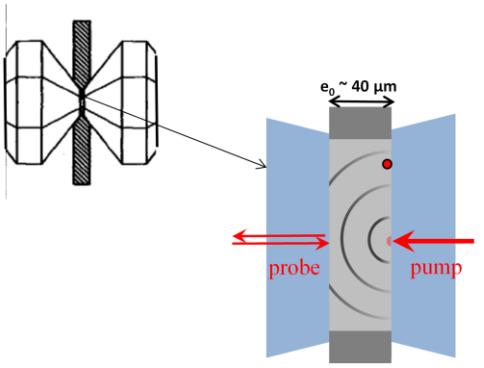
[Phonons 2023, XVII CONFERENCE ON PHONON SCATTERING IN CONDENSED MATTER
Conservatoire National de Arts et Métiers (CNAM), Paris, France, 2-7, july 2023
Session 16h30-18h00, TU4: New phonon techniques, materials and phenomena]

Hello everybody,
my name is Simon Ayrinhac
I come from the IMPMC laboratory located in Sorbonne Université in Paris.
I want to thanks the organizing commitee of Phonons-2023
to give me the opportunity to present my work.

Picosecond acoustics at extreme conditions



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

P (DAC) : 0-100 GPa
T (resistive heating) : 300-700 K
T (laser heating) : 1200-5000 K
(see S. Boccato talk)

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Picosecond acoustics is an optical pump-probe technique
which permits to generate and detect sound waves
In a large variety of materials.

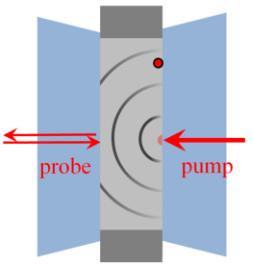
It can be coupled with diamond anvil cells resistively heated or laser heating,
to perform measurements on a large pressure and temperature range.
Typically 0-100 Gpa and 300-700 K.
The DAC combined with laser heating was presented by my colleague Silvia Boccato.

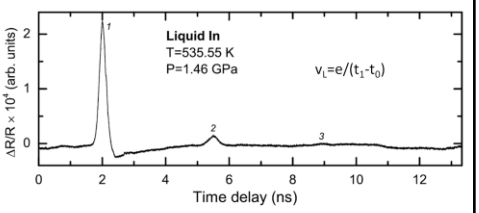
References

[1] Silvia Boccato, “Picosecond acoustic measurements at extreme pressure and temperature conditions”, Monday 15:40 - 16:00, July 3, 2023, session MO4: Time resolved phononics and nonlinear phononics.

Picosecond acoustics at extreme conditions

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





Versatile probe to study a large variety of samples,
→ **liquid metals** are especially well suited
- pump is easily absorbed (optical absorption length ~10nm @λ=800nm)
- no pressure transmitting medium to ensure hydrostatic conditions
- longitudinal waves (thermoelastic properties)

Ayrinhac JAP **129**, 185903 (2021)

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Picosecond acoustics (PA) is a versatile technique

used to study the propagation **of acoustic waves** in a large variety of samples : liquid, solid, isotropic, anisotropic, transparent or opaque, nanomaterials, single or polycristalline solids.

However, liquid metals are especially well suited for this technique,

because pump beam is easily absorbed, no need of metallic transducer (the optical absorption length is around 10 nm) ;

- There is no need pressure transmitting medium to ensure hydrostatic conditions, because the sample is itself liquid ;

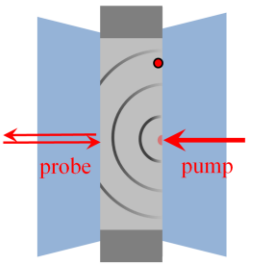
In liquids there is only longitudinal waves which permits to determine easily all the thermoelastic properties of the liquid.

The longitudinal velocity is obtained by temporal measurements.
I show here a typical signal in indium obtained at high pressure and temperature, with 3 echoes.

So basically we monitor the position of the main peak as a function of P and T and the sound velocity is obtained by the time of flight Delta t with v=e/Delta t.

Picosecond acoustics at extreme conditions

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



Versatile probe to study a large variety of samples,
→ **liquid metals** are especially well suited

Hg, Ga, In, Bi, EGa-In-Sn (galinstan)

Ayrinhac *et al* JCP **140**, 244201 (2014)
Ayrinhac *et al* JPCM **27** 275103 (2015)
Ayrinhac *et al* PRM **6**(6) 063403 (2022)

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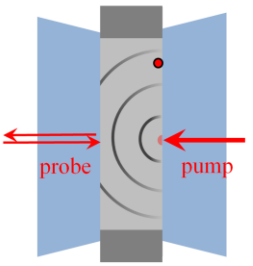
Over the past 10 years, in this context I studied many liquid metals, such as Hg, Ga, In, Bi, eutectic alloy EGa-In-Sn (also called galinstan).
The work on Bi and Galinstan is still in progress.

