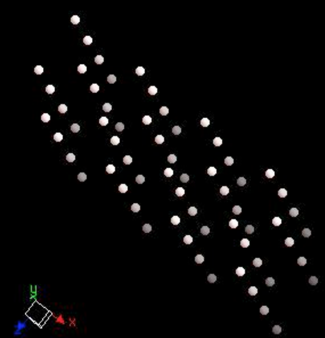
Simple Elements at high densities: En-Route to metallic hydrogen and insulating lithium

Shanti Deemyad
Department of Physics, Harvard University

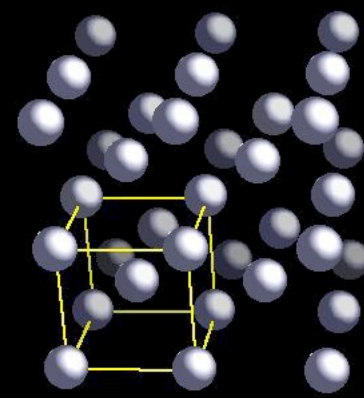
Solid Hydrogen at ambient pressure

- Boiling point ~20K
- Melting point ~14 K
- Molecular solid
- Insulator



Solid Lithium at ambient pressure

- Boiling point ~1118 K
- Melting point ~553 K
- Atomic solid
- Metal



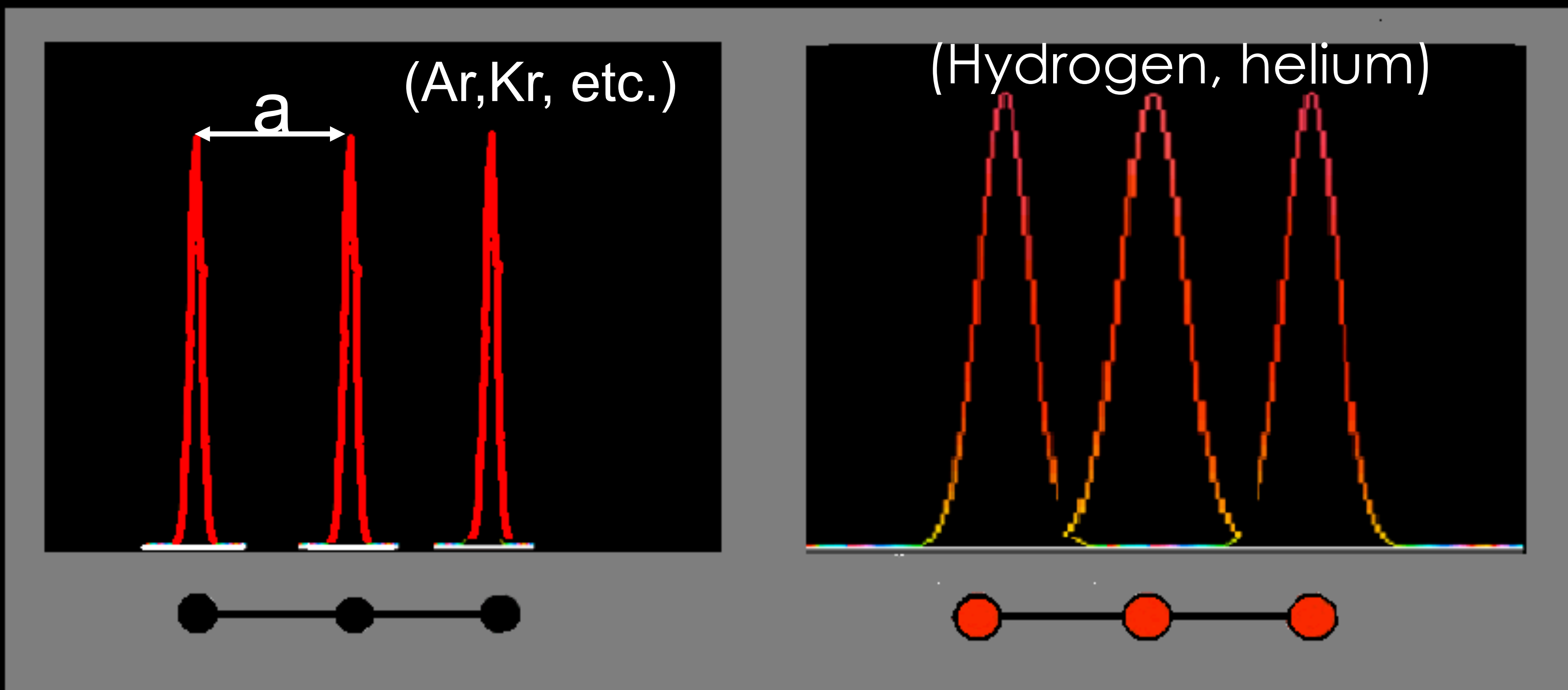
Translational zero point motion at T=0K

Classical solid

$\lambda_{de\ Broglie} << a$

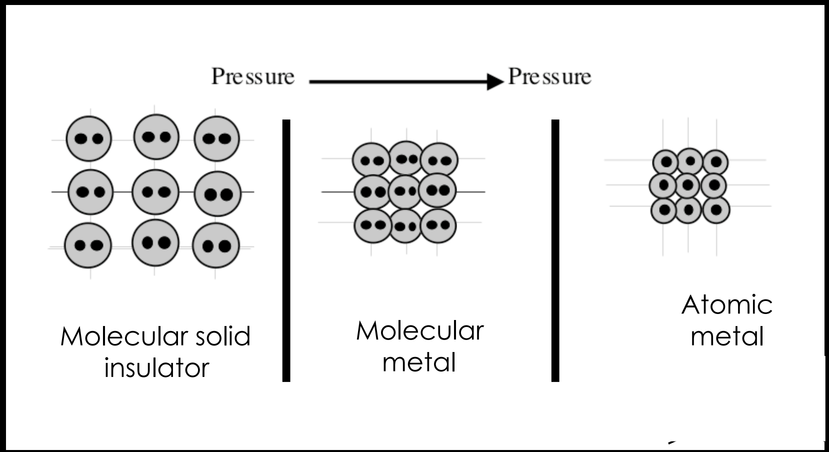
Quantum Solid

$\lambda_{de\ Broglie} \sim 0.1a$



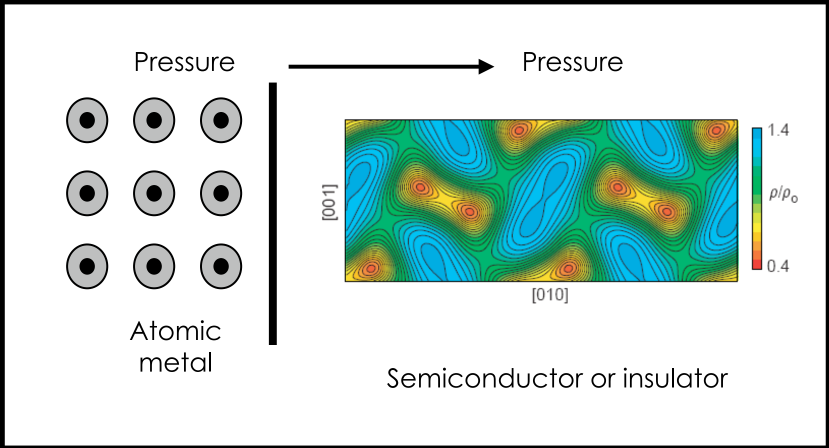
In quantum solids Lattice expands to prevent overlap of hard cores

Hydrogen



- High temperature superconductivity in atomic metallic hydrogen *Ashcroft , 1968*
- Metastability, *Brovman, Kagan, Kholas, 1972*
- Two component superconductivity & superfluidity in high-pressure liquid H. *Babaev, Sudbe, Ashcroft 2004*
- Maximum in the melt line*, Bonev 2004*

Lithium



- Superconductivity with T_c as high as 80 K *Chrisensen and Novikov 2001*
- Metal insulator transition and pairing, *Neaton and Ashcroft 1999*
- Maximum in the melt line above 20GPa. *Temblyn et al. 2008*

1. Pressure-induced superconductivity in lithium

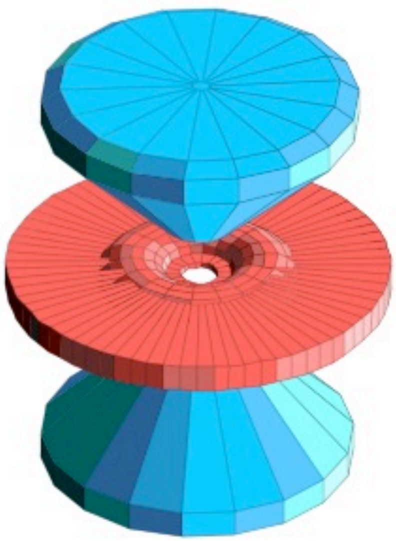
2. Maximum in melt line of hydrogen

1 Mbar = 100GPa ~1,000,000 atm

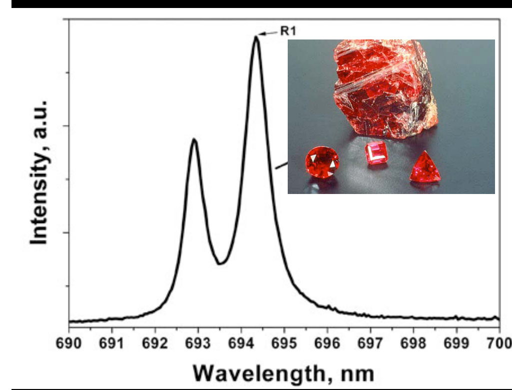
P[redacted]

Diamonds and Gasket

(about 3-4 mm linear dimensions)



Diamond Anvil Cell (about the size of a coca-cola bottle)



$$P(GPa) = \frac{1904}{b}\left\{\left[1 + \left(\frac{\Delta\lambda}{\lambda_0}\right)\right]^{b} - 1\right\}$$

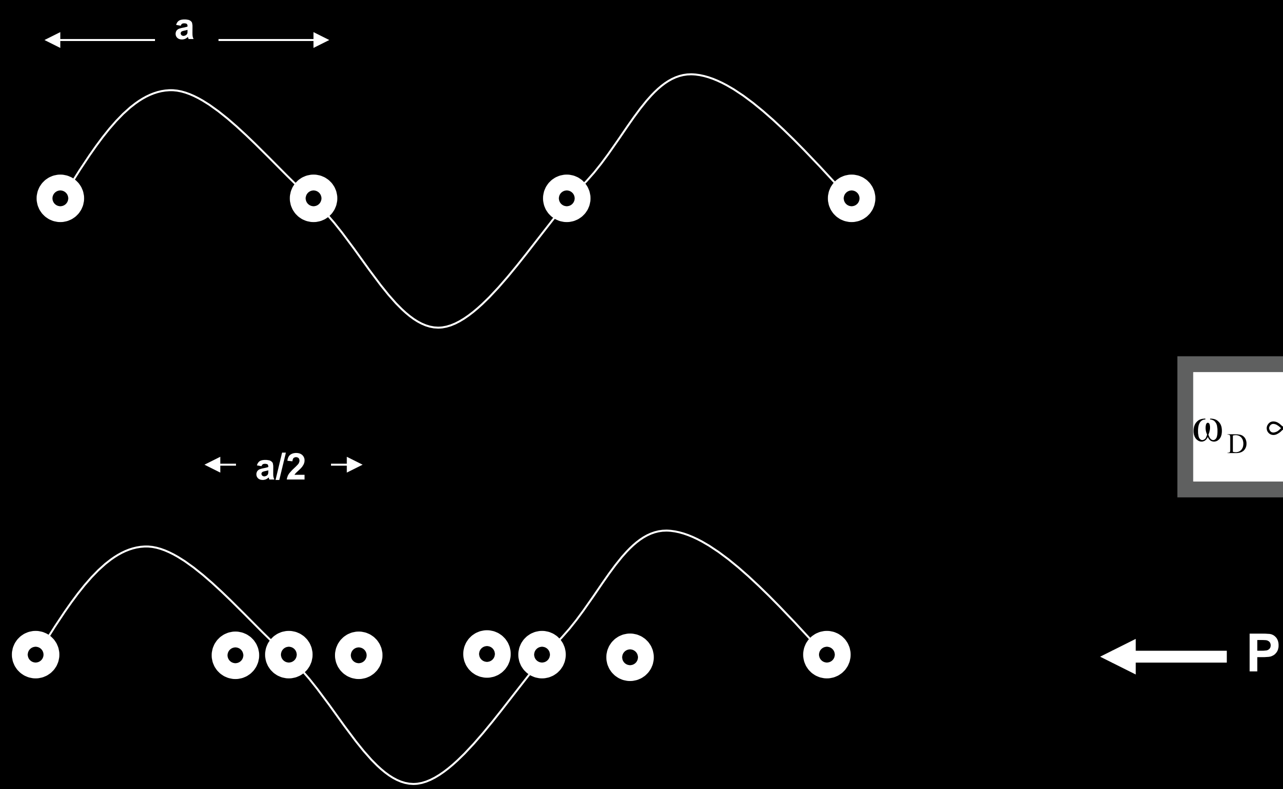
1. Pressure-induced superconductivity in lithium

2. Maximum in melt line of hydrogen

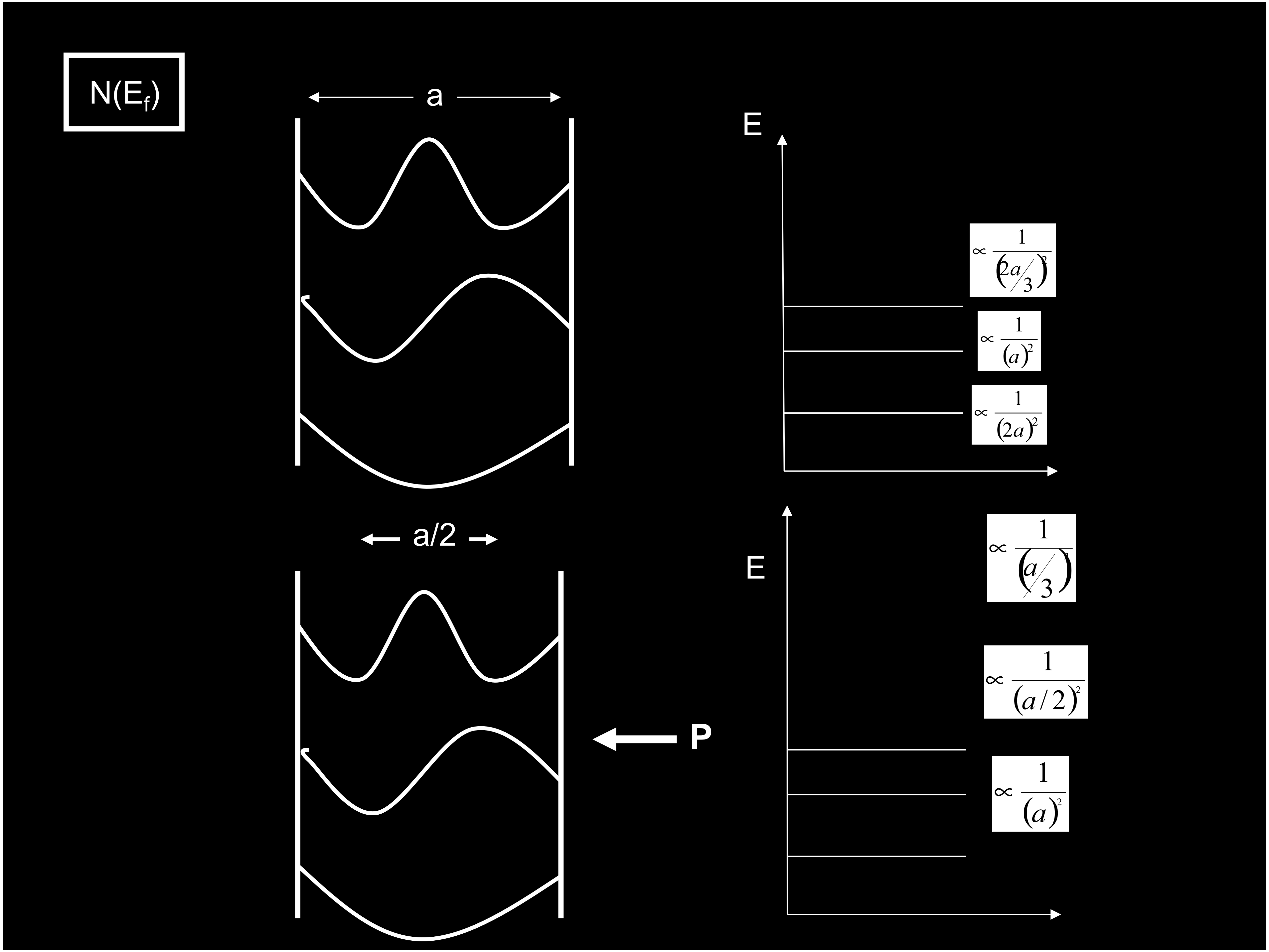
Conventional BCS-type superconductivity

$$T_c = 1.14\hbar\omega_D \exp\left(-\frac{1}{N(E_f)U}\right)$$

w_D



$$\omega_D \propto K_{max} = \frac{\pi}{a}$$



N(E$_f$)
a
E
$\propto \frac{1}{(2a/3)^2}$
$\propto \frac{1}{(a)^2}$
$\propto \frac{1}{(2a)^2}$
a/2
P
E
$\propto \frac{1}{(a/3)^2}$
$\propto \frac{1}{(a/2)^2}$
$\propto \frac{1}{(a)^2}$

