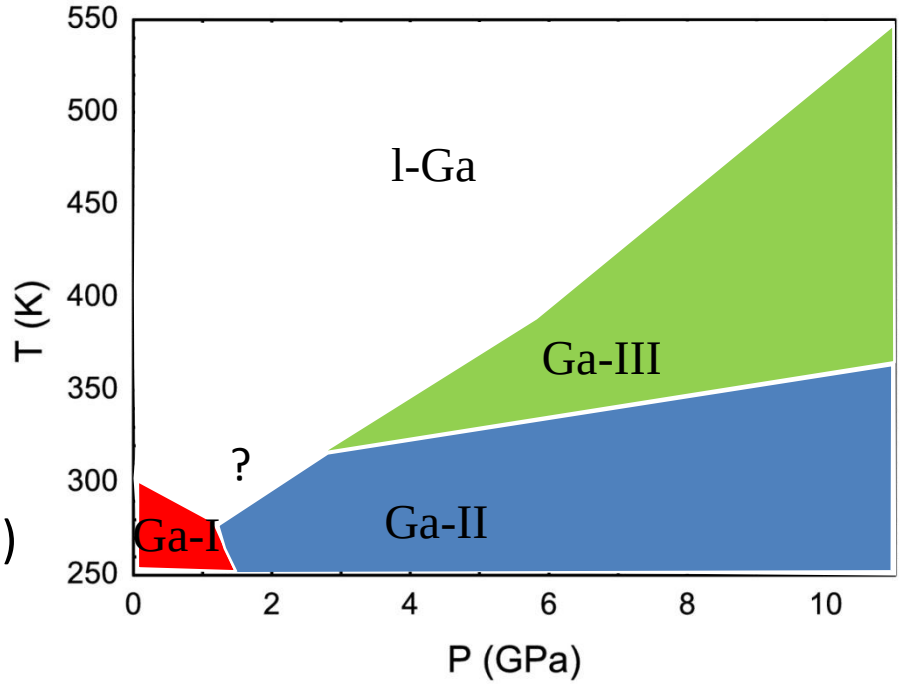
C.Tien *et al* PRB **74,** 024116 (2006)

~ 0-2GPa, ~300 K, LLPT in stable phase ?

experiments

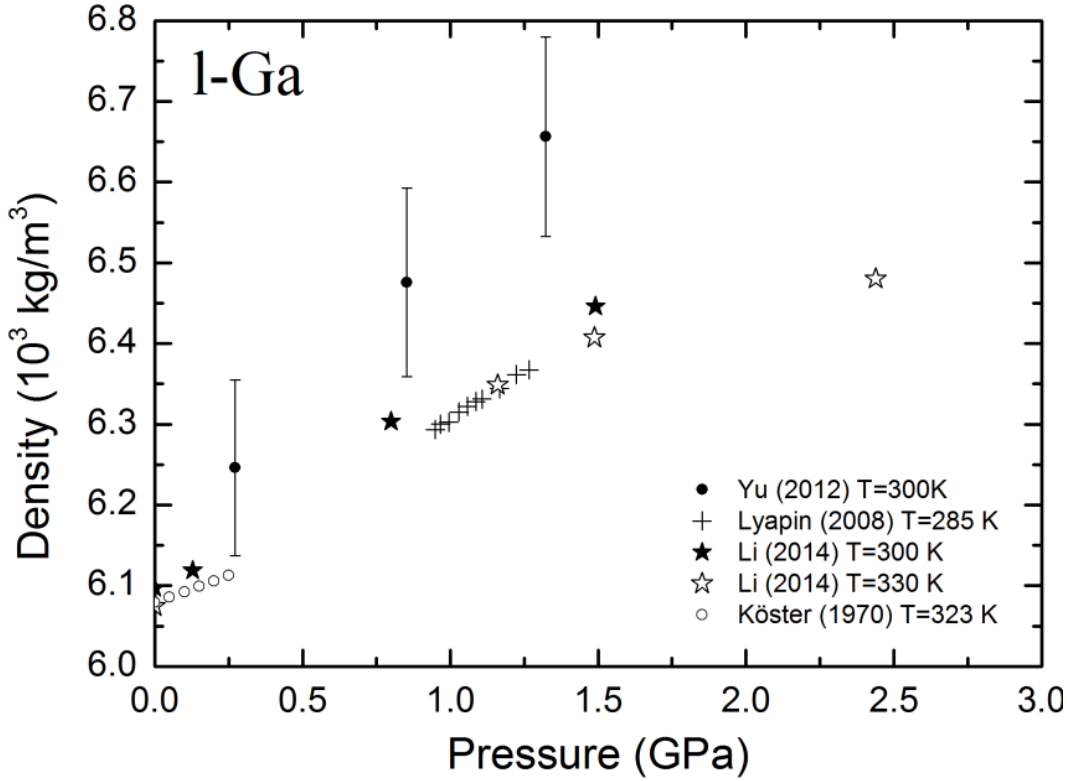
R.Poloni *et al* PRB **71**, 184111 (2005)

R.Li *et al* APL **105,** 041906 (2014)