Picosecond acoustics at extreme conditions

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



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Ayrinhac *et al* JPCM **27** 275103 (2015)
Ayrinhac *et al* PRM **6**(6) 063403 (2022)

I will focus my talk on alkali metals (Rb & Cs) at HP

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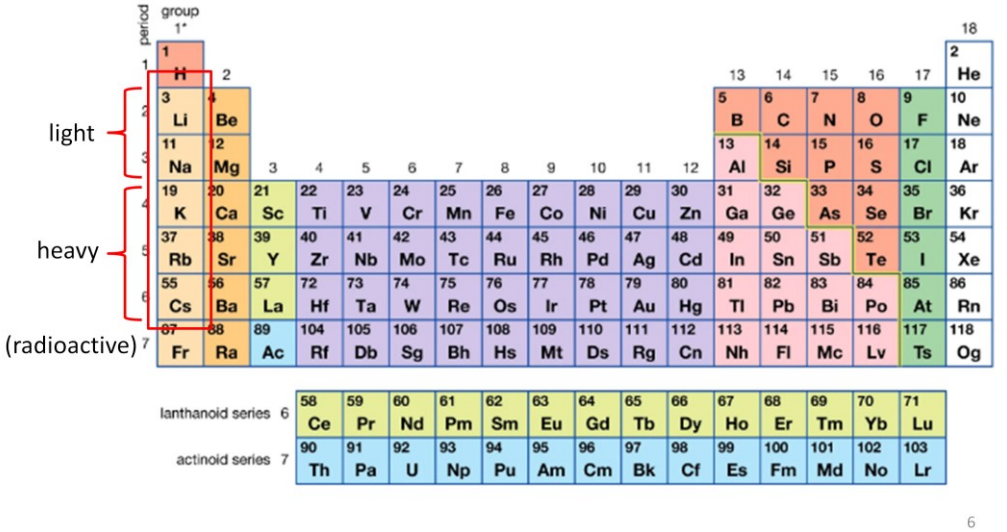
I have also studied liquid Rb and liquid Cs at high pressure,
and I will focus my talk on these 2 elements.

Simple metals ?

alkali elements : simple metals, one valence e^-

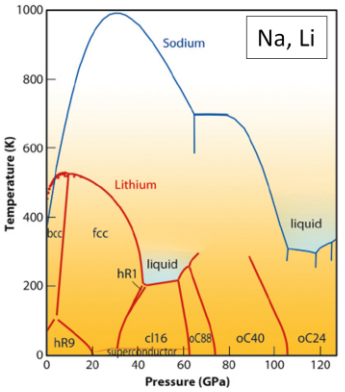


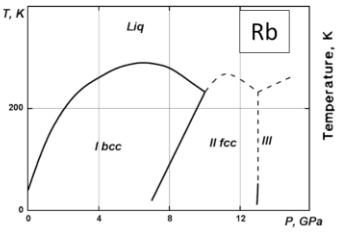
Alkali elemets are the elements in the first column of the periodic table
They are the prototype of **simple metals.**
They possess one valence electron,
So They are highly reactive, and corrosive.

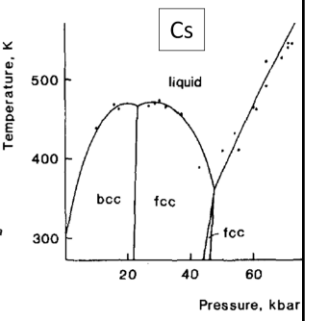
Simple metals ?

alkali metals : simple metals, one valence e^-

Phase diagrams







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

7

However, at high pressure, their behaviour becomes more complex.
For example they possess very complex phase diagram, as illustrated here, with many minima and maxima
as shown here for Li, Na, K, Rb and Cs.
Sodium and Lithium melt at very high pressure which is very unusual.