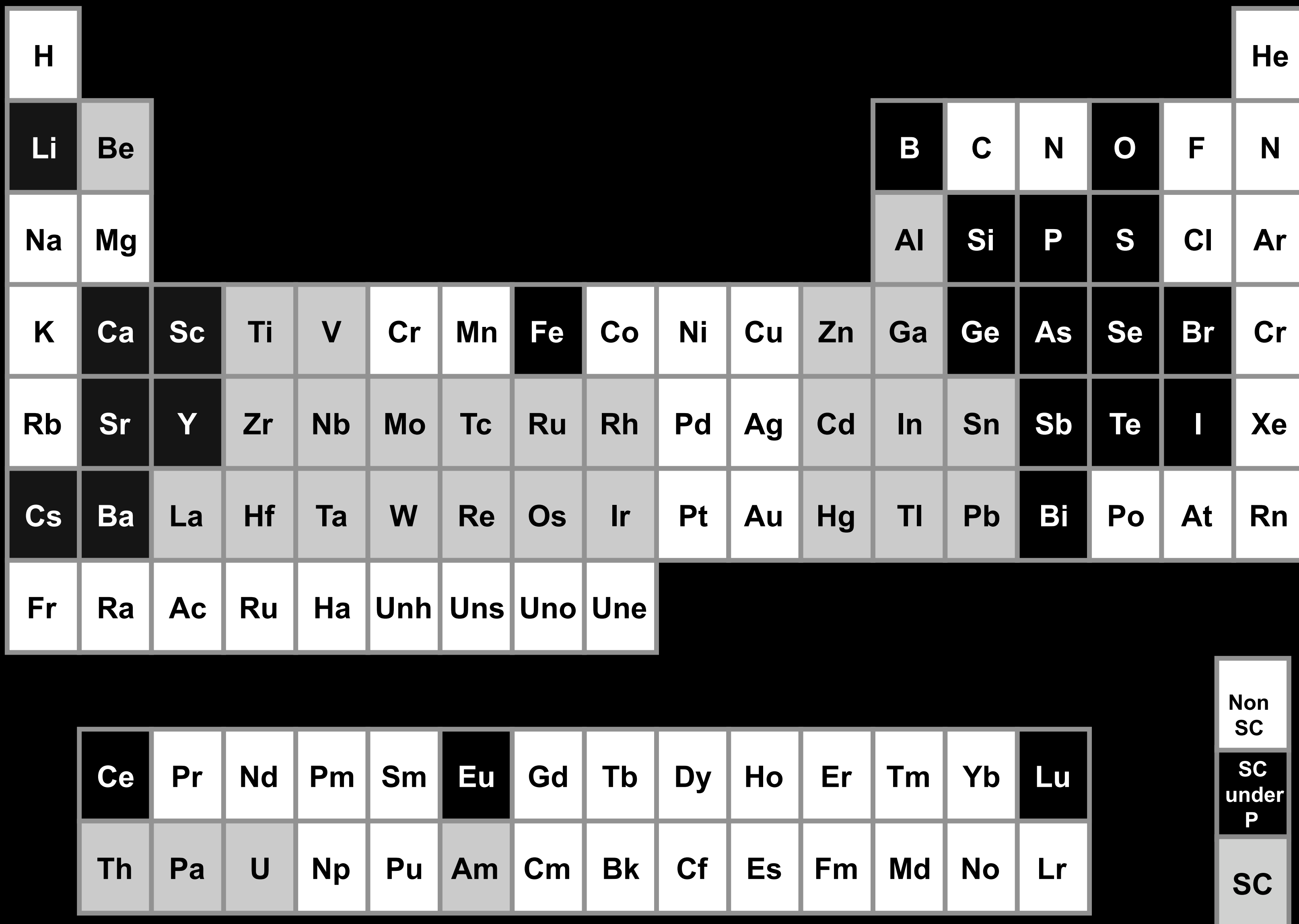
Increases under pressure

$$T_c = 1.14\hbar\omega_D \exp\left(-\frac{1}{N(E_f)U}\right)$$

In most cases both decrease under pressure

T_c decreases with pressure for most known conventional superconductors.

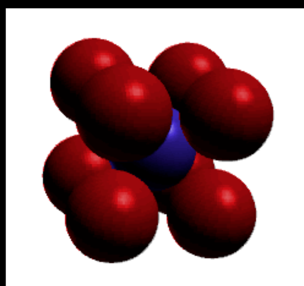
Table of Superconducting Elements

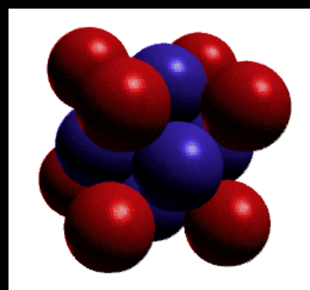


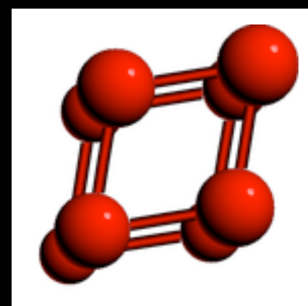
Lithium

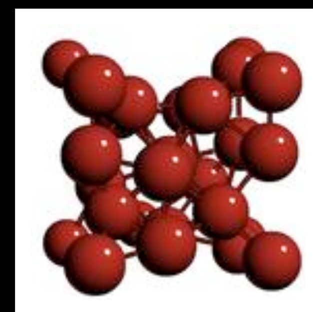
T ≈ 180 K

(7.5GPa) (39.8GPa) (42.5GPa)







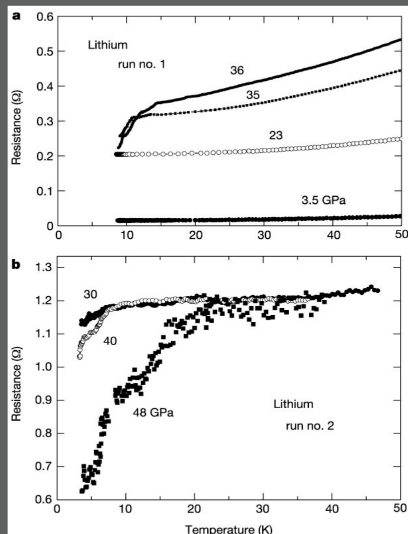


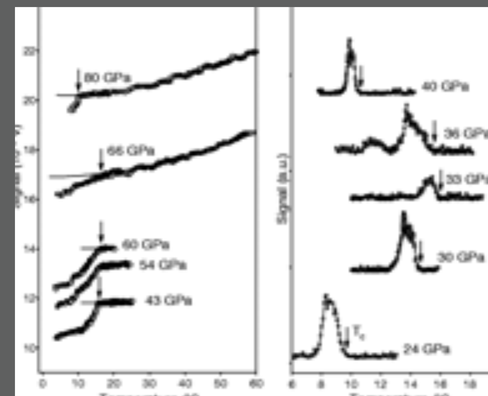
bcc ⟶ fcc ⟶ hR1 ⟶ cI16

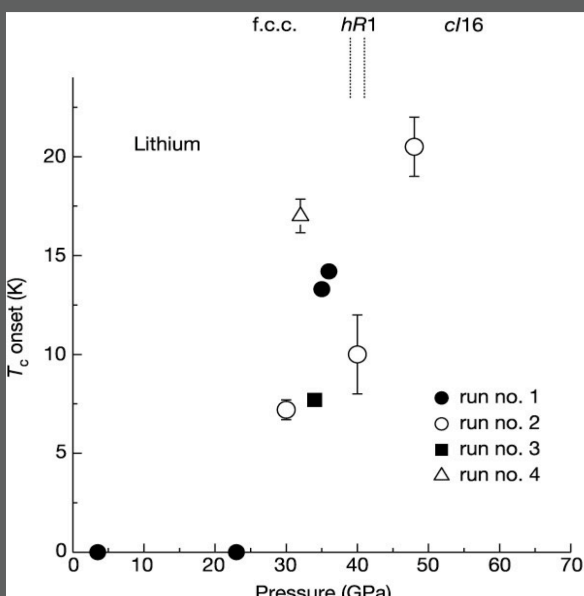
T < 75 K : Martensitic transition bcc → 9R

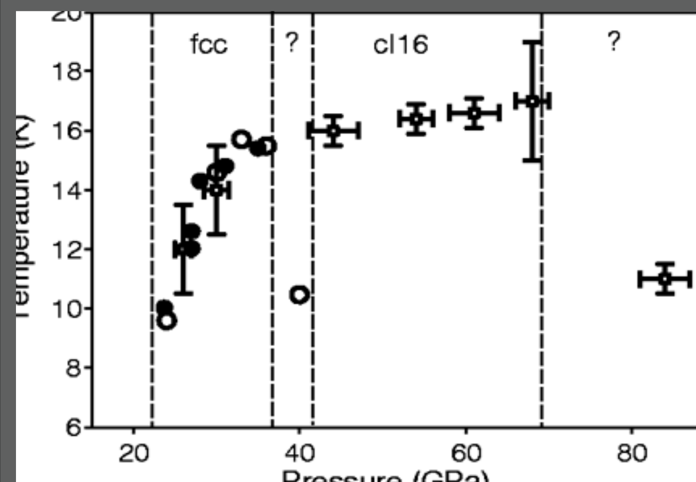
M. Hanfeld et al. Nature **408**: 174 (2000).

Superconductivity in Lithium









V.V. Struzhkin et al. Science **298**: 1213(2002).

K. Shimizu.et al. Nature **419**: 597. (2002).

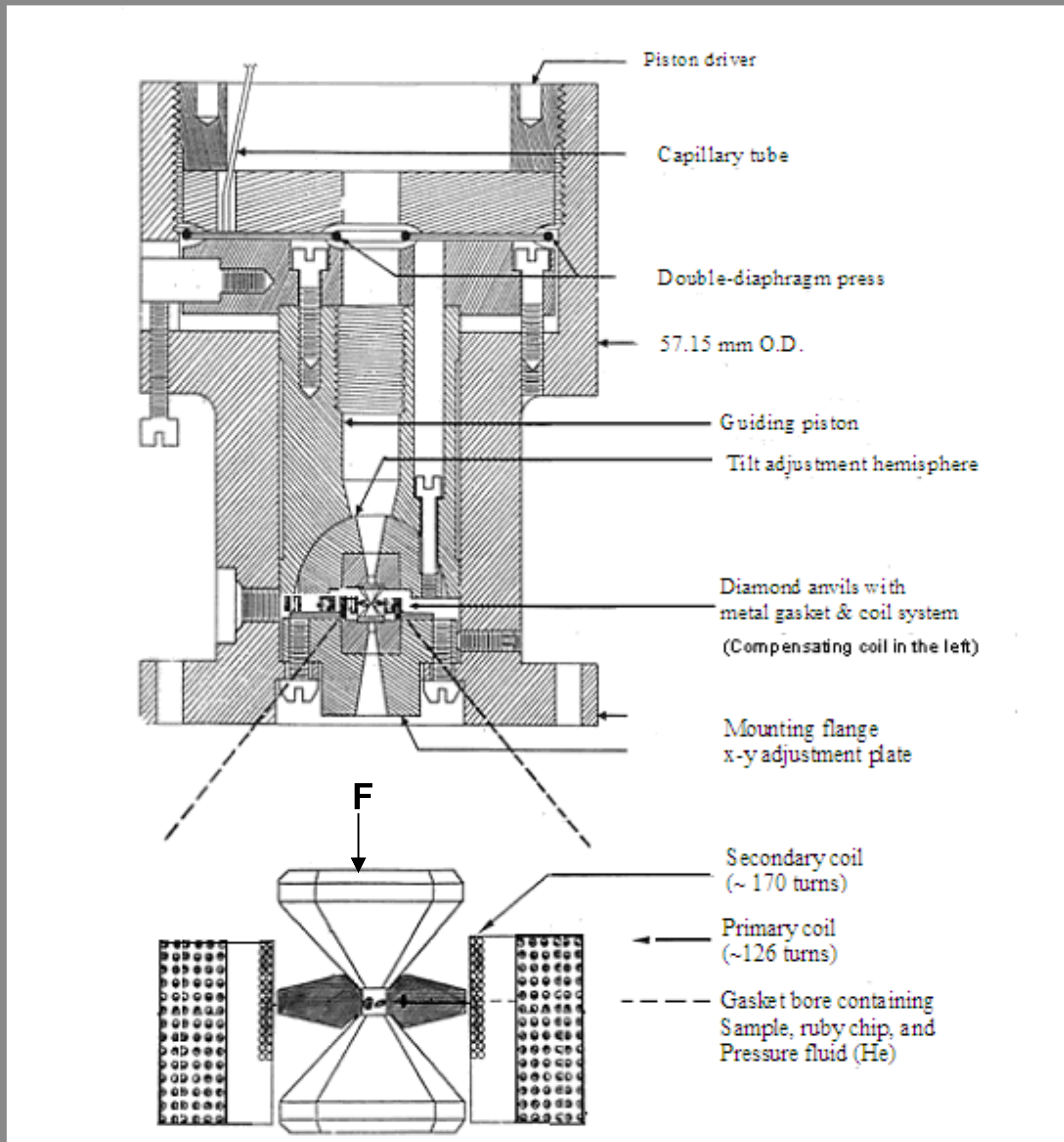
Shear stresses and high pressure studies of superconductors:

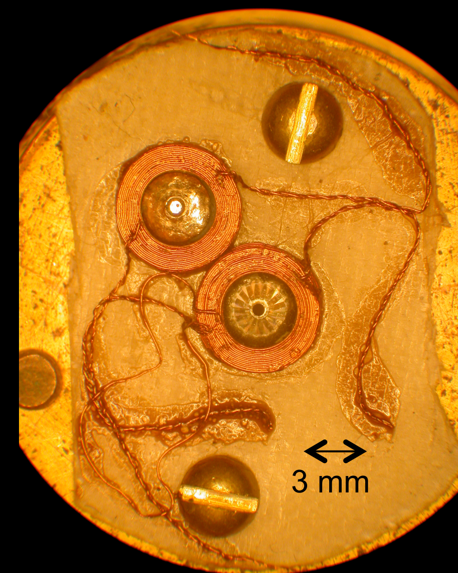
- Many of the properties of materials under pressure depend on whether the pressure is transmitted in a truly hydrostatic way or not.

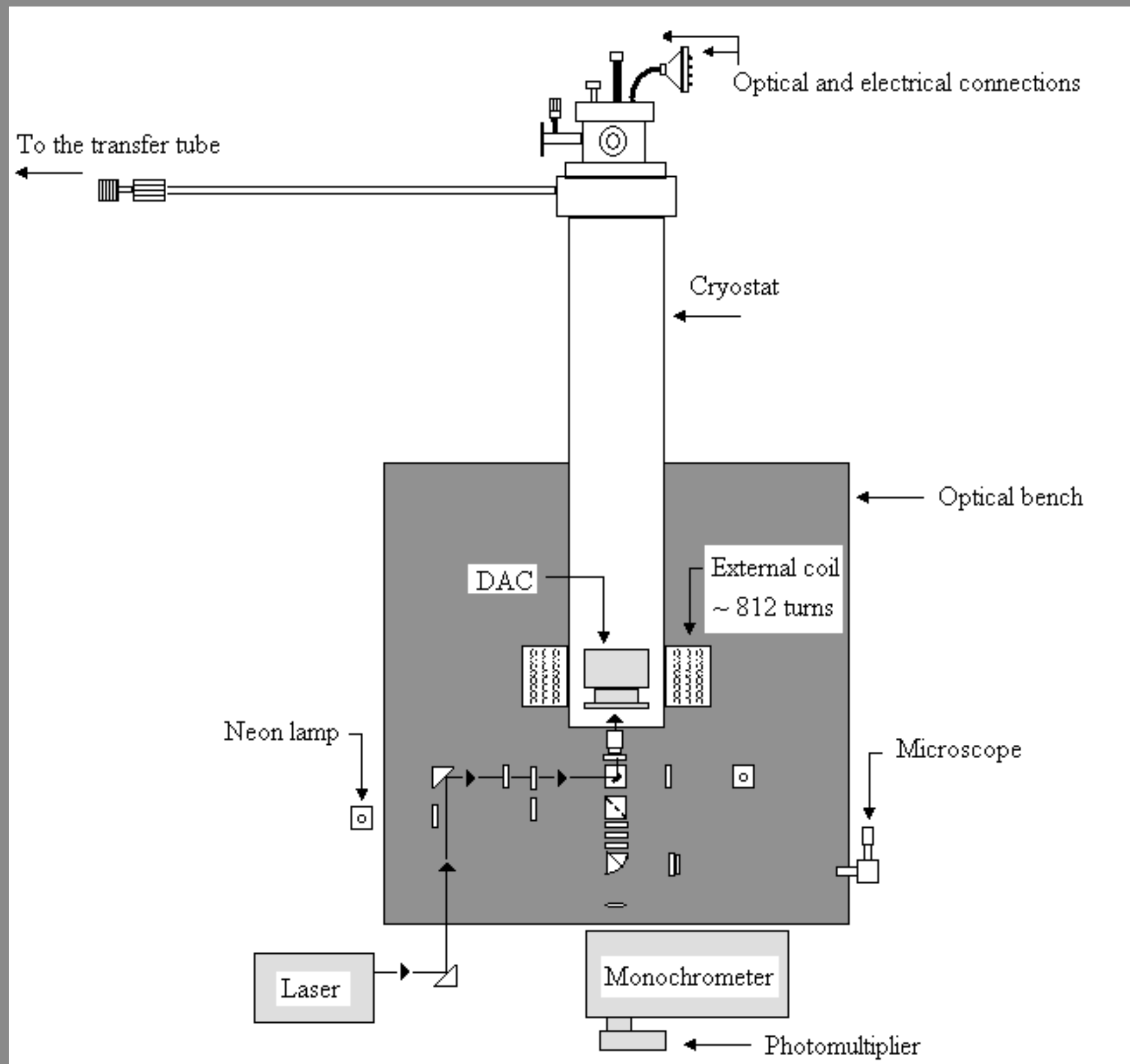
- Shear-stresses generated in non-hydrostatic pressure media influence the pressure dependence of T_c.