→ **Is there a liquid-liquid transition in stable liquid ?**

Density



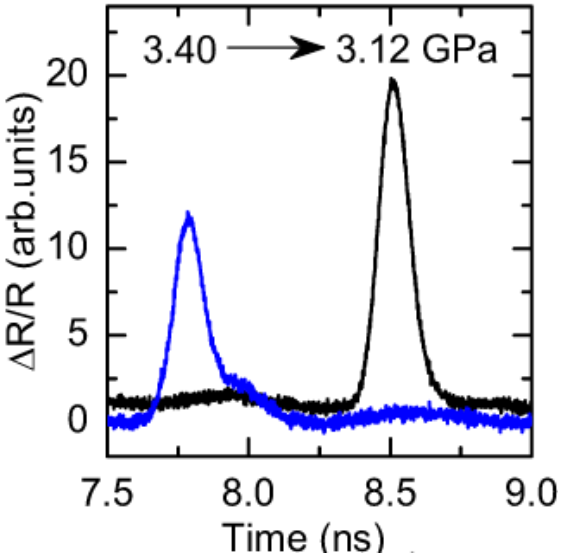
→ large discrepancies between data obtained by various techniques

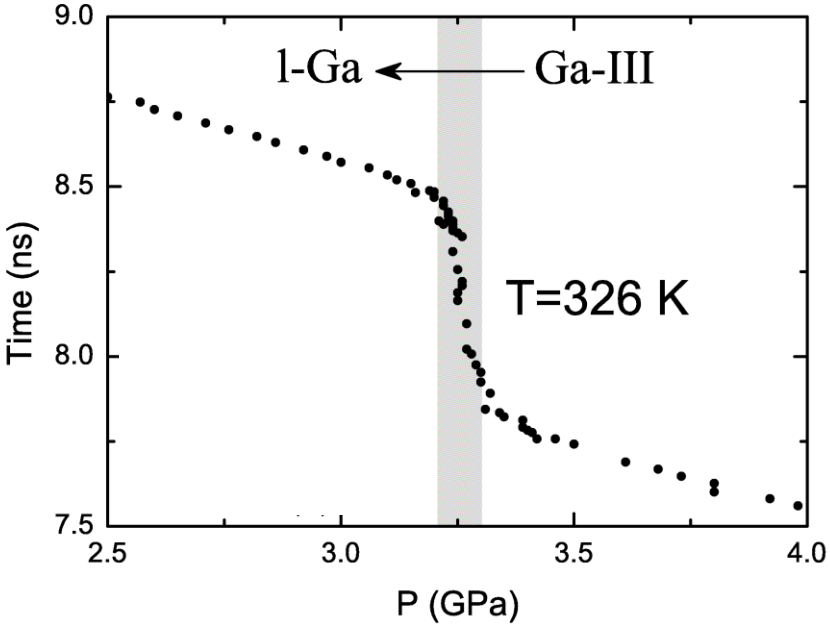
→ EOS still controversial

→ **an accurate EOS is needed**

Yu *et al,* JAP **111** 112269 (2012)
Lyapin *et al,* JETP **107** 818 (2008)
Li *et al,* APL **105** 041906 (2014)
Köster *et al,* BBPC **74** 43 (1970)