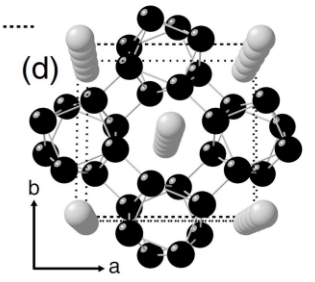
Incommensurate host-guest structures (h-g)

In h-g the elemental crystal structure form a "host" lattice, inside which reside "guest" atoms, which themselves form a regular crystal structure

h-g of Rb-IV

McMahon *et al* PRL **87** 055501 (2001)

Na-V, K-III, Rb-IV



8

Some phases exhibit very complicated structures.
For example under some conditions of P and T there is the apparition of host-guest structures.
It means that the elemental crystal structure form a "host" lattice,
inside which reside "guest" atoms, which themselves form a regular crystal structure.
The host lattice has **channels** where the guest atoms form chains.
=> This is a common feature of alkali metals at high pressure (Na, K, Rb).

Incommensurate host-guest structures (h-g)

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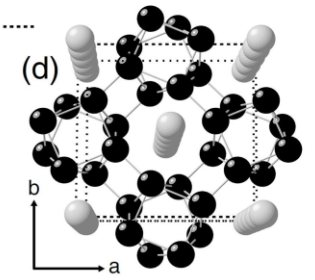

→ The guest atoms form a lattice with lattice parameter c_G that need not be commensurate with the host lattice parameter c_H.

9

The incommensurability means that the guest atoms form a lattice with lattice parameter c_G that
need not be commensurate with the host lattice parameter c_H.

Incommensurate host-guest structures (h-g)

In h-g the elemental crystal structure form a "host" lattice, inside which reside "guest" atoms, which themselves form a regular crystal structure

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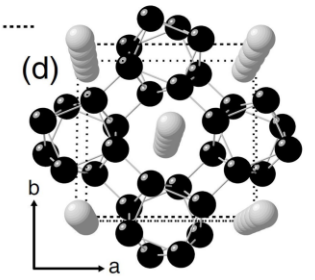
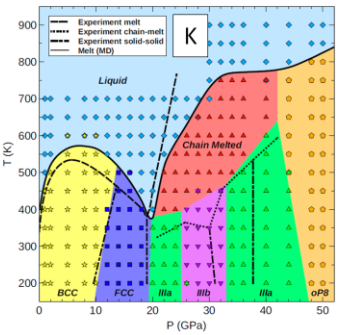


McMahon et al **93** 055501 (2004)
McBride *et al* **91**, 144111 (2015)
Robinson *et al*, PNAS **116** 10297 (2019)

Chain-melted phase : one sublattice is disordered



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Then, as discovered by McMahon et al in 2004,
The host-guest structure can become a chain-melted phase :
one sublattice is disordered and the other remains ordered.

Recently, Robinson and coworkers reproduced the whole phase diagram of K with calculations based on machine learning [1].
They showed that order is lost along and between chains and this is a true thermodynamic phase of matter…

References

[1] http://dx.doi.org/10.1073/pnas.1900985116

Incommensurate host-guest structures (h-g)

In h-g the elemental crystal structure form a "host" lattice, inside which reside "guest" atoms, which themselves form a regular crystal structure

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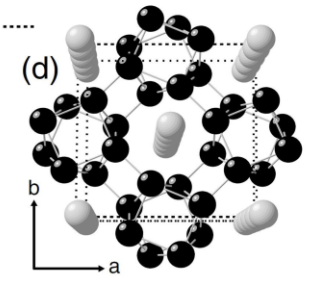
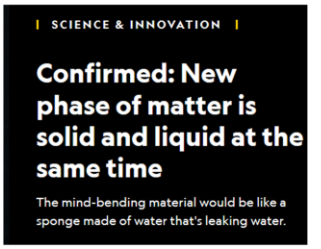


McMahon et al **93** 055501 (2004)
McBride *et al* **91**, 144111 (2015)
Robinson *et al*, PNAS **116** 10297 (2019)

Chain-melted phase : one sublattice is disordered

"solid and liquid at the same time" !

National Geographic (April 2009)



11

… which can be considered solid and liquid at the same time.
This work was reported in the National Geographic magazine in April 2009 [1].

References

[1] https://victorsplayground.wordpress.com/

Liquid-liquid phase transition (LLPT)

LLPT is a transition from one liquid state to another with the same composition but distinct local ordering

Review : H. Tanaka, « Liquid–liquid transition and polyamorphism », *The Journal of Chemical Physics*, **153**(13) 130901 (2020).