- Conditions which are very nearly hydrostatic may be obtained over the widest range of temperature and pressure using helium as pressure transmitting medium.

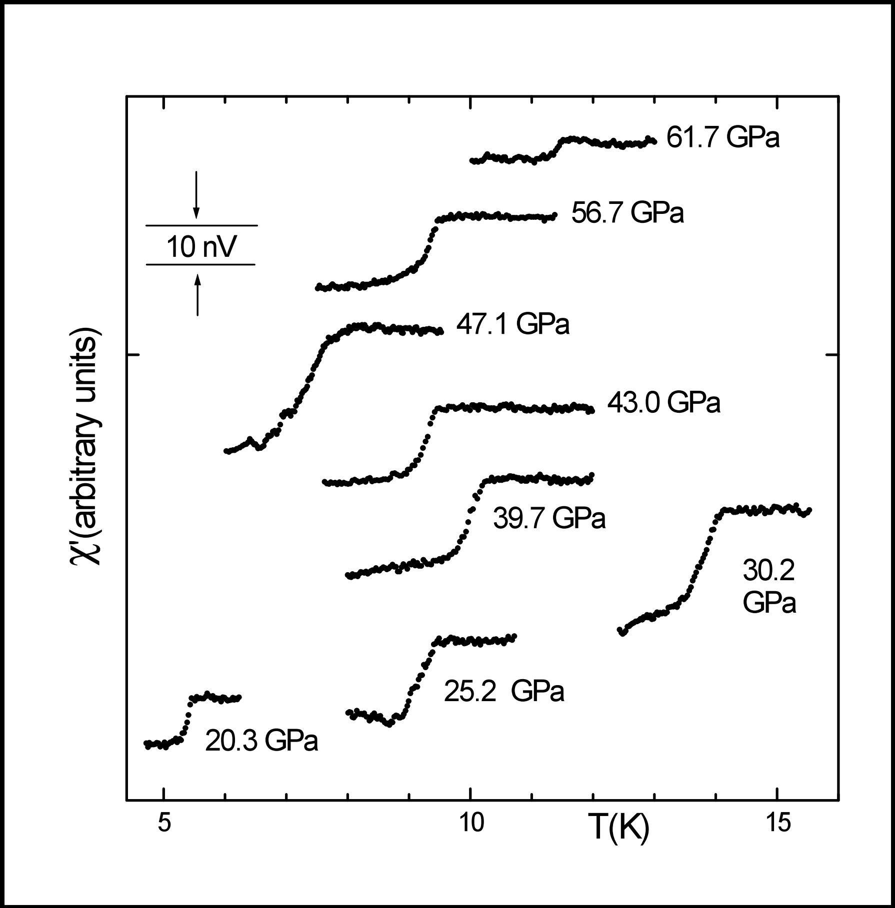
The diamond-anvil cell

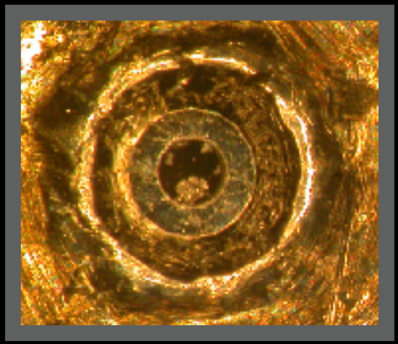





Optical and electrical connections
To the transfer tube
Cryostat
Optical bench
DAC
External coil
~ 812 turns
Neon lamp
Microscope
Laser
Monochrometer
Photomultiplier

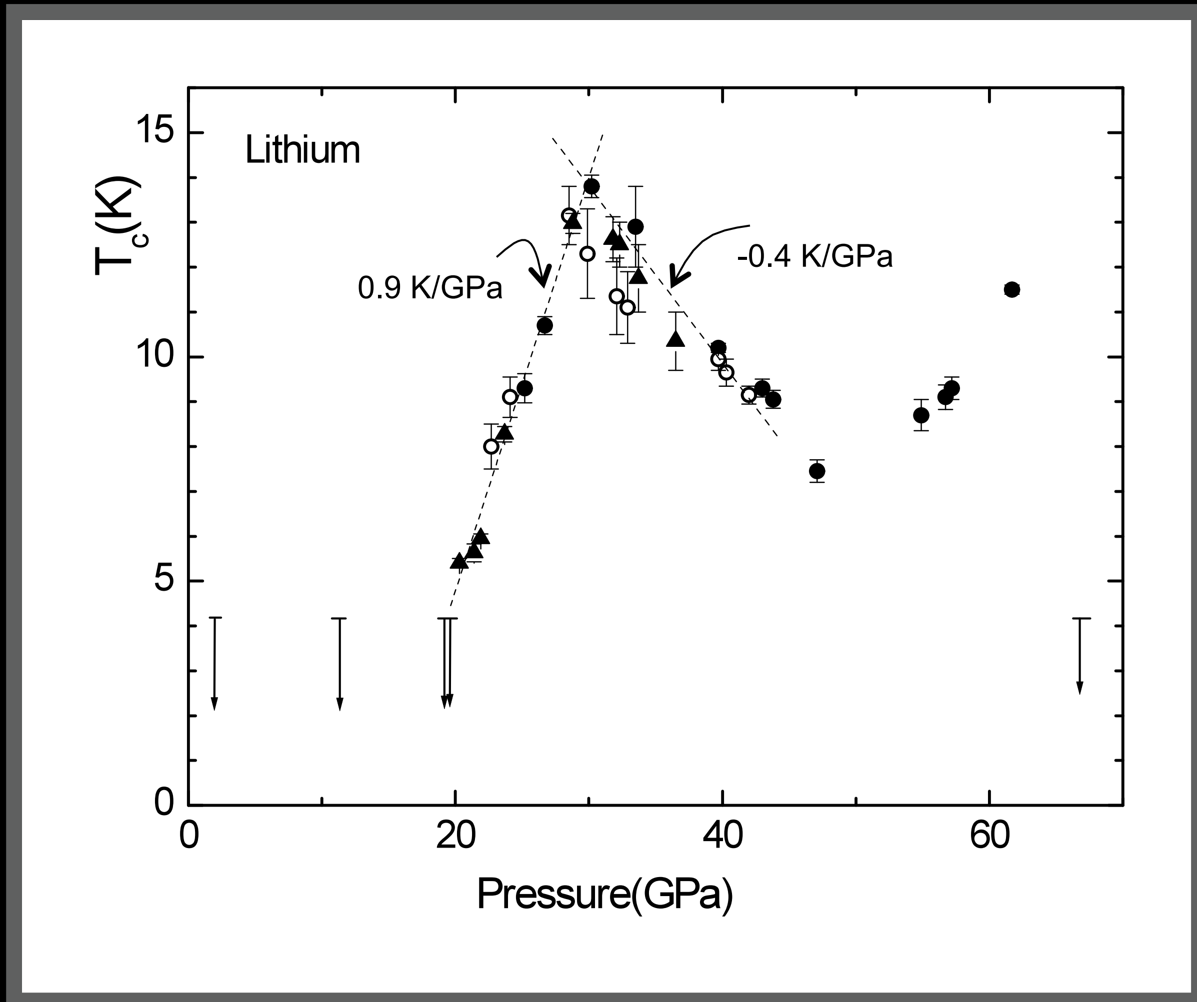
Lithium



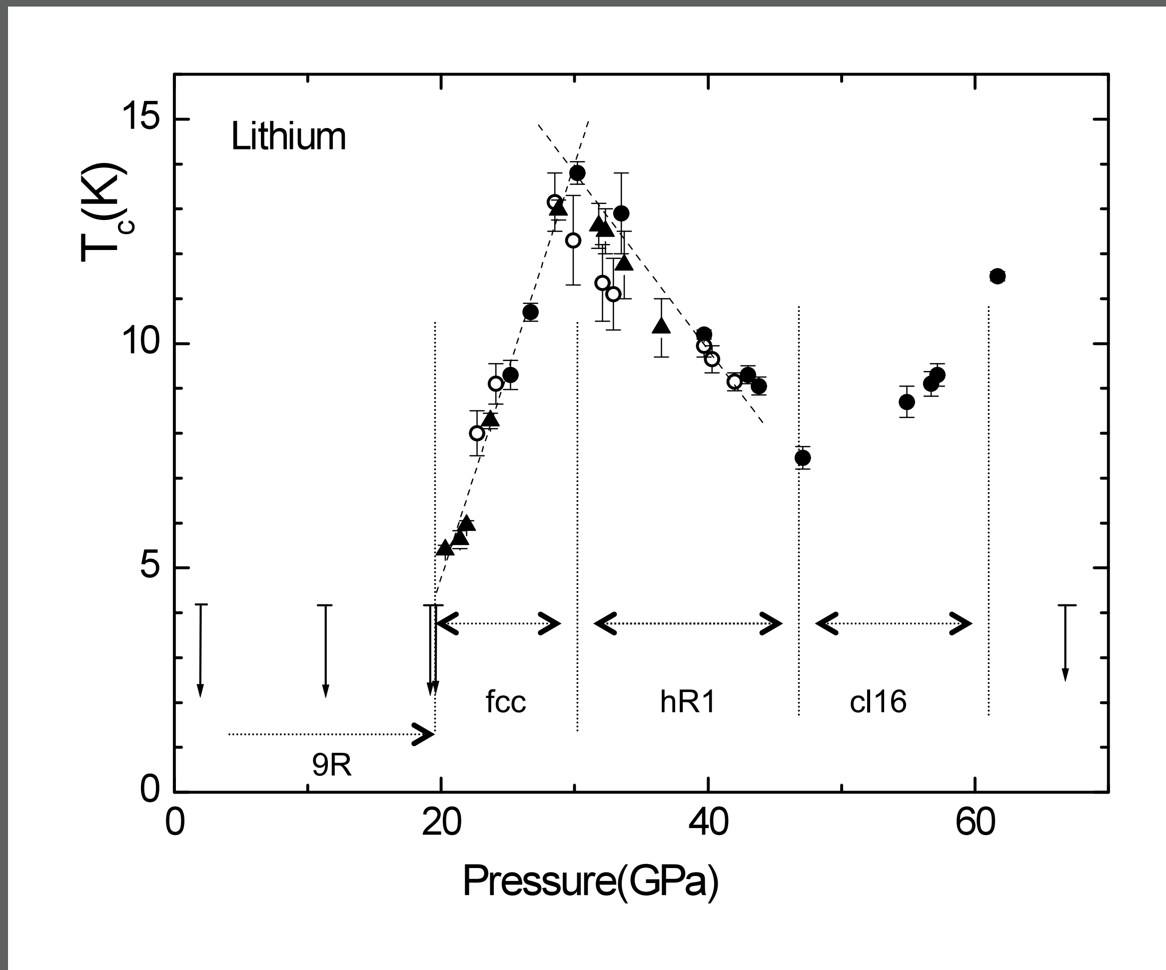


Ambient Pressure

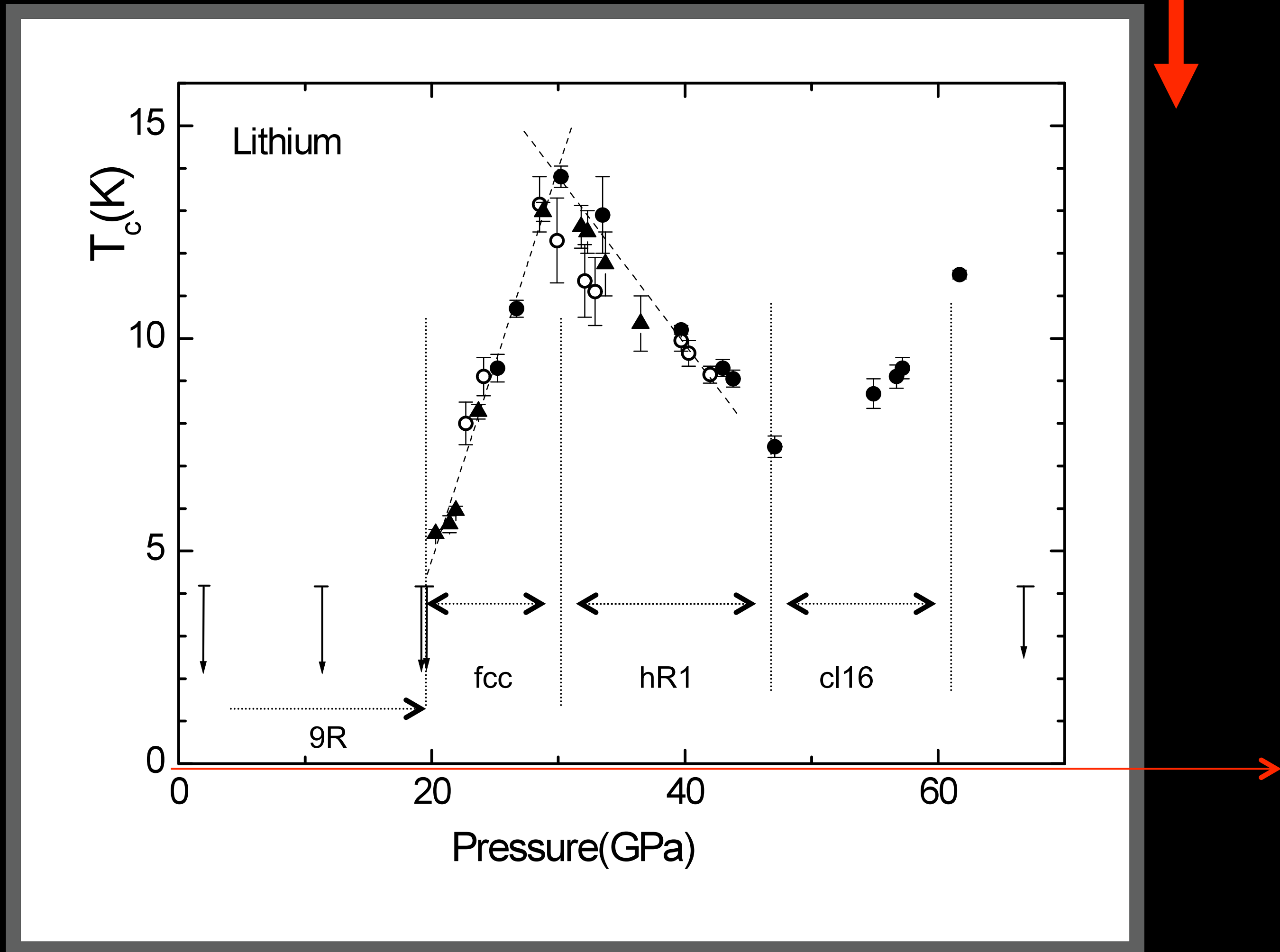
30 GPa



S. Deemyad and J. S. Schilling, Phys. Rev. Letter **91**, 167001 (2003).


Lithium
T_c(K)
Pressure(GPa)
fcc
hR1
cI16
9R
0
5
10
15
0
20
40
60

Metal semiconductor transition (Shimizu 2009)



Summary

- The superconducting phase diagram of lithium, $T_c(P)$, was determined up to 67 GPa under nearly hydrostatic conditions.

- Superconducting transition of lithium was disappeared above 67 GPa and T>4K.

- Search for paired state in lithium and possible insulator-metal transition in lithium is still to be found.