Melting line in liquid Ga

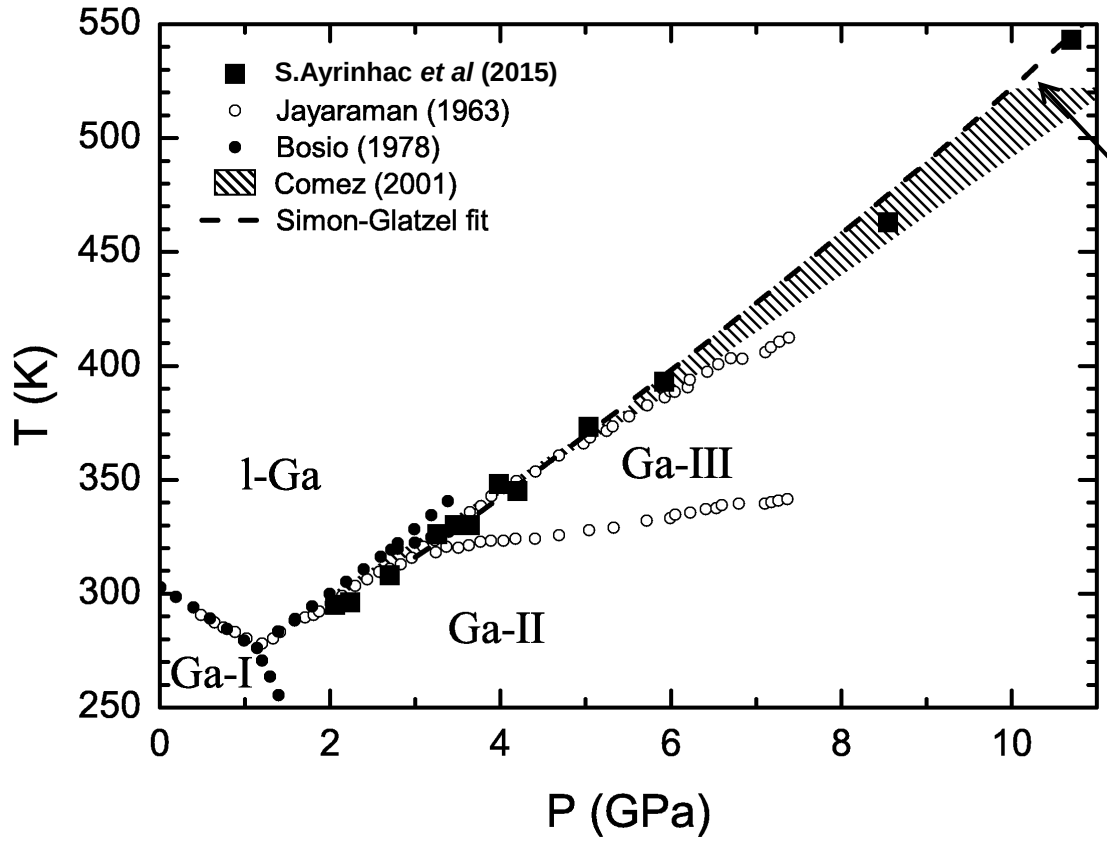




Phase transition solid ⟶ liquid

Melting line in liquid Ga

New determination of the melting line of liquid Ga



Simon-Glatzel equation

$$T = T_t \left[\frac{P - P_t}{a} + 1 \right]^{1/c}$$

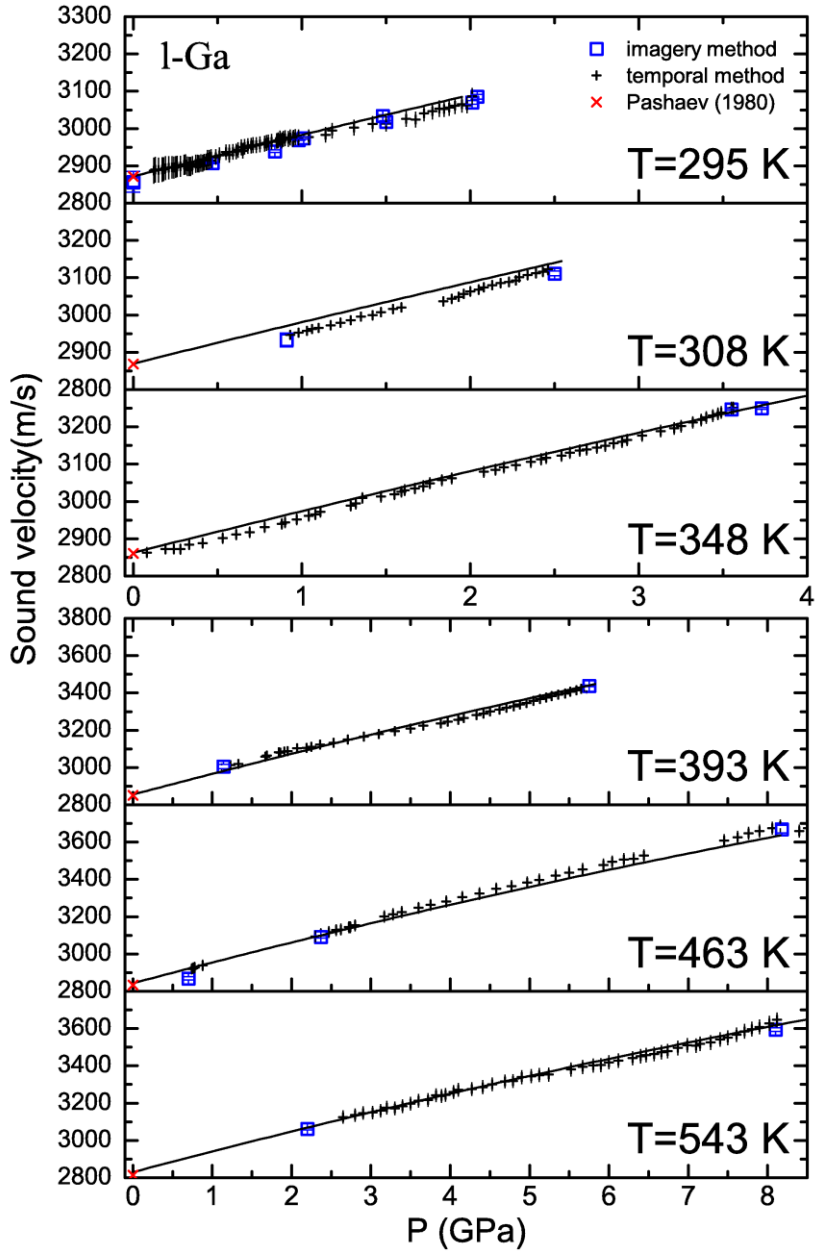
Parameters (fit) :

a= 24 GPa

c= 0.51

Adiabatic sound velocities

S. Ayrinhac *et al,* JPCM **27** 275103 (2015)



in liquid Ga, up to 8 GPa and 540 K

→ no abrupt or gradual transition in this range of P and T

→ no liquid-liquid phase transition

Equation of state from acoustics

→From adiabatic sound velocity
to isothermal equation of state

Davis & Gordon JCP **46** 2650 (1967)
Daridon *et al*, *International journal of thermophysics* **19** 145 (1998)

input

$v_S(P,T)$
(smoothed and interpolated)