- first-order liquid-liquid transitions (exp. evidence)
  - elemental phosphorus
    Katayama *et al*, *Nature*, **403** 170 (2000)
  - elemental sulphur
    Henry *et al*, *Nature*, **584** 382 (2020)

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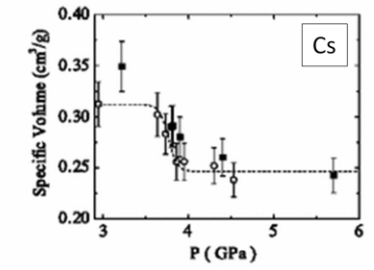
In addition, a hot topic in condensed matter is the existence of **liquid-liquid phase transition.**
Liquid–liquid phase transition (LLPT) is a transition from one liquid state to another with the same composition but distinct local ordering.
An excellent review on this topic was done recently by Tanaka.

In two thousand, a first order LLPT was found experimentally by Katayama and coworkers in elemental liquid phosphorus.
First order means that there is a discontinuity in the volume at the transition.
More recently in 2020, a similar transition was observed by Henry et al in sulphur.
There is also theoretical clues on the existence of the LLT.

However, LLPT is **also** detected or expected in alkali liquid metals, such as Cs and Rb.

Liquid-liquid phase transition (LLPT)

→ transformations in liquid Cs were detected by X-ray @P=2 GPa & P=3-4 GPa, T=500 K



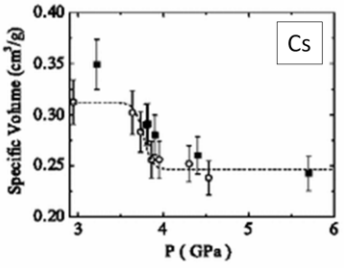
Falconi *et al* PRL **94**, 125507 (2005)
Falconi *et al* PRB **73**, 184204 (2006)

13

Transformations in liquid Cs were detected by X-ray scattering at P=2 GPa and P=3-4 GPa at T=500 K.
I show here the specific volume as a function of P around 4 Gpa.
Falconi and coworkers found that there is a steep transition at 4 GPa.

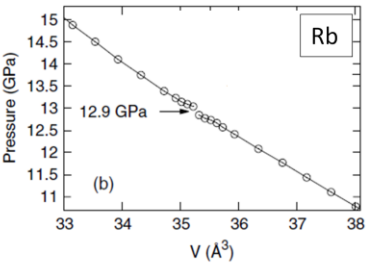
Liquid-liquid phase transition (LLPT)

→ transformations in liquid Cs were detected by X-ray @P=2 GPa & P=3-4 GPa, T=500 K



Falconi *et al* PRL **94**, 125507 (2005)
Falconi *et al* PRB **73**, 184204 (2006)

→ a LLT is detected in *ab initio* MD @P=12.9 GPa, T=573 K



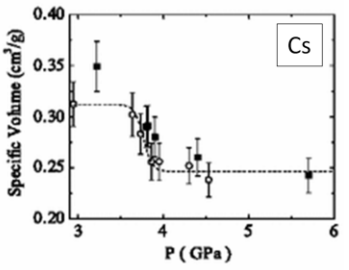
Bryk *et al* PRL **111** 077801 (2013)
Gorelli *et al* JPCL **9** 2909 (2018)

14

In the same way, as shown by Bryk et al,
there is a discontinuity in the volume at 12.9 GPa and T=573 K.

Liquid-liquid phase transition (LLPT)

→ transformations in liquid Cs were detected by X-ray @P=2 GPa & P=3-4 GPa, T=500 K



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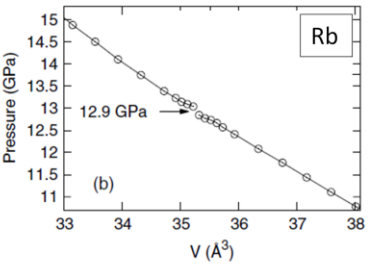

Bryk *et al* PRL **111** 077801 (2013)
Gorelli *et al* JPCL **9** 2909 (2018)

The question : Can we detect these LLPT by picosecond acoustics combined with DAC ?

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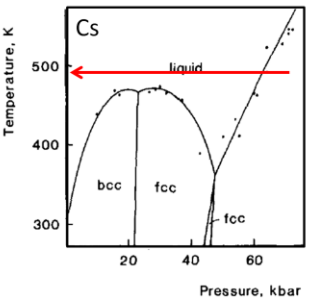
However many of LLPT are controversial on an experimental point of view.
For example Hattori [1], performing density measurements by another method in Caesium, did not find a discontinuity in volume.

So it is interesting to perform sound velocity measurements because sound velocity is a sensitive probe of phase changes.
So The question is : Can we detect these LLPT by picosecond acoustics combined with DAC ?

References

[1] Hattori PRB **97** 100101 (2018).