1. Pressure-induced superconductivity in lithium

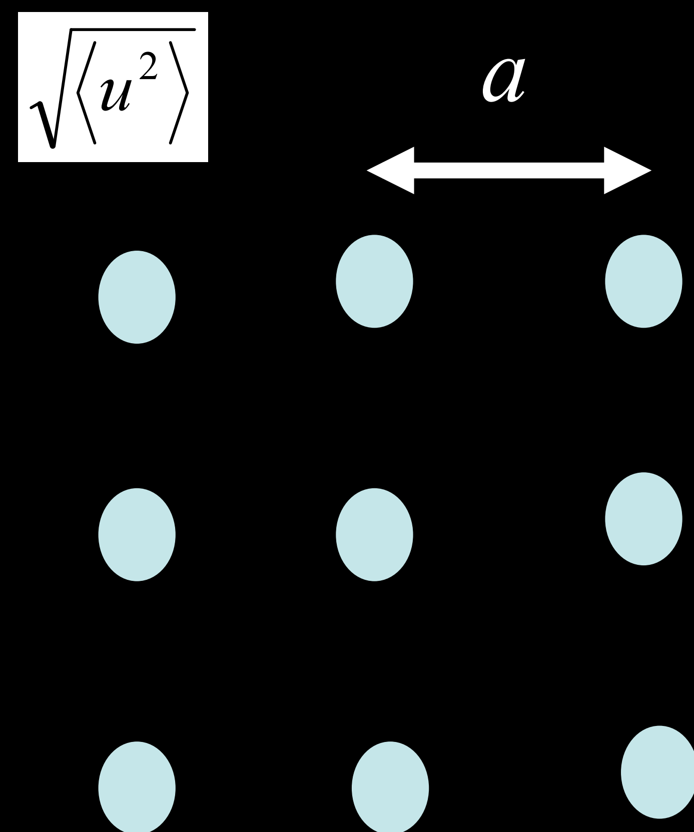
2. Maximum in melt line of hydrogen

Lindemann criterion for melting

At $T \geq T_m$:

$$\frac{\langle u^2 \rangle}{a^2} \geq 0.01$$

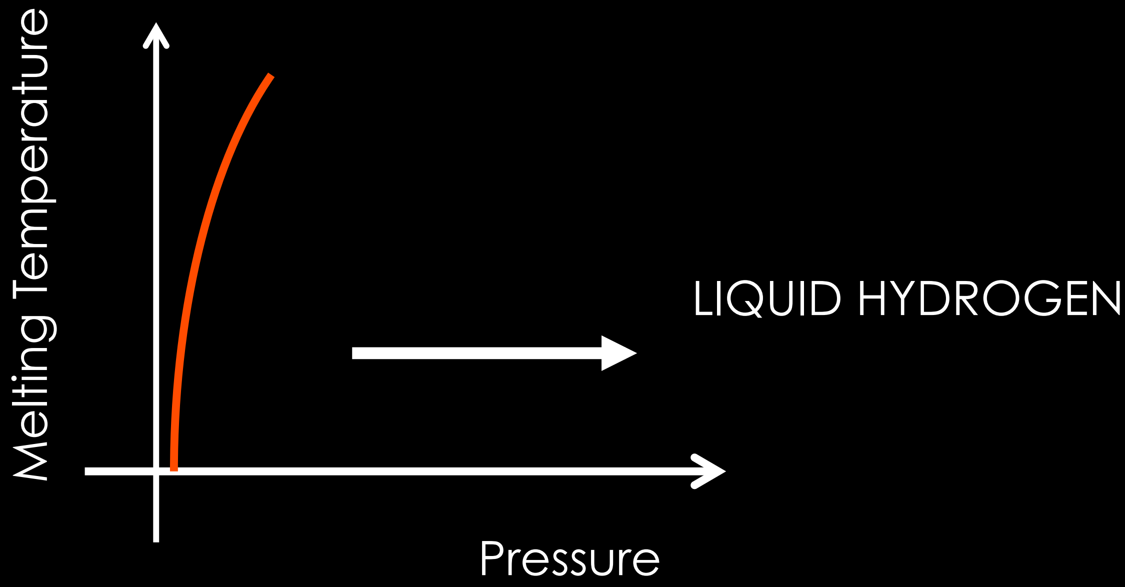
$$kT_m \propto c\,\omega_D{}^2 a^2$$



Liquid atomic metallic hydrogen

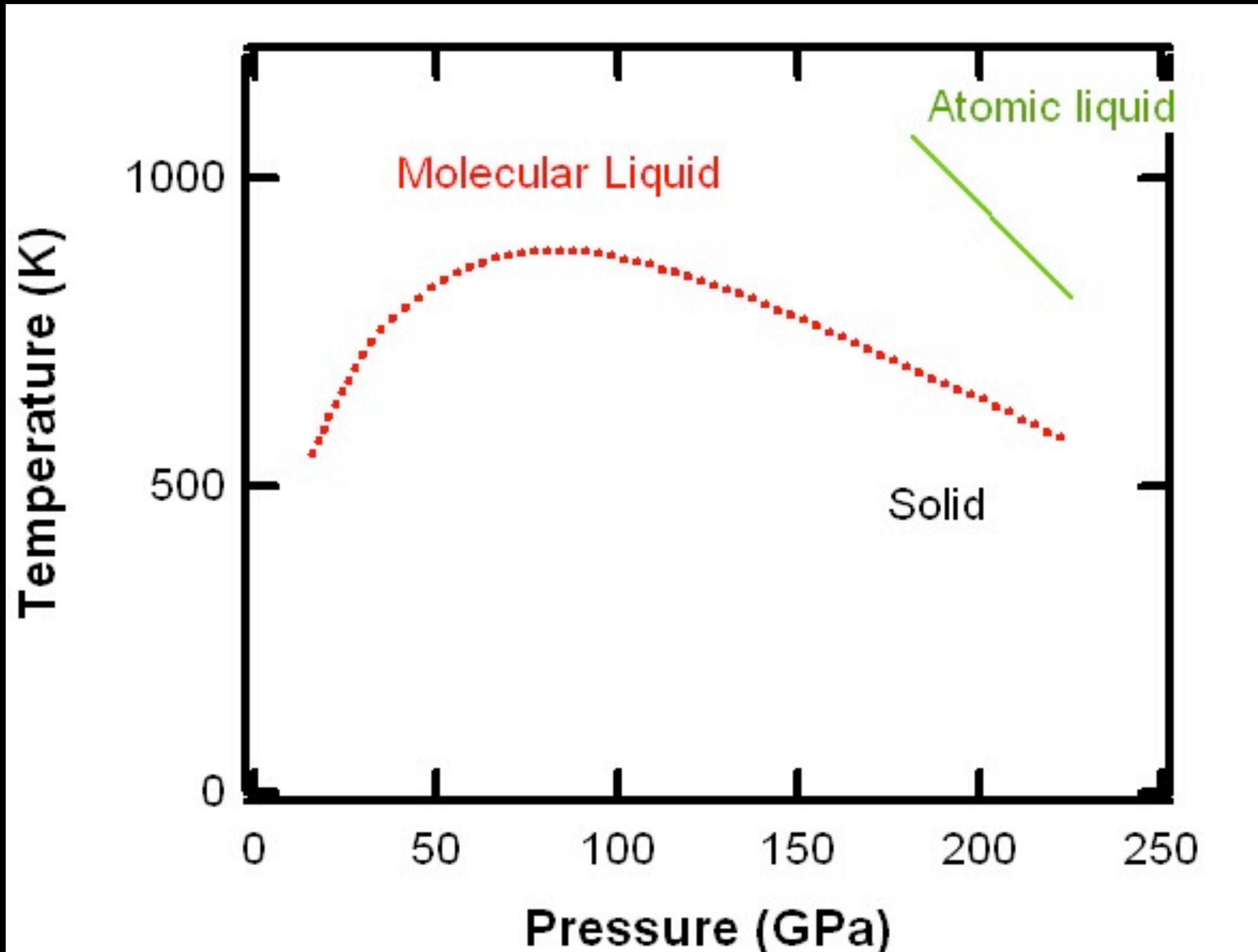
Hydrogen has a very large hidden translational zero-point energy in the internal vibration ~1/2 ev

This may be "liberated" if the molecules dissociate. → Quantum melting

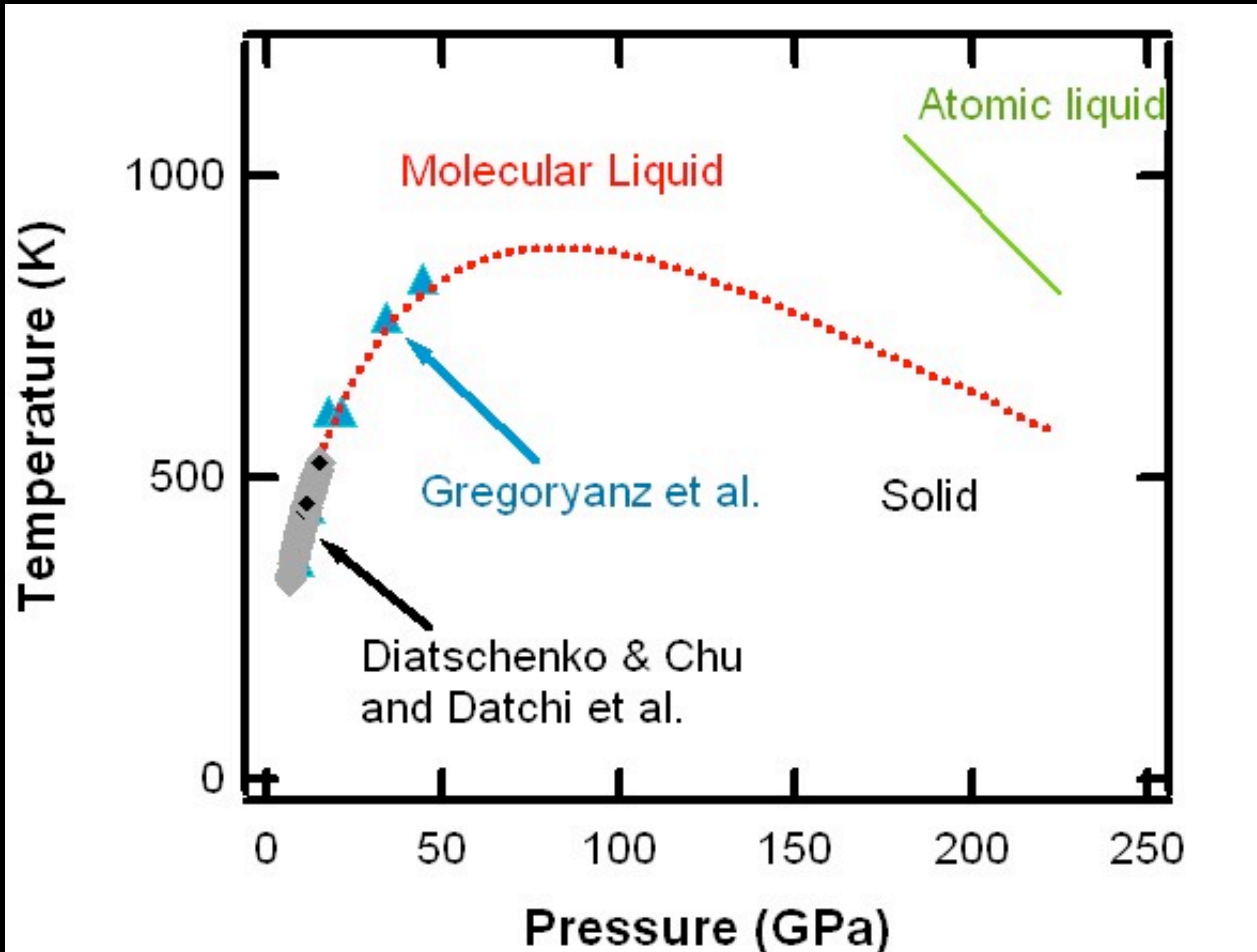


Low Temperature Liquid Metallic Phase at High Pressure???

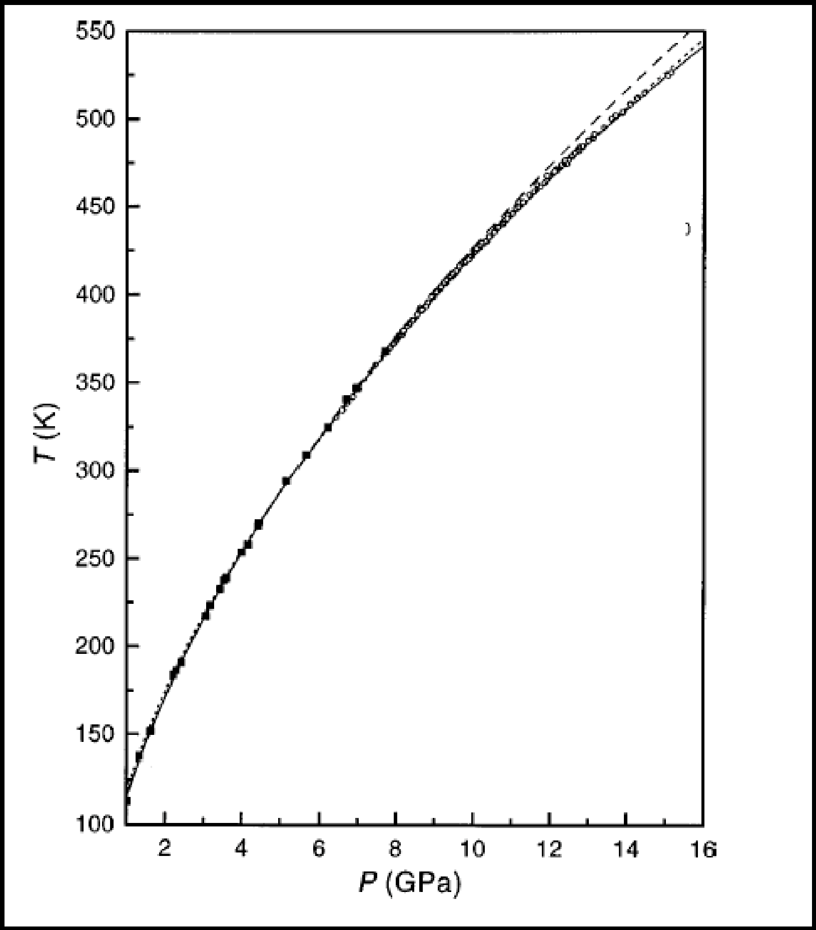
Maximum in the Melting Line



Bonev et al 2004

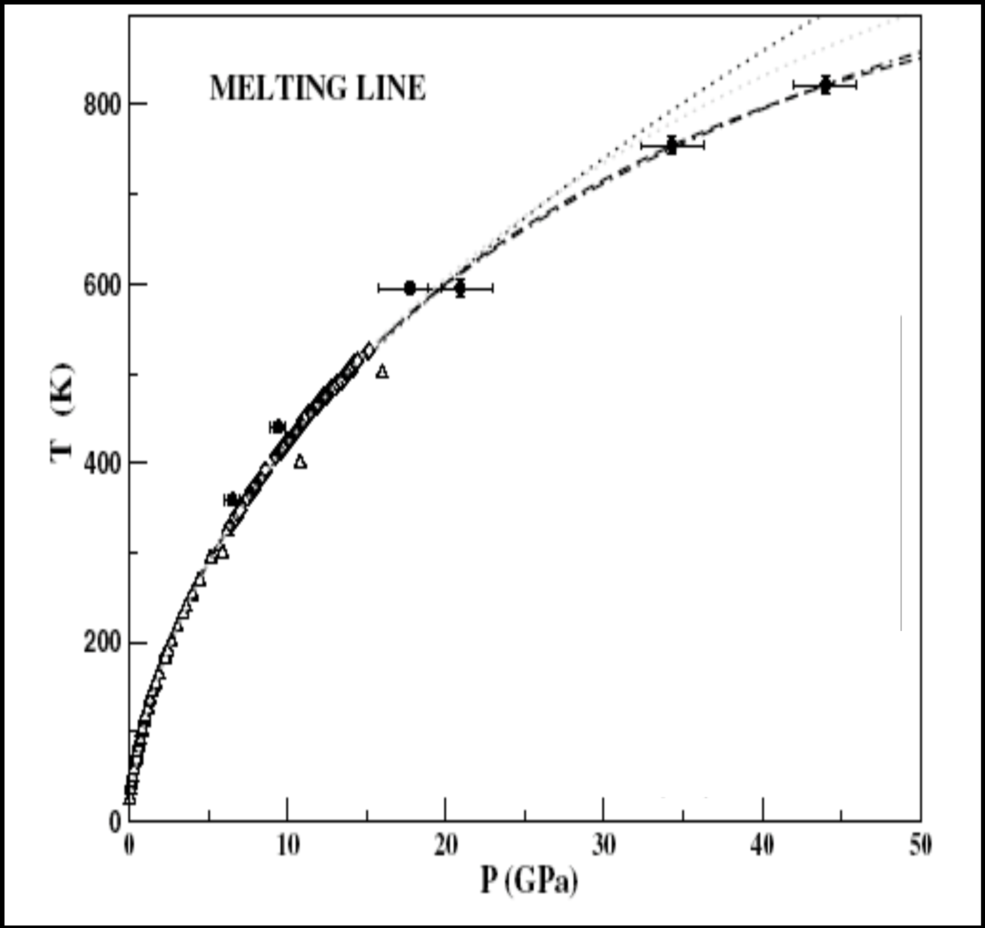

Atomic liquid
Molecular Liquid
1000
500
0
Temperature (K)
Gregoryanz et al.
Solid
Diatschenko & Chu
and Datchi et al.
0
50
100
150
200
250
Pressure (GPa)

Datchi, Loubeyre,LeToullec
PRB 61.6535 (2000)