$\rho(P_0,T)$

$\alpha_P(P_0,T)$

$C_P(P_0,T)$

1. $\beta_T = \beta_S + \dfrac{T\alpha_P^2}{\rho C_P}$

2. $\alpha = -\dfrac{1}{\rho}\left(\dfrac{\partial\rho}{\partial T}\right)_P$

3. $\left(\dfrac{\partial Cp}{\partial P}\right)_T = -\dfrac{T}{\rho_2}\left[\left(\dfrac{\partial\alpha_1}{\partial T}\right)_P + \alpha_1^2\right]$

output

$\rho(P,T)$

$\alpha_P(P,T)$

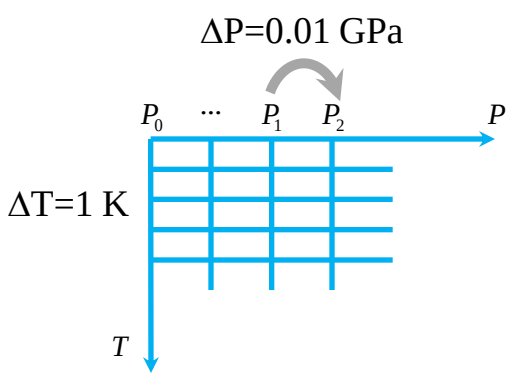
$C_P(P,T)$

$B_T(P,T)$

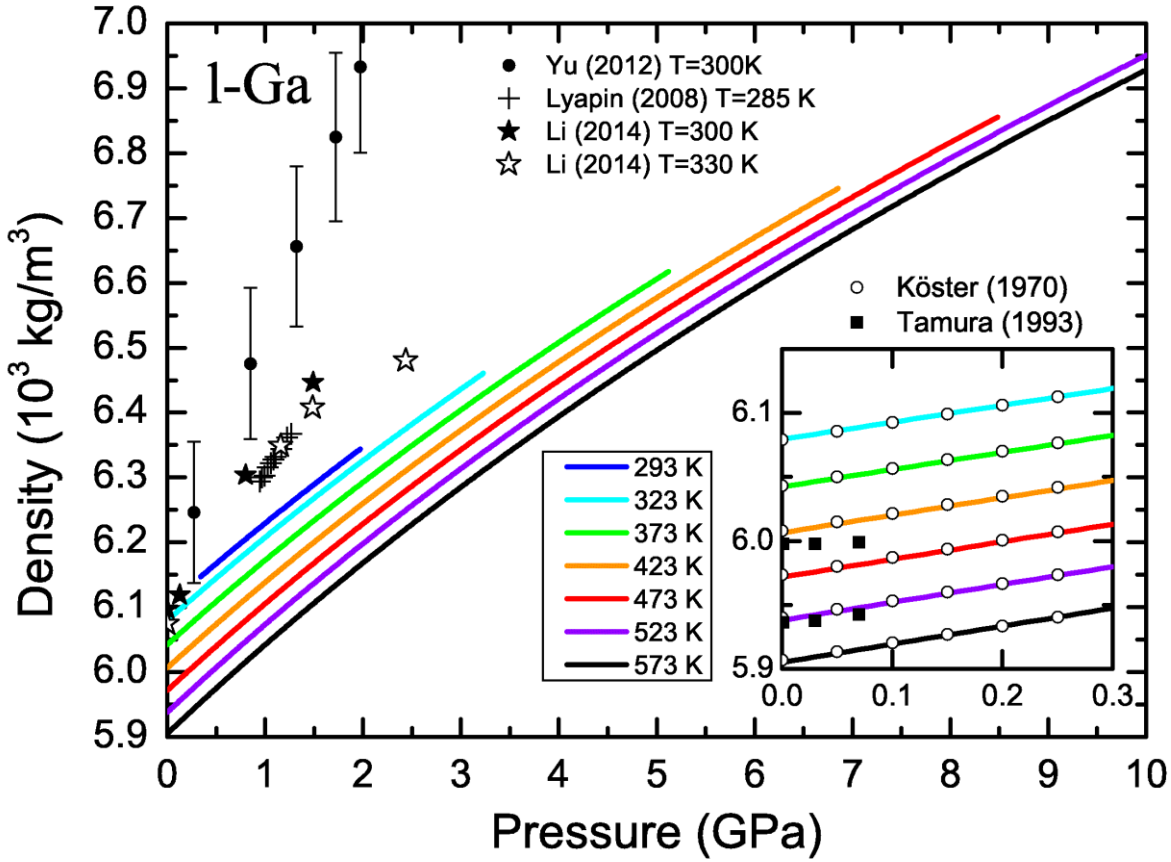
$C_V(P,T)$

$\gamma(P,T)$

...



Density of liquid Ga



→ our data from sound velocity are in excellent agreement with Köster

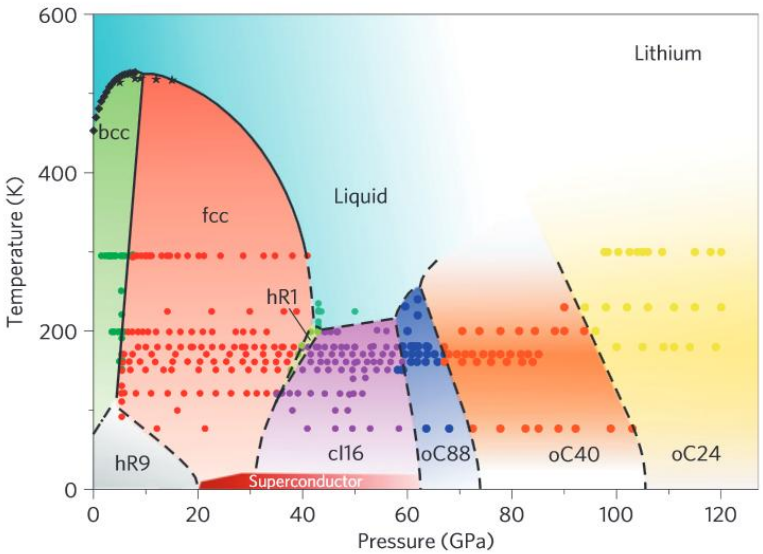
→ other thermodynamic quantities in liquid gallium