Liquid caesium



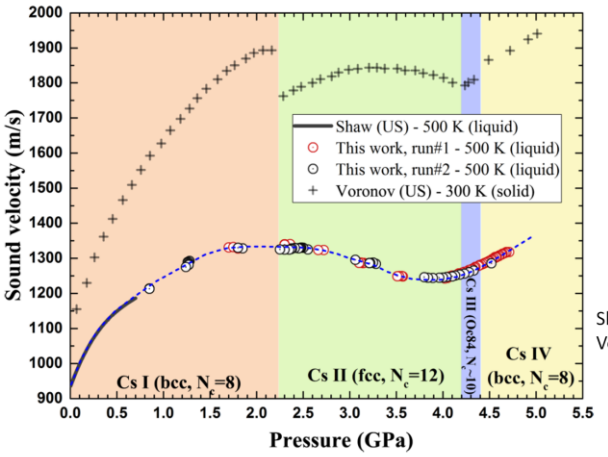
(DAC loaded in a dry glove box)

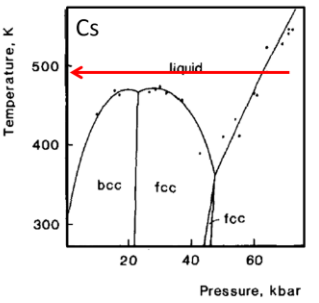
16

The idea was to measure sound velocity with picosecond acoustics just above the maximum of the melting curve at 500 K
(obviously at the same temperature than Falconi), with decreasing pressure
Because the thickness of the sample remain constant when pressure decreases.

Liquid caesium

Decremps *et al.*, PRB **98** 184103 (2018)





Shaw *et al*, PRB, **32** 7937 (1985)
Voronov *et al* JETP **95** 77 (2002)

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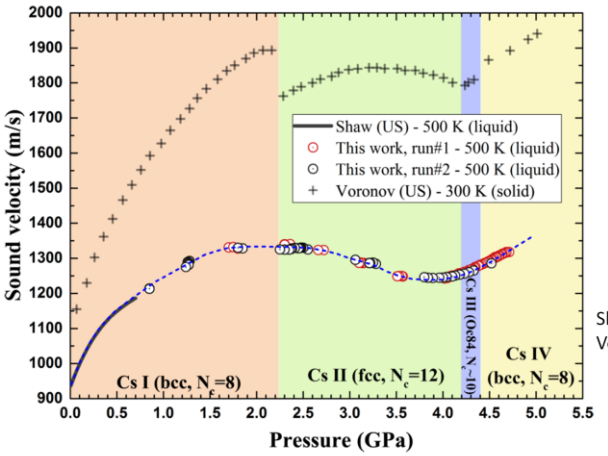
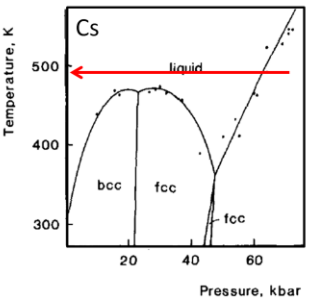
I show here the sound velocity we obtained as a function of pressure (in 2 runs).
Our data are compared to the sound velocity measured in the solid by Voronov.

We found an oscillation, and it highlights the strong similarity between the sound velocity in liquid and solid.
It means that the properties of the liquid Cs are similar to the underlying solid.

Liquid caesium

Decremps *et al.*, PRB **98** 184103 (2018)





Shaw *et al*, PRB, **32** 7937 (1985)
Voronov *et al* JETP **95** 77 (2002)

➢ **No first-order LLPT but a gradual crossover between 2 liquids**

Max @2 GPa → structural origin

Min @4 GPa → electronic transition in solid Cs (*6s-5d* transfer)

Takemura *et al* PRL **49** 1772 (1982)

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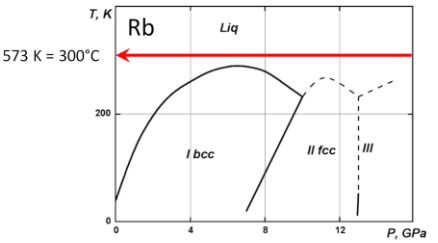
-> We did not find a first-order LLT but a gradual crossover between 2 liquids.

•It seems that the maximum at 2 GPa corresponds to the bcc-fcc solid-solid phase transition, this bump have a structural origin.