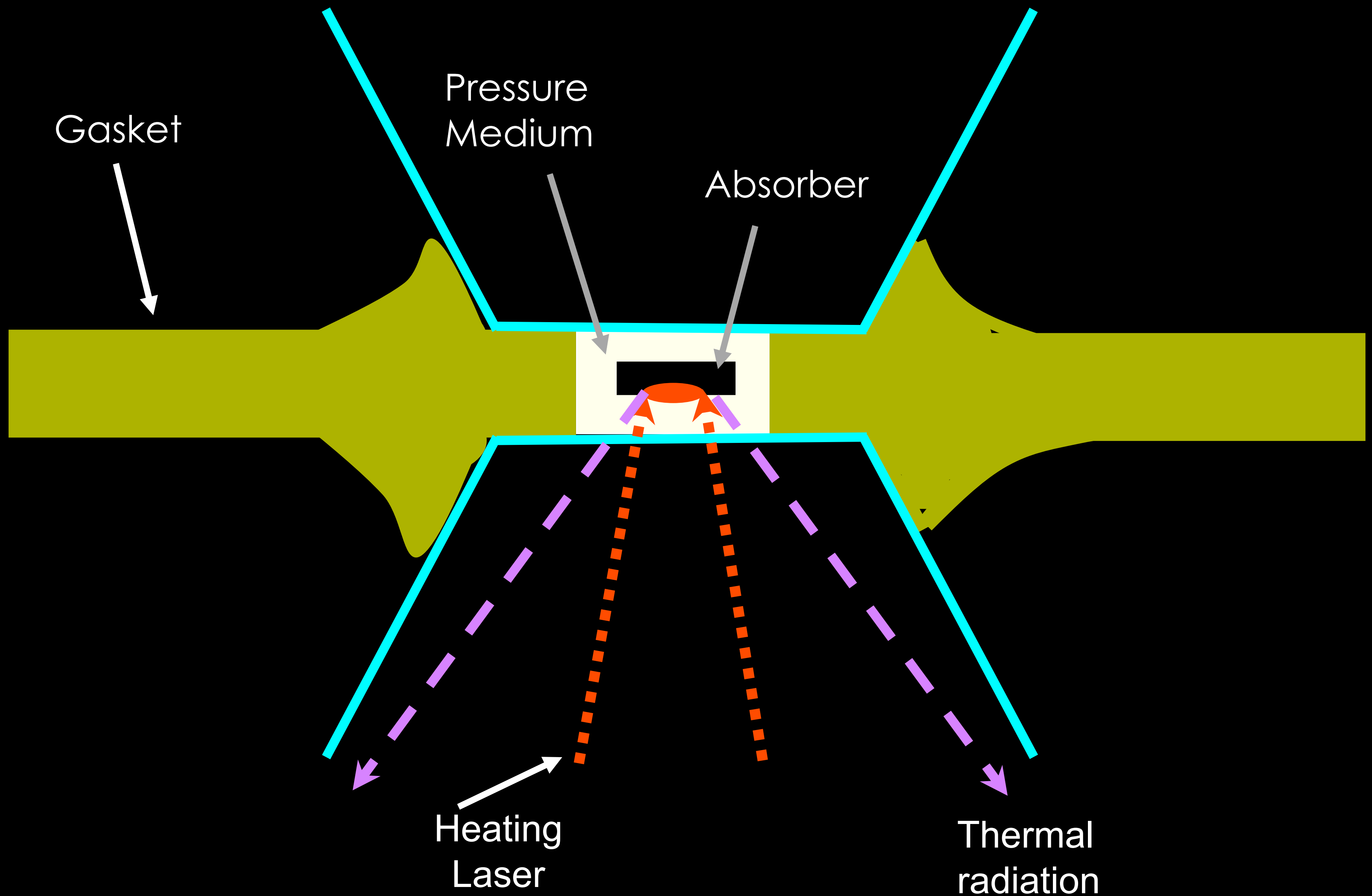
- Up to P=16 GPa
- CW resistive heating and Au lined gasket to inhibit the diffusion
- Direct observation of melting by crystallization.
- Limitation: Diffusion of hydrogen

Gregoryanz et al.
Phys. Rev. Lett. 90,
175701-4 (2003).



- Up to P= 45 GPa
- CW resistive heating with Re gasket and unidentified liner to inhibit hydrogen diffusion
- Using the shift in hydrogen vibron for detection of melting justified by overlapping with previous studies at two pressure points.
- Limitation: loss of vibran shift above 45GPa.

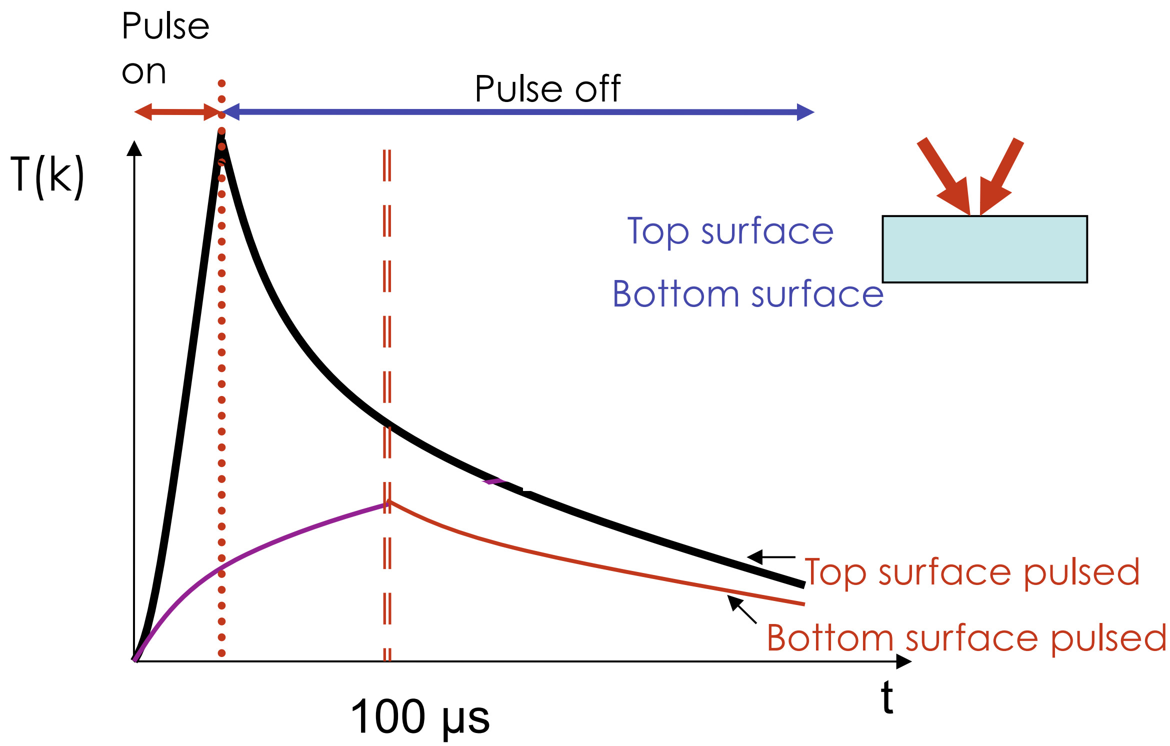
Laser Heated Diamond Anvil Cell

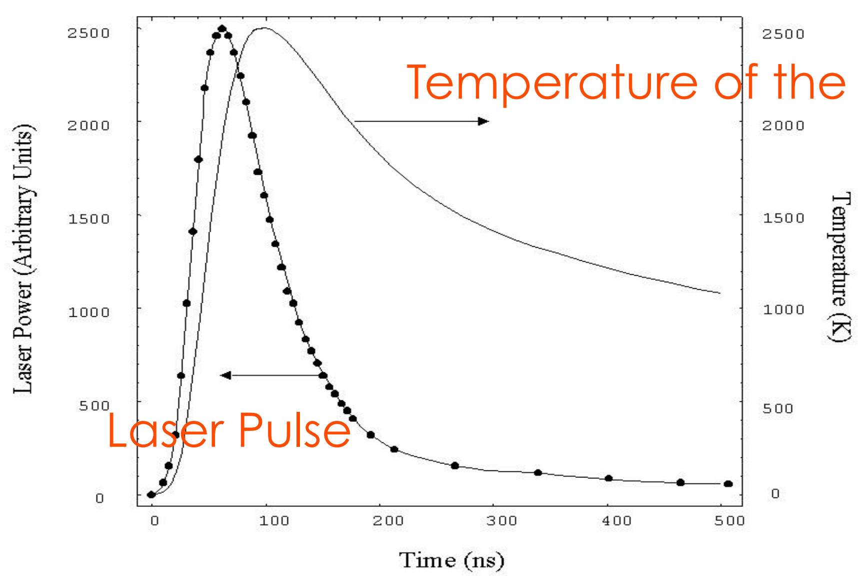


100ns Pulsed laser heating

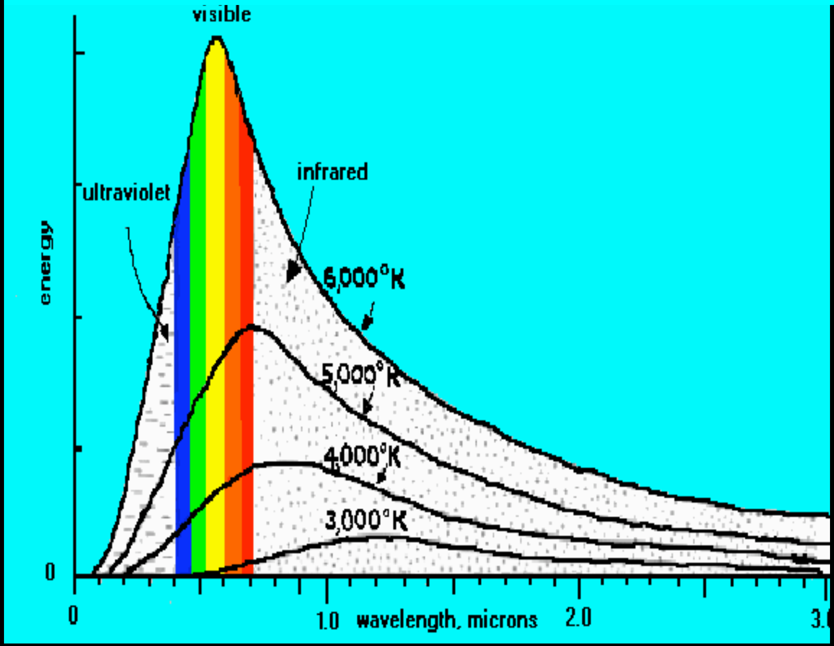
Small time scale~**<u>100ns</u>**

Long enough for thermal equilibrium and short for heat conduction


Pulse on
Pulse off
T(k)
Top surface
Bottom surface
Top surface pulsed
Bottom surface pulsed
100 µs
t

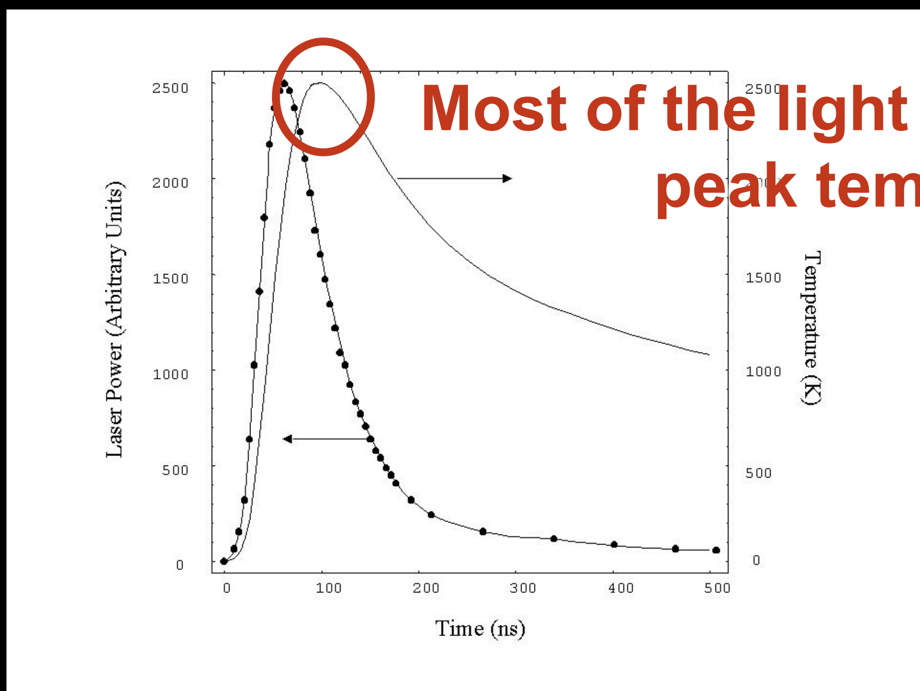

Temperature of the sample
Laser Pulse
Laser Power (Arbitrary Units)
Temperature (K)
Time (ns)
0
100
200
300
400
500
500
1000
1500
2000
2500

Evolution of thermal radiation spectra with changing temperature according to Planck's law