S. Ayrinhac *et al,* JPCM **27** 275103 (2015)

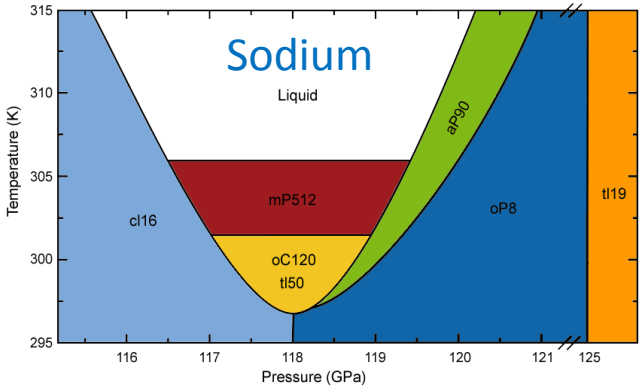
Perspectives and work in progress

alkali metals (Li, Na, K, Rb, Cs)
- complex phase diagrams
- liquid or insulating/transparent @ HP
- unusual properties at high P

→ highly reactives



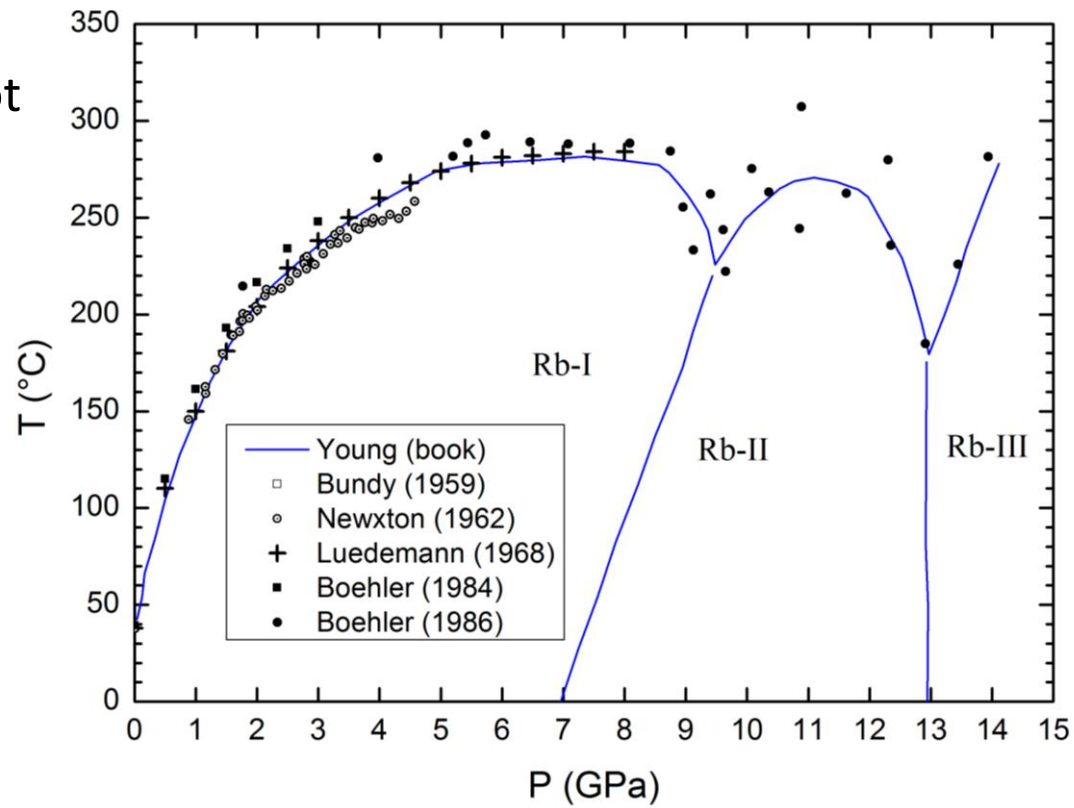
C.L. Guillaume *et al, Nature Physics* **7** 211 (2011)



E. Gregoryanz *et al*, *Science* **320**, 1054 (2008)

Liquid rubidium

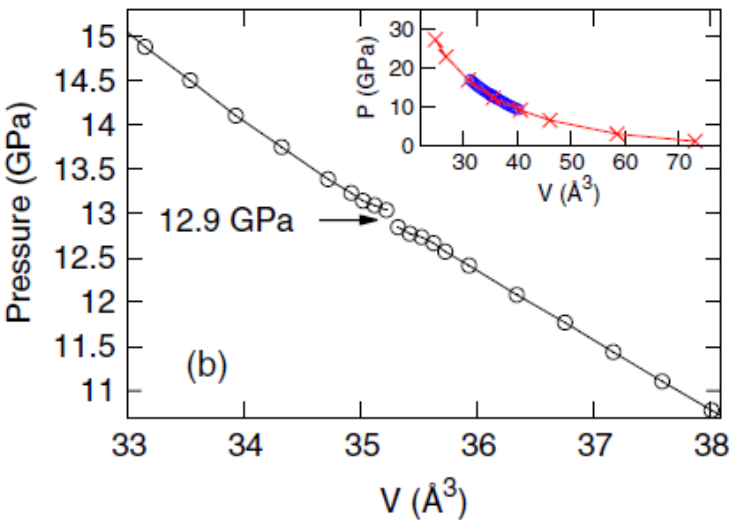
→ complex phase diagram, not well determined