•The minimum in sound velocity at 4 GPa occurs at the same pressure than an electronic transition in solid Cs (collapse of the 6s electronic orbital onto the 5 d orbital – s-d transfert / s-d hybridization)

Liquid rubidium



Tonkov *et al* (book, 2004)

Demanding experiments :
DAC loading in a dry glove box

9 runs :
- 3 runs useful only
- 4 diamonds broken
- P calibrant lost

19

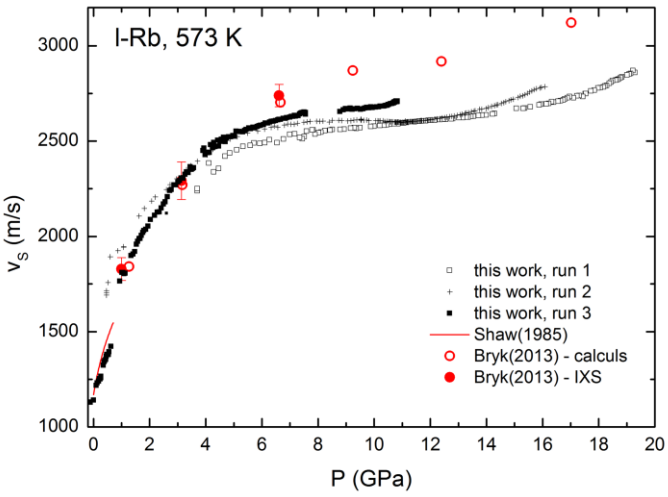
So we performed the same measurements in liquid Rb.

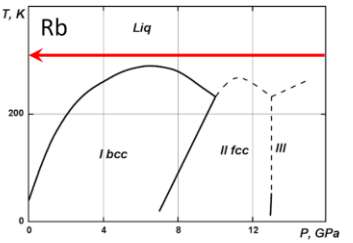
As in caesium, the experiments are demanding because the DAC is loaded in a dry glove box.
The experiments were more demanding than Cs.
I performed nine runs, 3 runs only were useful, and 4 diamonds were broken at HP.
At some pressure point, P calibrant were lost, so we measured the Raman of the diamond directly at the contact of the sample (but it is not so accurate)
And use a calibration curve.

Liquid rubidium

Ayrinhac *et al* **4**, 113611 (2020)

- temporal method : thickness = constant when P ↓
- automatic pressure driver → P ↓ controlled ramp





Tonkov *et al* (book, 2004)

Demanding experiments :
DAC loading in a dry glove box

9 runs :
- ➢3 runs useful only
- ➢4 diamonds broken
- ➢P calibrant lost

Shaw *et al*, PRB, **32** 7937 (1985)
Bryk *et al* PRL **111** 077801 (2013)

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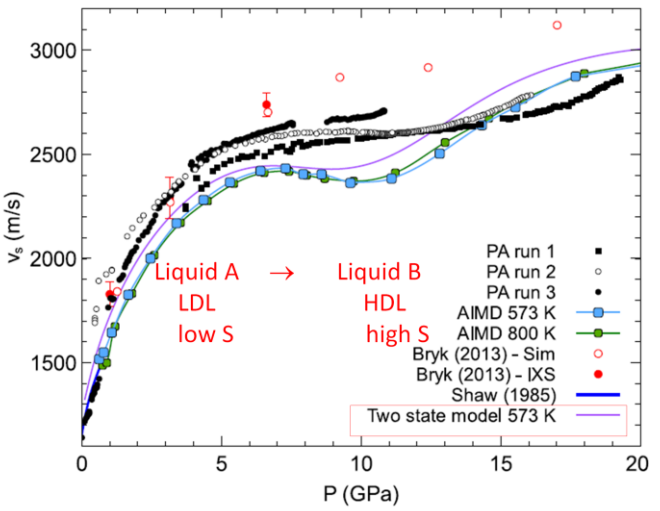
I show here the sound velocity as a function of P.
The sound velocity increases steeply when the pressure increases, then there is a huge **plateau**
(or an oscillation like in Cs, but it is inside the uncertainty).
The thickness is not well known, however relative sound velocity measurements are very accurate.
So no first-order LLT was detected, but a gradual transition like in Cs.

Liquid rubidium

Ayrinhac *et al* **4**, 113611 (2020)



Ackland *et al PRB* **104**, 054120 (2021)

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A thermodynamic model which consider a <u>mix of two different liquids</u> reproduce well the data (in pink).
The oscillation is explained by a gradual transition from a low-density to a high-density liquid,
But the liquid A have a low entropy and the liquid B have a high entropy.