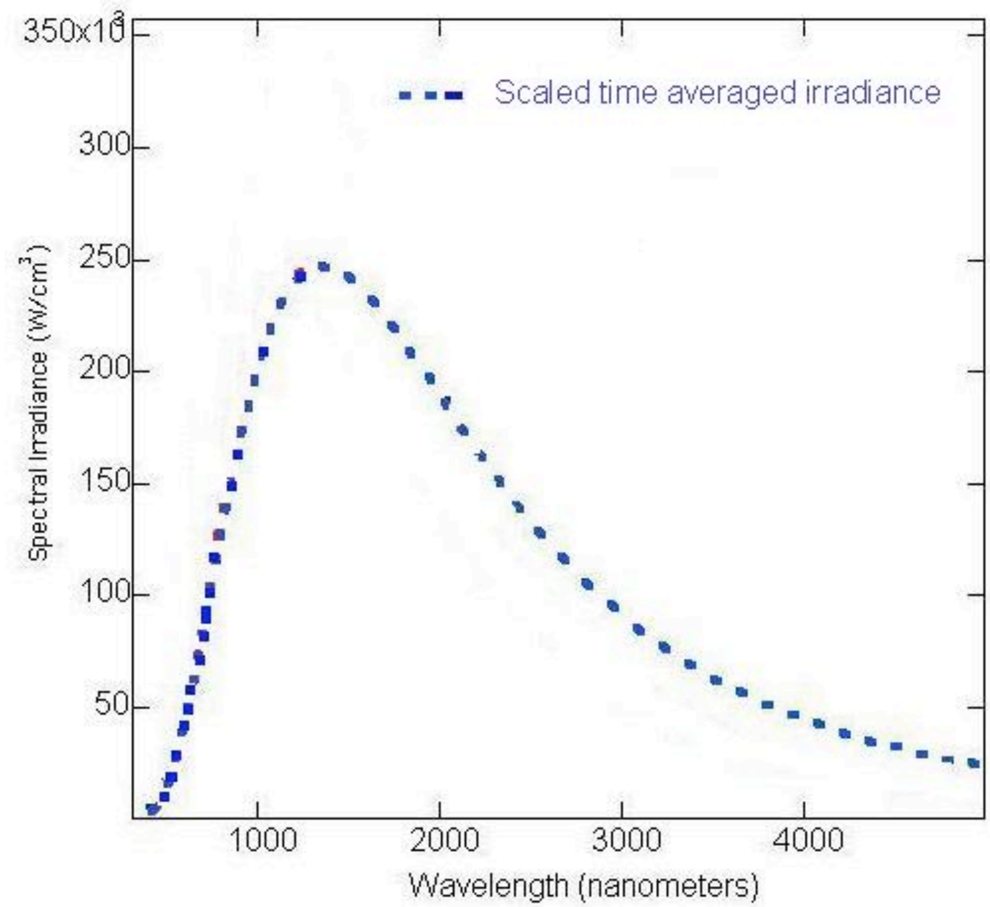


Rekhi et al. 2003
Deemyad et al. 2005

$$N_\lambda = \frac{B_\lambda}{(hc/\lambda)} \propto T^4$$

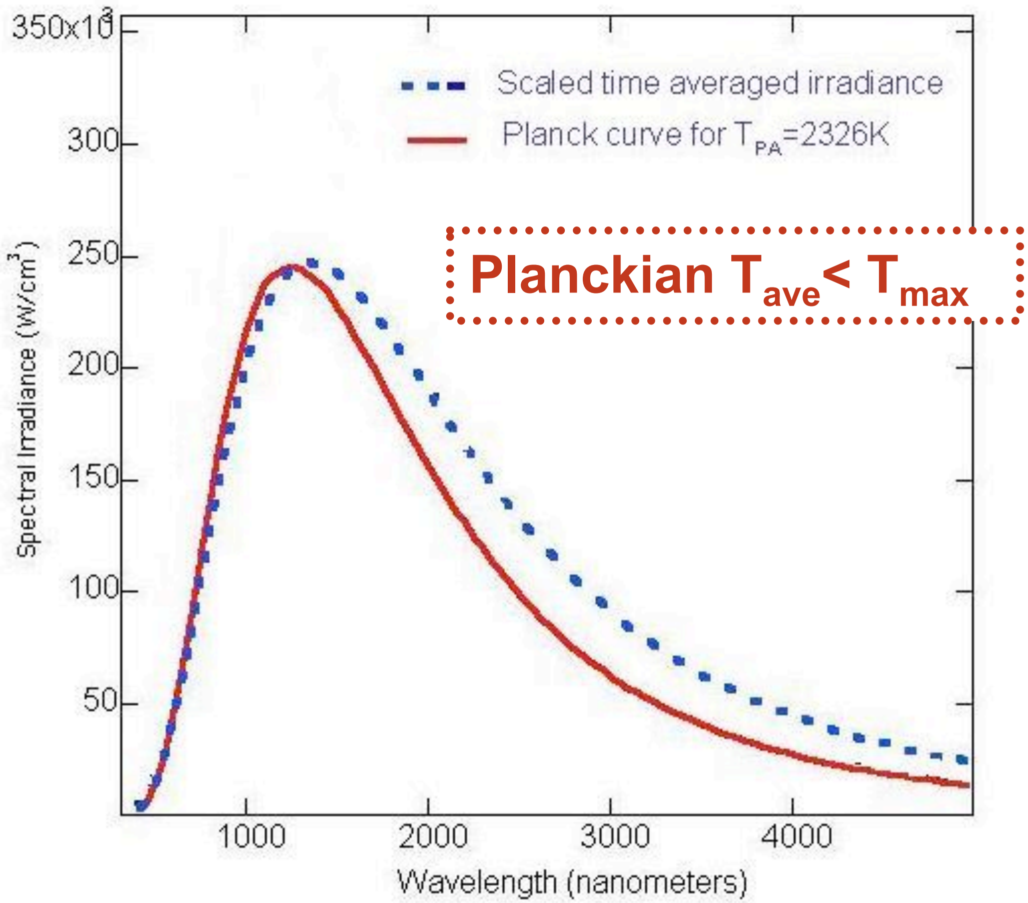


Most of the light comes from the peak temperature

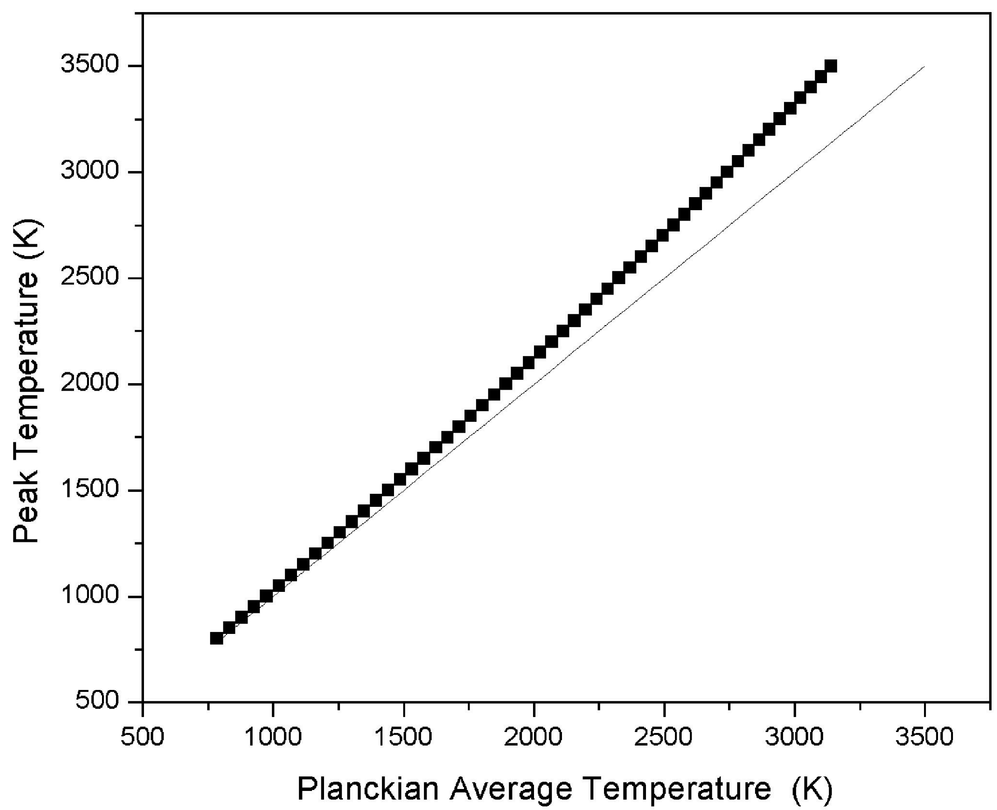


350x10³
300
250
200
150
100
50
1000
2000
3000
4000
Spectral Irradiance (W/cm³)
Wavelength (nanometers)
Scaled time averaged irradiance

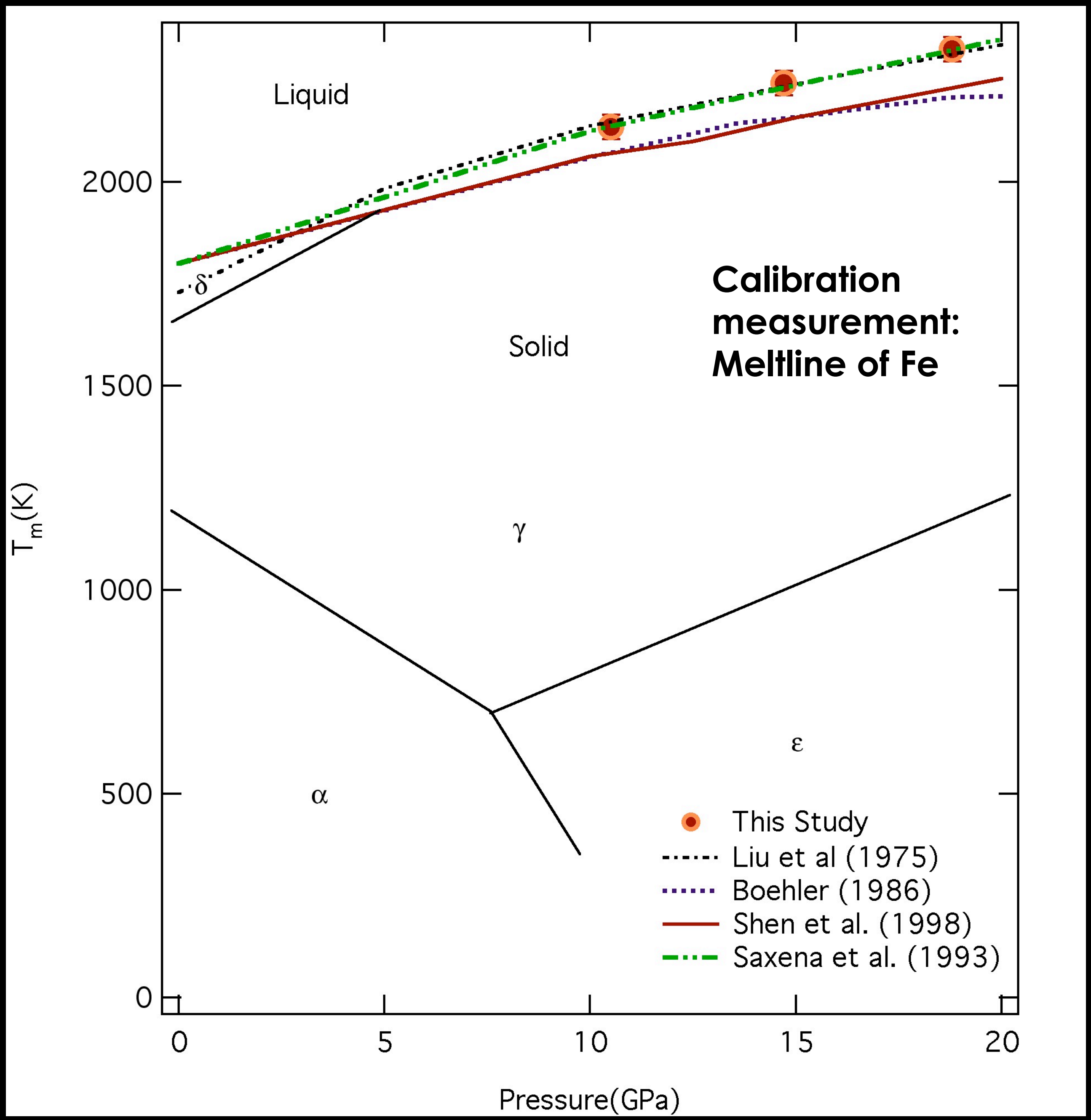
Rekhi et al.

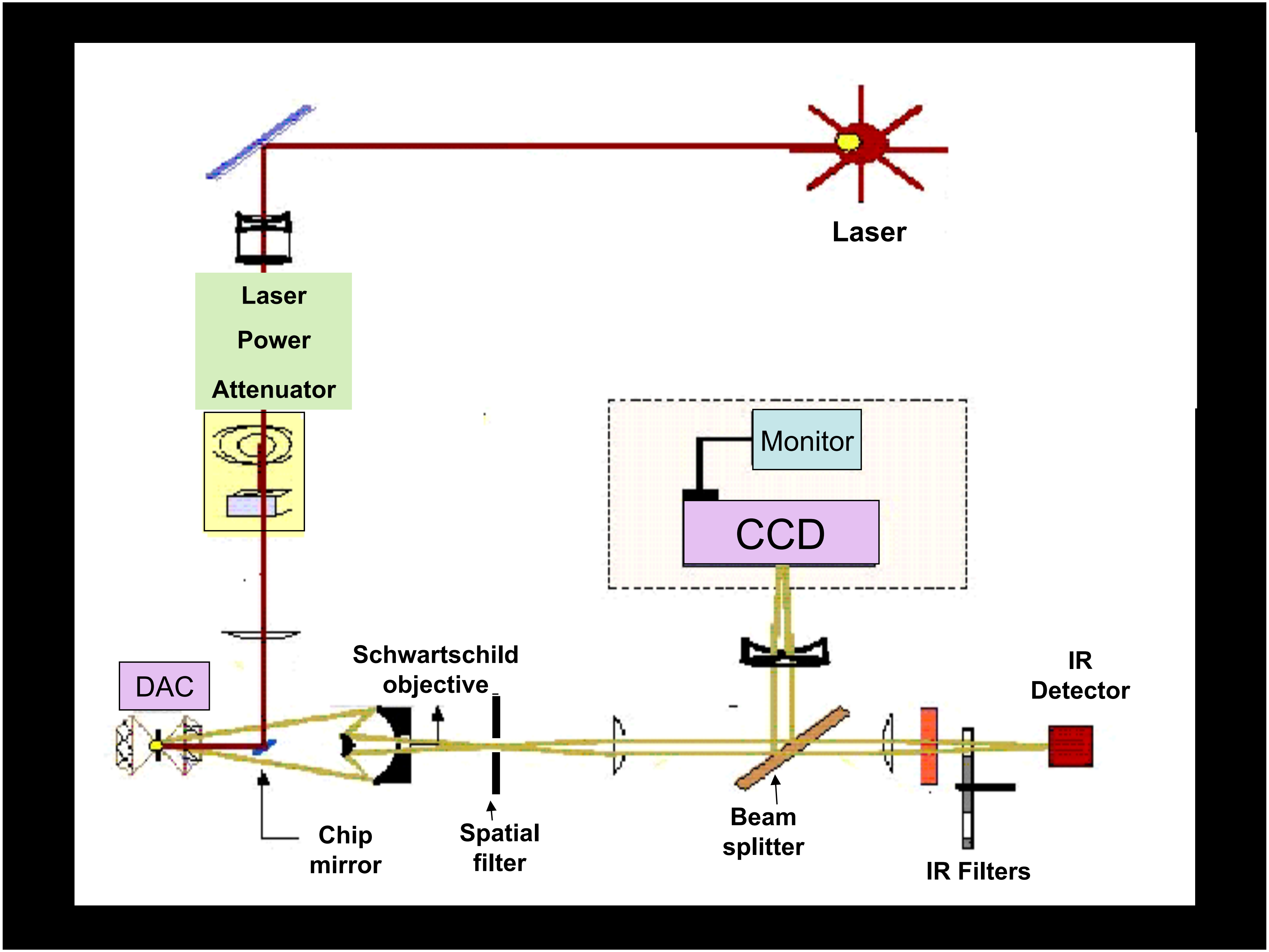

350x10³
300
250
200
150
100
50
1000
2000
3000
4000
Wavelength (nanometers)
Spectral Irradiance (W/cm³)
Scaled time averaged irradiance
Planck curve for T_PA=2326K
Planckian T_ave< T_max

Rekhi et al.

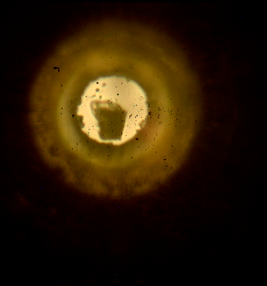


Peak Temperature (K)
3500
3000
2500
2000
1500
1000
500
500
1000
1500
2000
2500
3000
3500
Planckian Average Temperature (K)


Liquid
Solid
Calibration measurement: Meltline of Fe
δ
γ
ε
α
2000
1500
1000
500
0
0
5
10
15
20
T_m(K)
Pressure(GPa)
This Study
Liu et al (1975)
Boehler (1986)
Shen et al. (1998)
Saxena et al. (1993)



Laser
Laser
Power
Attenuator
Monitor
CCD
DAC
Schwartschild
objective
IR
Detector
Chip
mirror
Spatial
filter
Beam
splitter
IR Filters



Loading and confirmation of sample presence:

1. Cryogenically loading 99.999% purity H_2.

2. Measuring the change in index of refraction when hydrogen is present between diamonds.

3. Observation of melting of sample at ~14K.

Presence of sample in the pressure cell at high pressure.

- Clear opening all around the absorber to the highest pressure.

- Sharp ruby R1 peak up to the highest pressure.

3. Overlapping melting point with previously reported data at ~45 GPa.

Detection of melting

Melting Plateau

Laser Speckle

Visual observation of melting

Raman

.....

Detection of melting

Melting Plateau

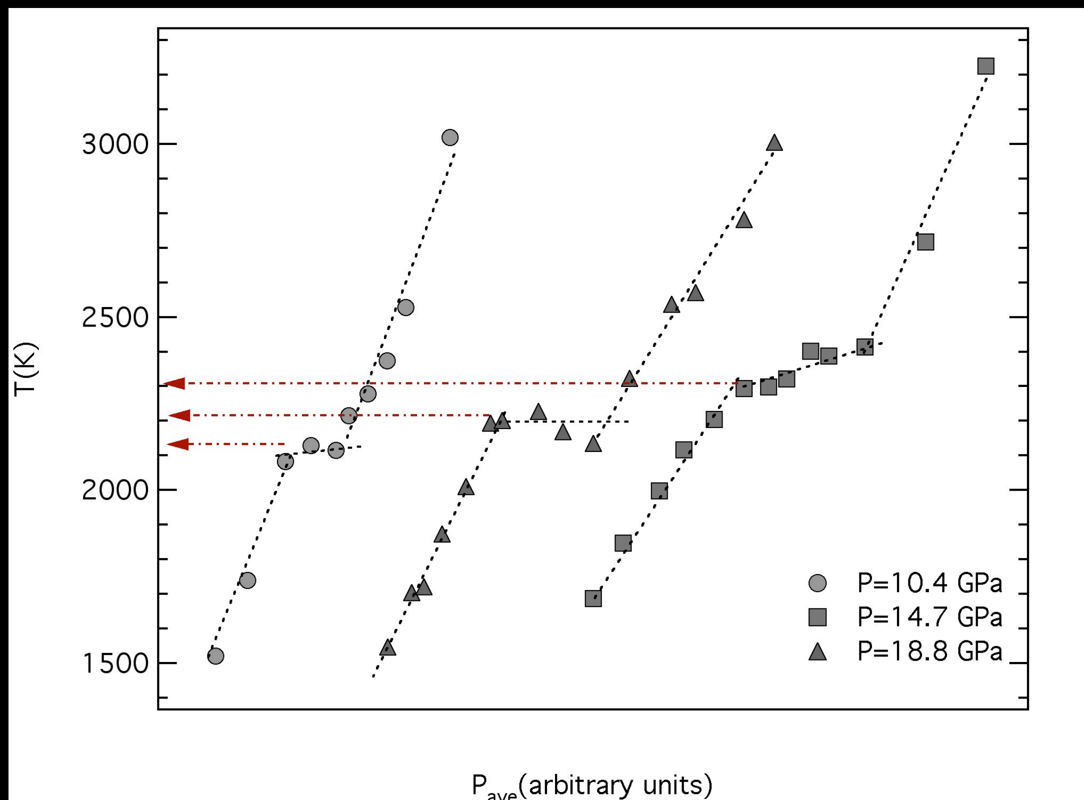
Laser Speckle

Visual observation of melting

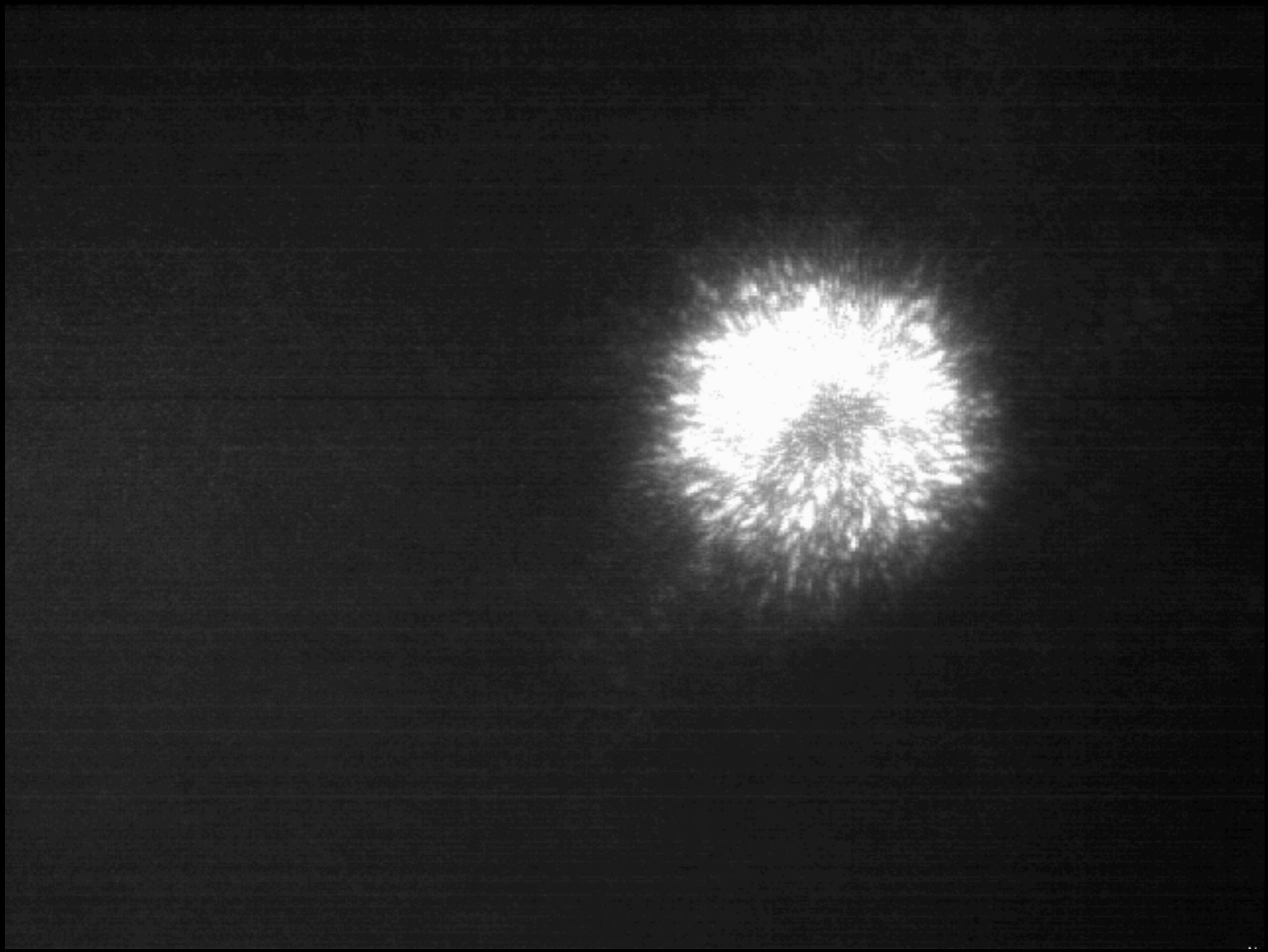
Raman

.....