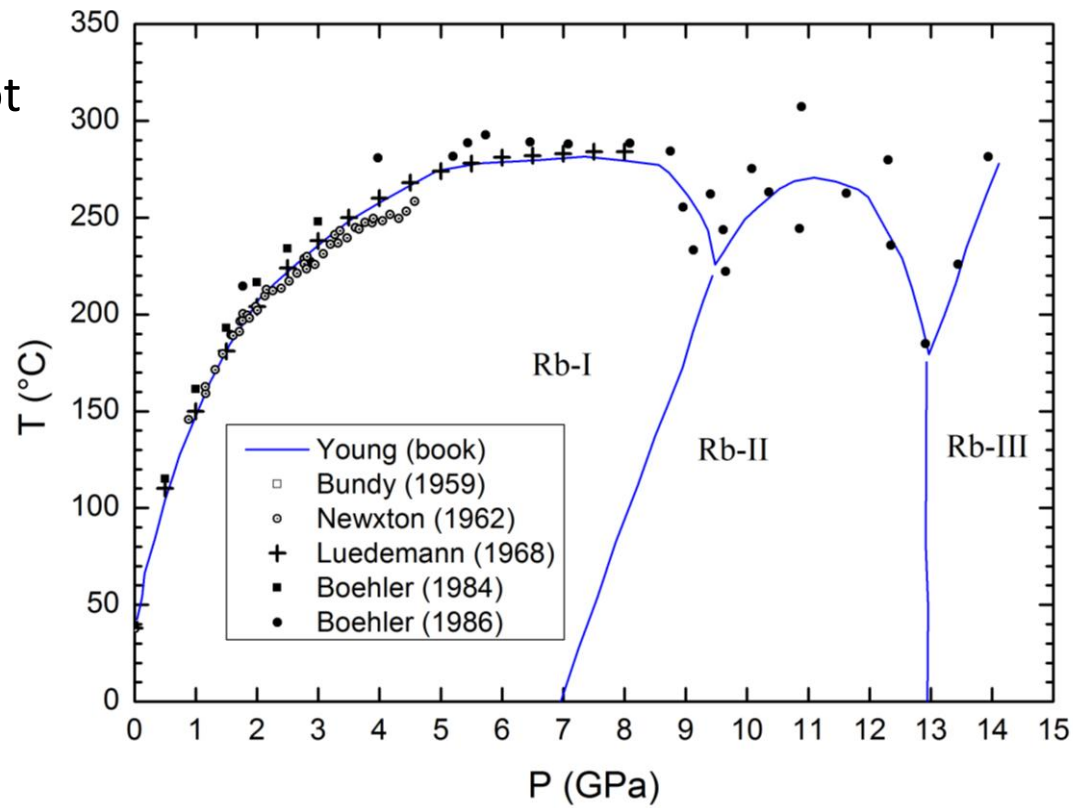


Liquid rubidium

→ complex phase diagram, not well determined

→ a liquid-liquid phase transition is observed in *ab initio* MD @P=12.9 GPa, T=300°C



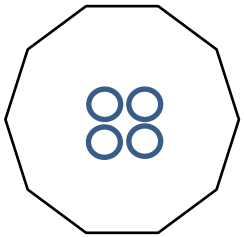


T.Bryk *et al* PRL **111** 077801 (2013)

liquid Rb

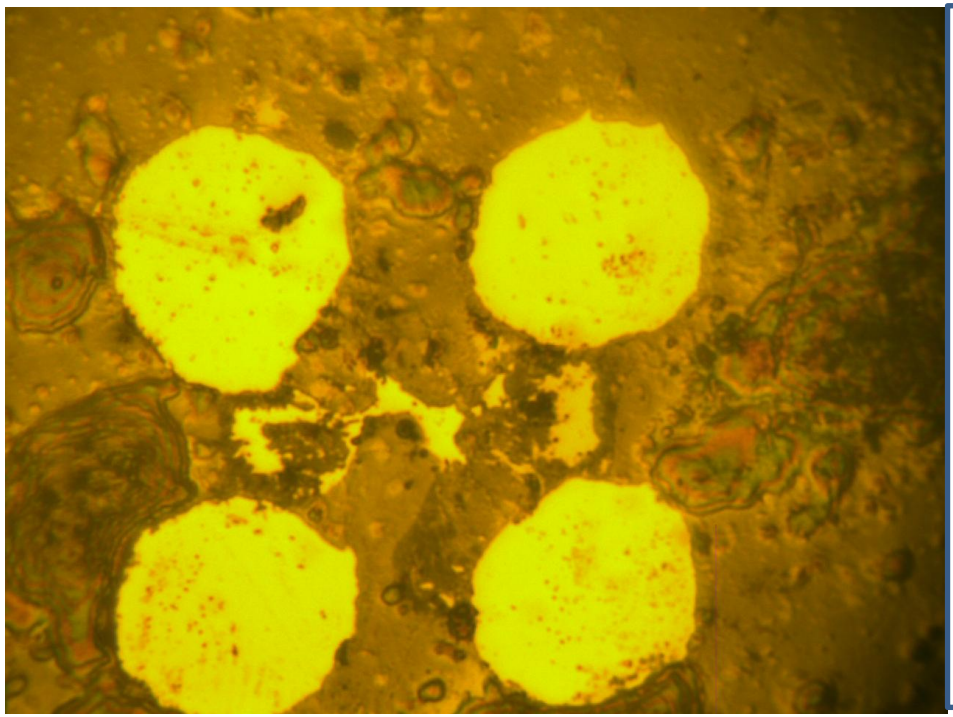
sample loaded under inert atmosphere in Re gasket