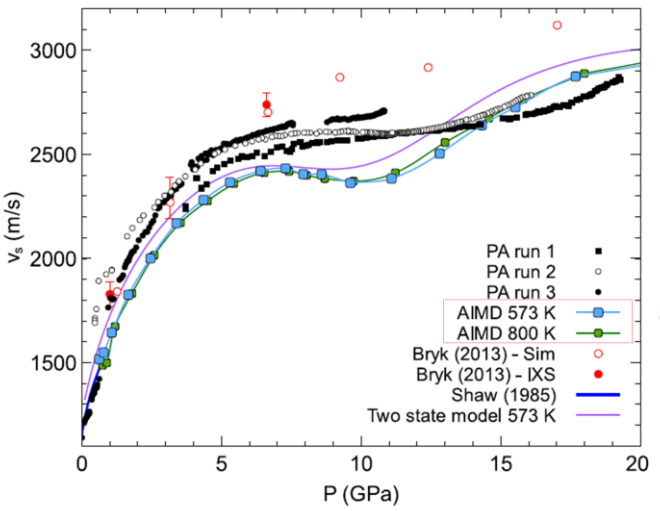
This model is discussed in details in the article of Ackland et al.

References

[1] Ackland *et al PRB* **104**, 054120 (2021)

Liquid rubidium

Ayrinhac *et al* **4**, 113611 (2020)



DFT calculations by V.N.Robinson and S. Scandolo

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DFT calculations were performed by my colleagues V. Robinson and S. Scandolo at 2 temperatures (573 K and 800 K).
They extract the sound velocity from the calculations, and they agree with our experimental data.

These simulations give us the possibility to have insights **on the microscopic nature of the transition**.

Rb (and Cs) as high-pressure electrides

An electride is an ionic compound where the anionic part is made up of isolated electrons

Neaton *et al* PRL **86** 2830 (2001)
Miao *et al Acc.Chem.Res.* **47** 1311 (2014)

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Liquid Rb (and Cs) can be seen as a high-pressure electride.
An electride is a ionic compound (solid state) where the anionic part is made up of isolated electrons.

At high pressure, the impenetrable cores get closer and are forced to overlap.
So the electrons are forced to migrate in the voids between the impenetrable ions, and behave like anions.

Rb (and Cs) as high-pressure electrides

An electride is an ionic compound where the anionic part is made up of isolated electrons

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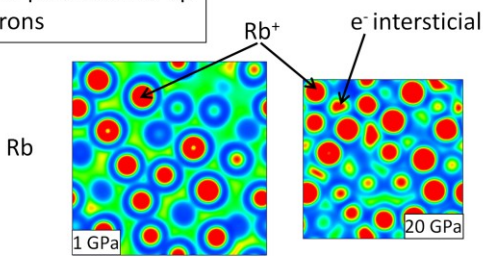

Ayrinhac *et al* **4**, 113611 (2020)