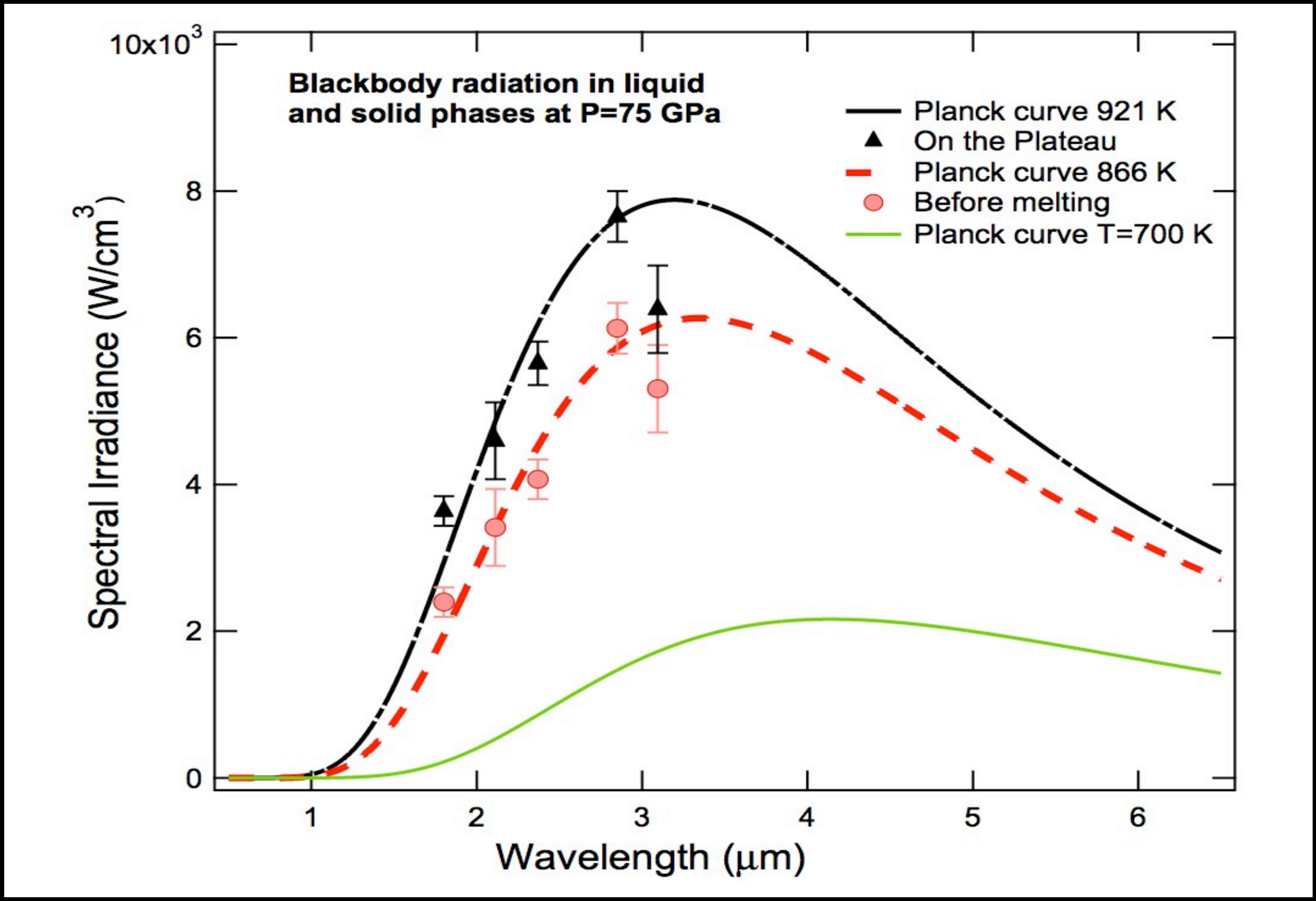
Detection of melting: Melting Plateau of Fe sample



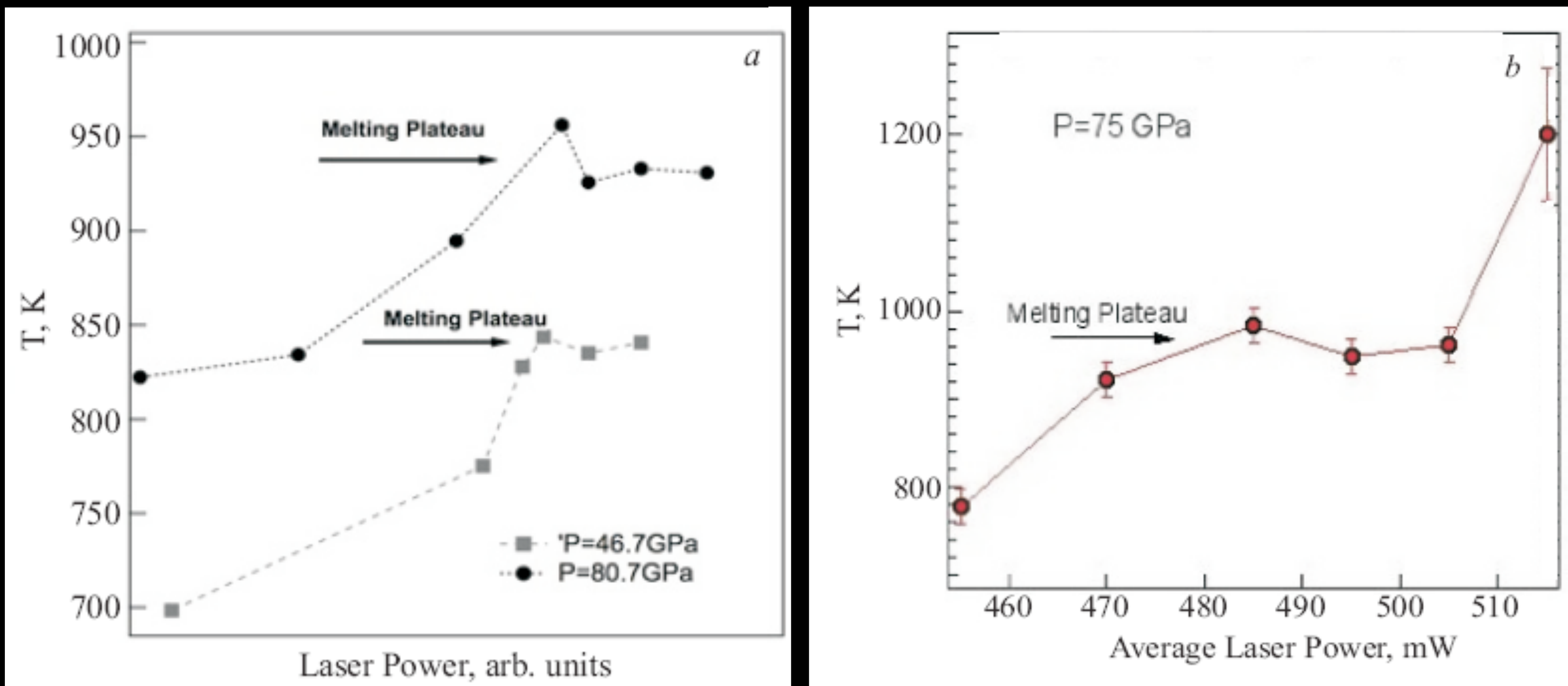
Detection of melting: Speckle motion

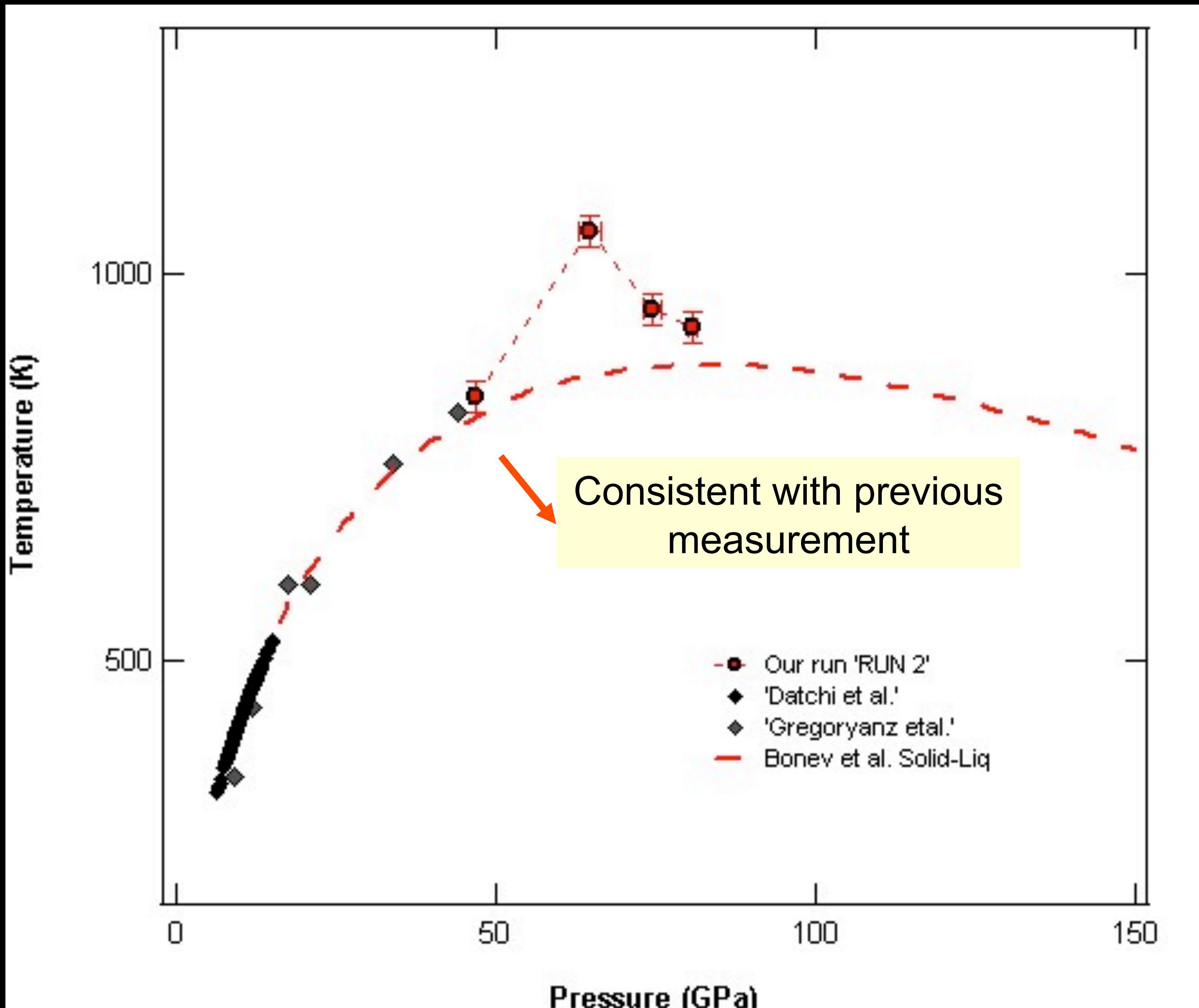


Temperature determination in hydrogen sample

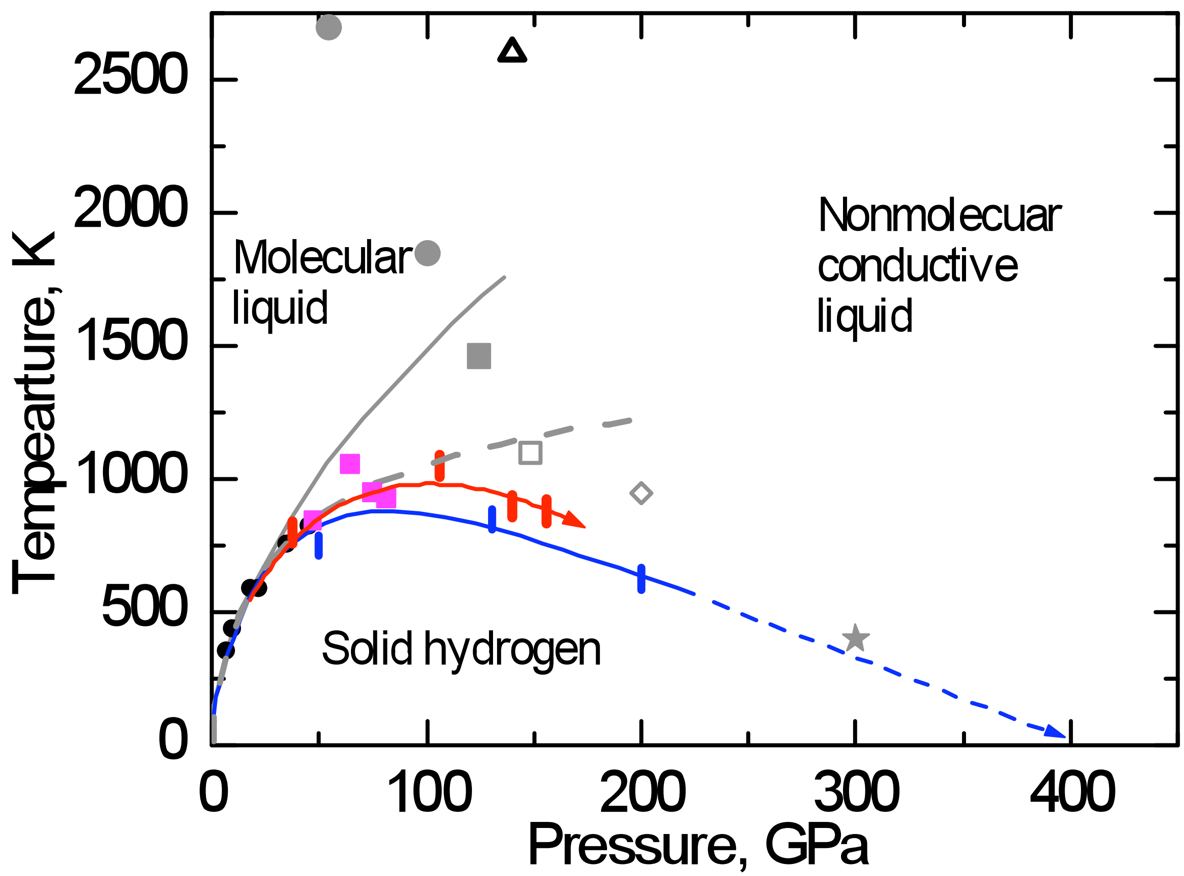


Melting plateau of hydrogen sample





Temperature (K)
1000
500
0
50
100
150
Pressure (GPa)
Consistent with previous measurement
Our run 'RUN 2'
'Datchi et al.'
'Gregoryanz etal.'
Bonev et al. Solid-Liq



Eremets et al.