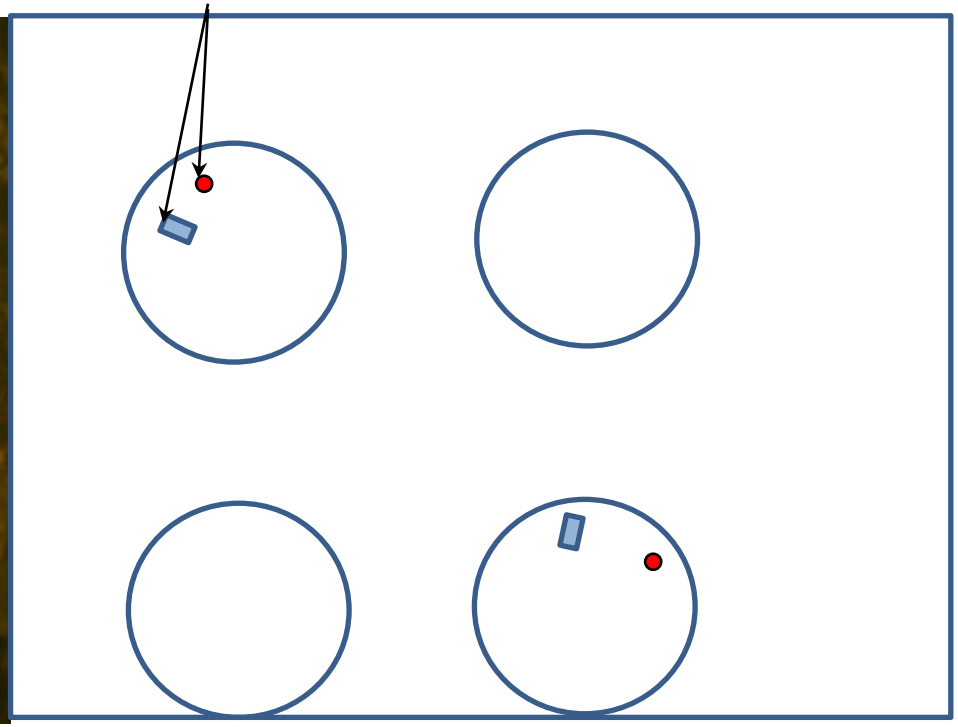
4 holes configuration (laser drilling)



(P,T) calibrants :