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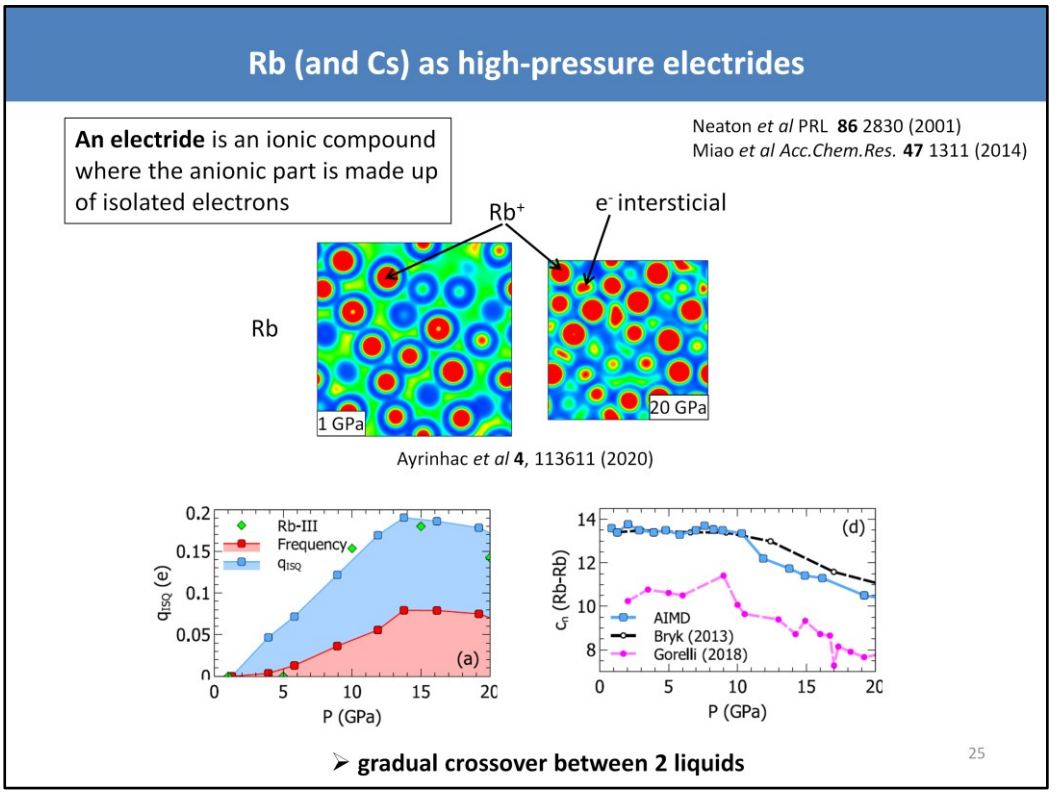
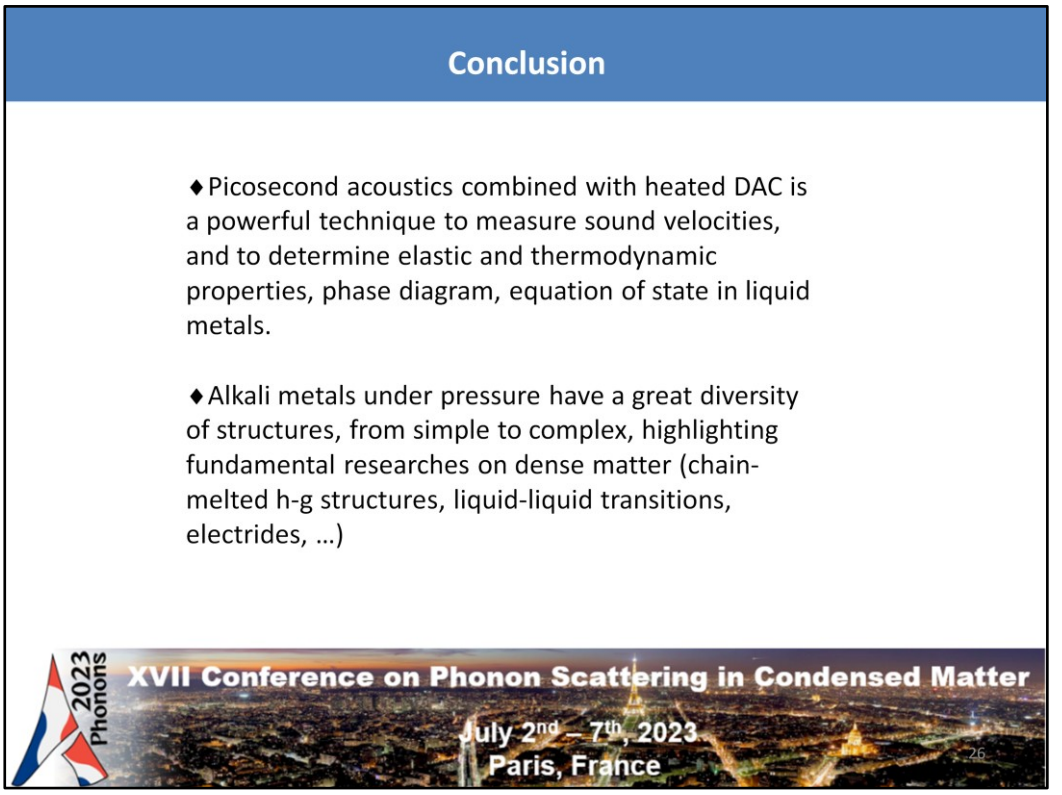
I show here 2 snapshots from the simulations at 1 GPa and 20 GPa.
They show the cores here of Rb plus, and the interstitial electrons here and here.
Colors code the electron localization function, red color means that the electron is localized.



As the pressure increases, the average electric charge localized in the voids increases to reach the value of the solid Rb-III.

At the same time, as the pressure increases, the coordinance numbre decreases from fourteen to ten.
This decrease indicates a gradual transition
From a simple close packed liquid to a complex liquid with a more open structure.

So the gradual crossover between 2 liquids can be explained y the electride nature of the high-pressure liquid.



So, as a conclusion :

• Picosecond acoustics combined with heated DAC is a powerful technique to measure sound velocities, and to determine elastic and thermodynamic properties, phase diagram, equation of state in liquid metals.

• Alkali metals under pressure have a great diversity of structures, from simple to complex, highlighting fundamental researches on dense matter (chain-melted h-g , liquid-liquid transitions, electrides, …)

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Thank you for your attention !