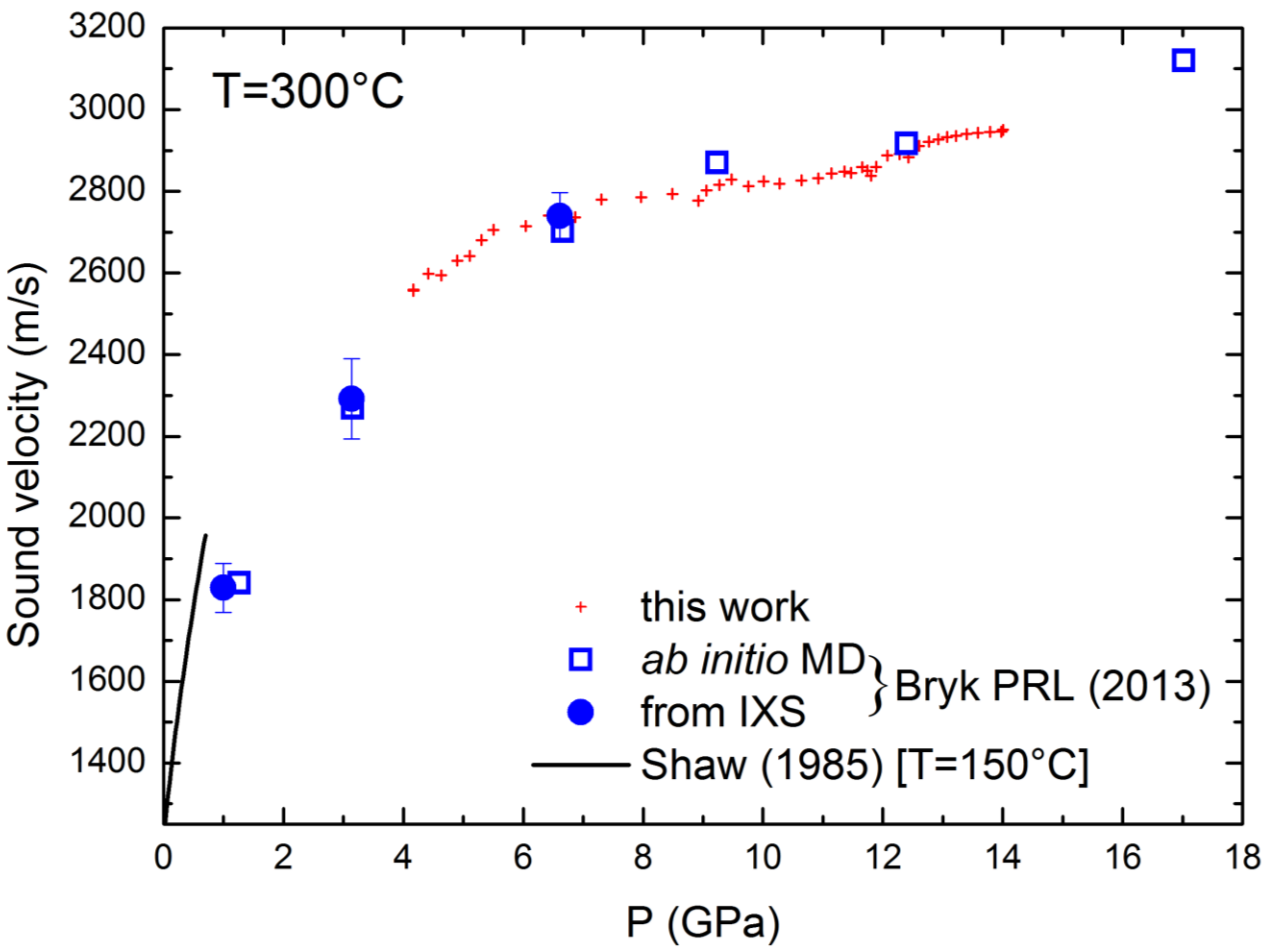
ruby + strontium tetraborate





(work-in-progress) sound velocity @T=300°C

- temporal method : thickness unknown → rescaled to known values



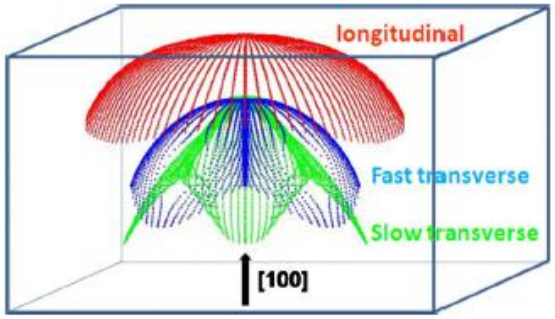
non monotonic behavior
→ plateau @ ~10 GPa?

THANK YOU
FOR YOUR ATTENTION

Surface imaging (100 μm × 100 μm) in anisotropic solid

F.Decremps *et al* PRB **82** 104119 (2010)

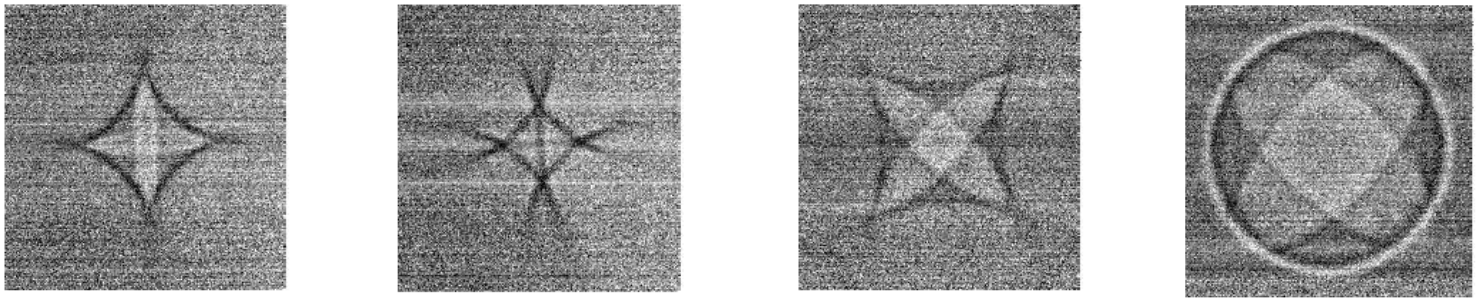
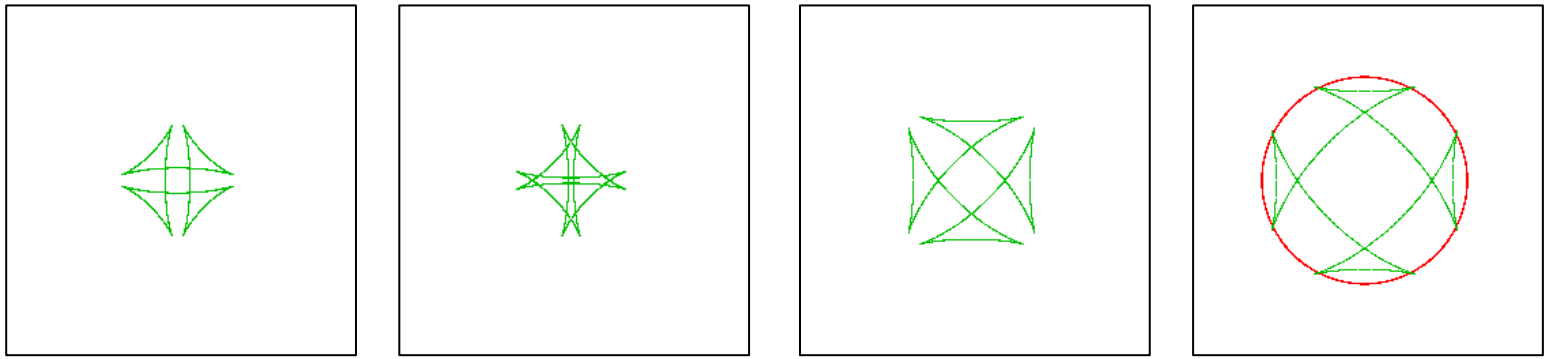
example in Si



$\rightarrow C_{ijkl}(P,T)$

$\rightarrow$ circles in liquids

Experiment



Simulation