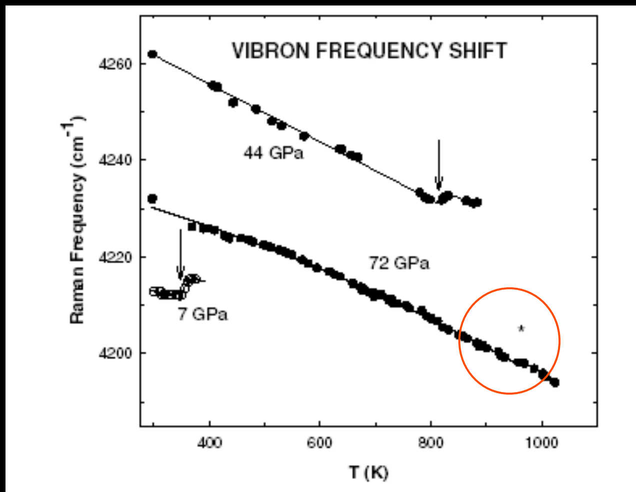
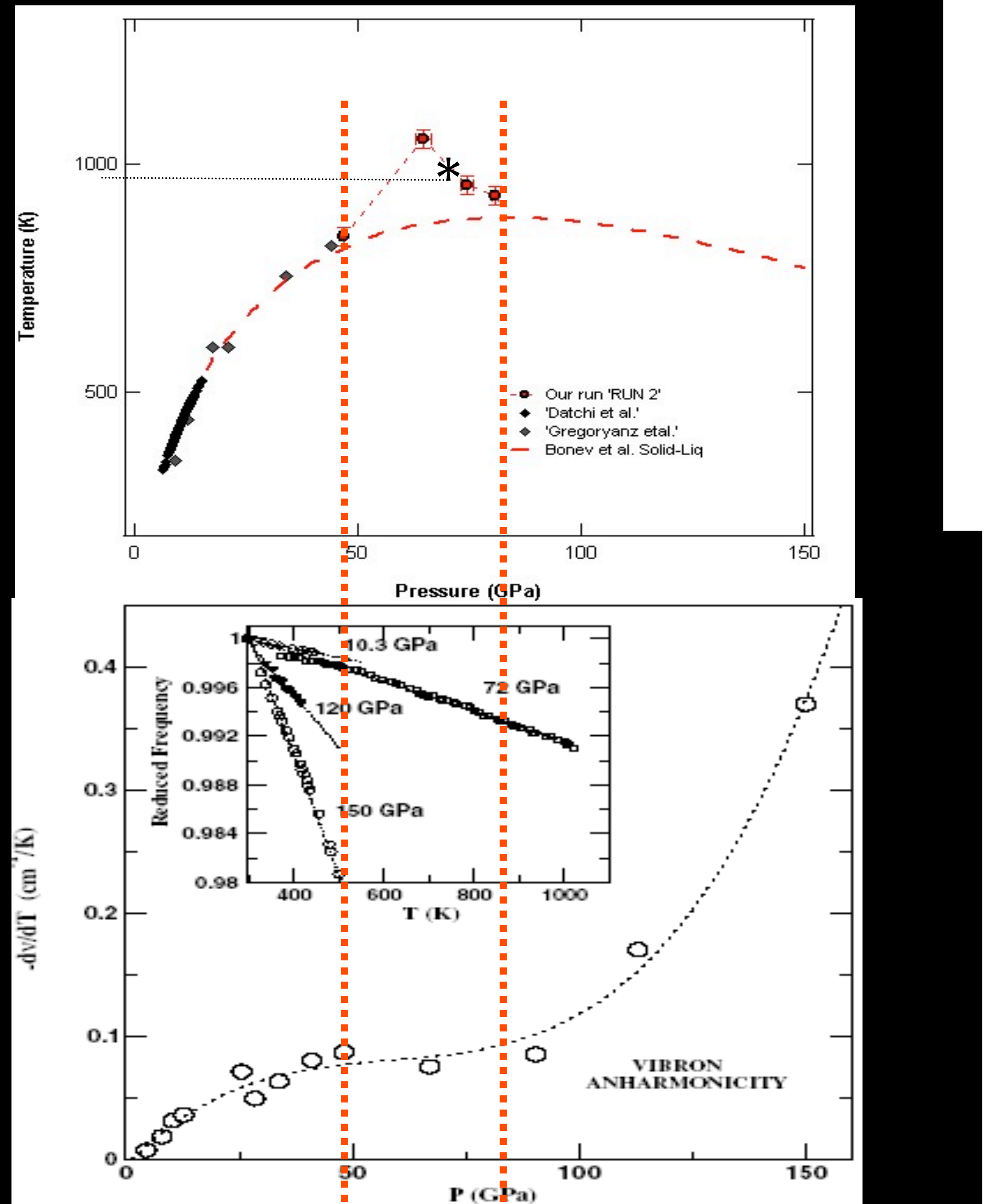
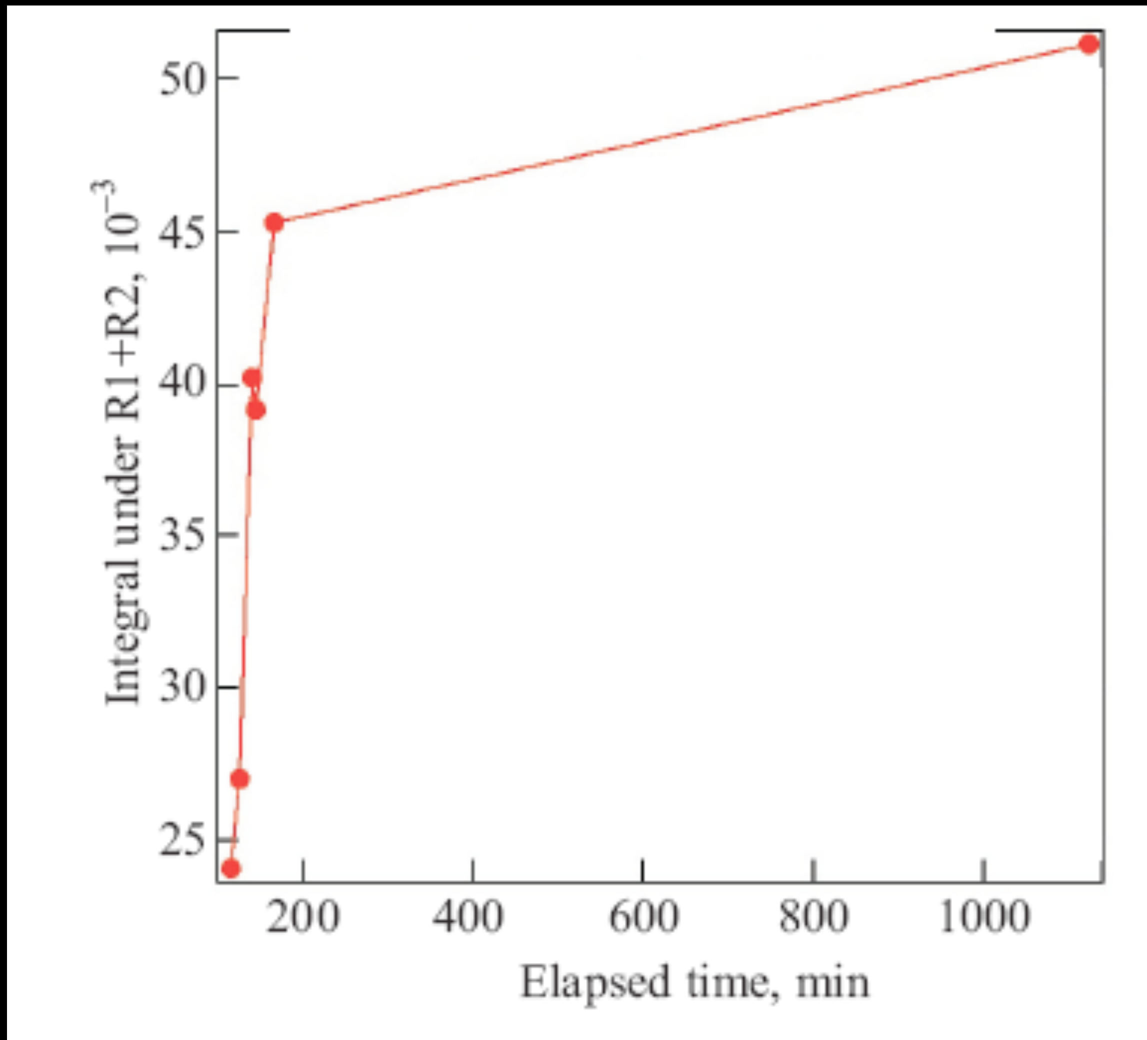


FIG. 2. Circles are measured Raman shifts as a function of temperature at 7, 44, and 72 GPa. Arrows show melting at 7 and 44 GPa and the asterisk indicates possible melting at 72 GPa. The data were taken between 73 and 69 GPa. The solid lines are guides to the eye.

Gregoryanz et al. 2003



Experiments limitation: Loss of ruby signal



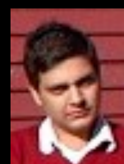
Summary

A maximum in melt line of hydrogen is predicted.

We have observed a peak in the melt line of hydrogen at P=63 GPa and T=1055 K

I. F. Silvera

S. Rekhi



J. Tempere

E. Sterer

J. S. Schilling

A. Papathanassiou

J. J. Hamlin

C. Barthel

Thank you!

[redacted]

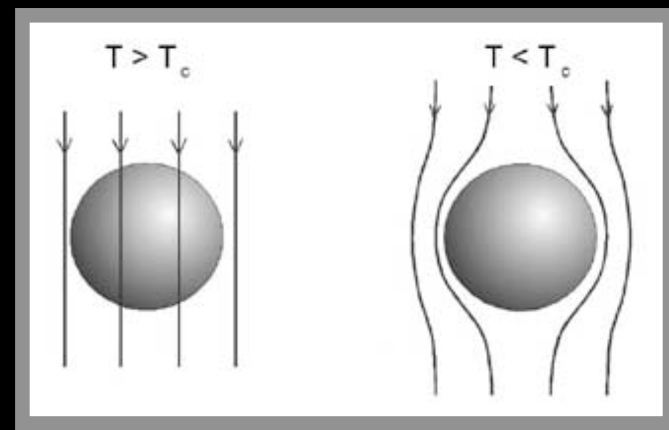
Formation of PtH at P<28GPa and room temperature (Hirao et al. 2008).

How would this effect our temperature measurement?

- PtH forms at pressures and temperatures way below all our measurement points.
- Irradiance of both Pt and PtH follows Planck law and therefore the only source of error would be the possible difference in the emissivities of the two.
- Differences in emissivities would not effect the trend of changes in the meltline and the overlap of our first data point with previous Raman studies confirms that the emissivites must be similar, as long as the previous melt line measured by Raman is accurate.

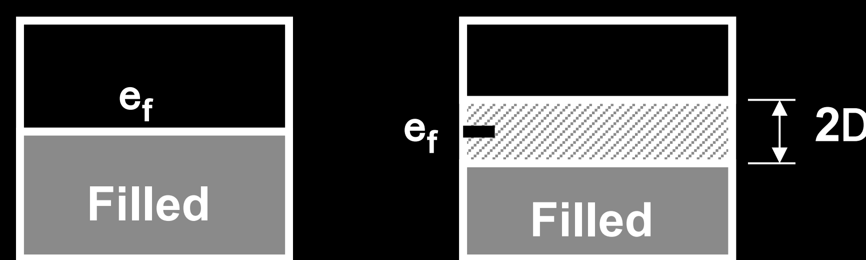
Superconductivity

- Zero DC Electrical Resistivity (r=0)

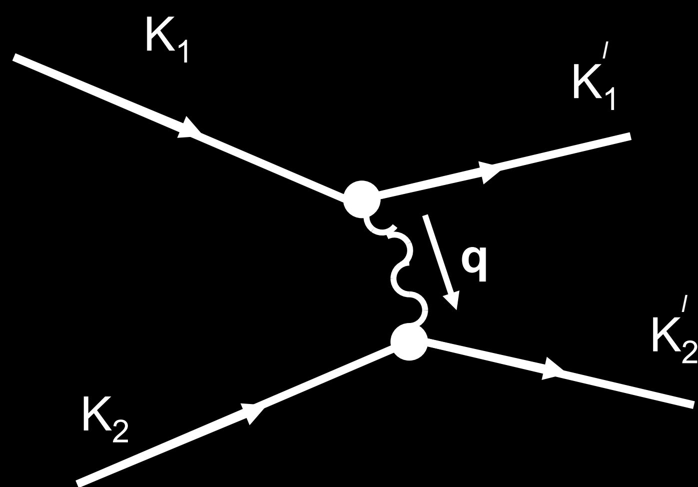


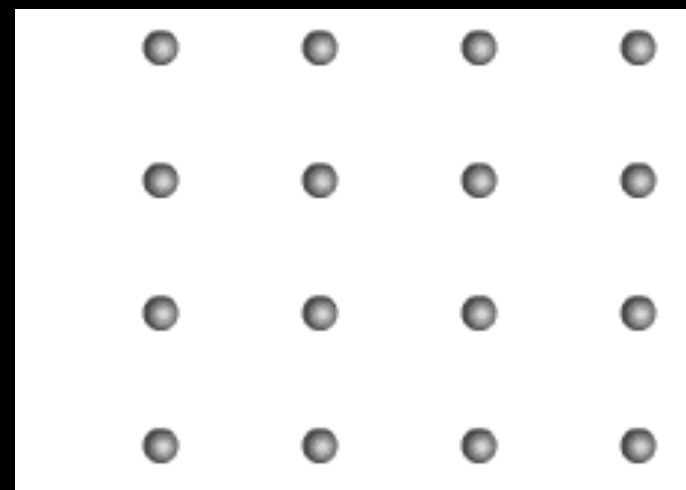
- Perfect Diamagnetism

- Energy Gap



Normal Superconductor





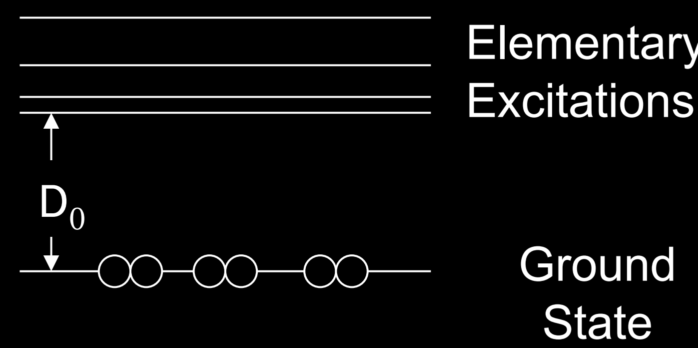
$$K_1 + K_2 = K'_1 + K'_2$$

$$|K_1| = -|K_2|$$

BCS Theory

$T \rightarrow 0\ K$

$$\Delta_0 \approx 2\hbar\omega_D \exp\left(-\frac{1}{N(E_f)U}\right)$$



$$T_c = 1.14\hbar\omega_D \exp\left(-\frac{1}{N(E_f)U}\right)$$

The Effect of Pressure on Quantum Solids

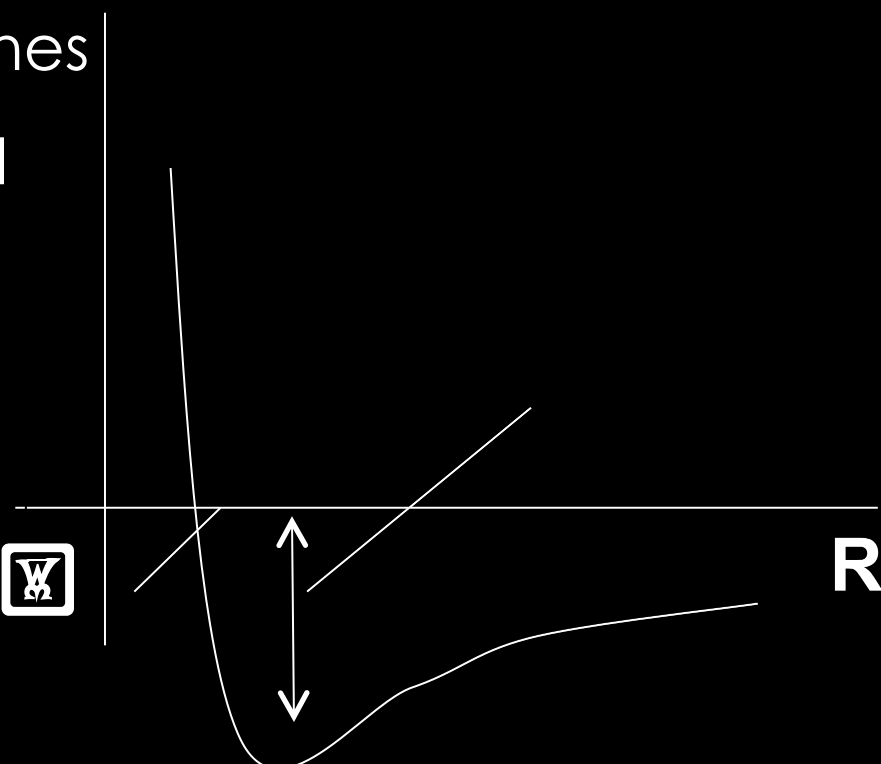
- The intermolecular pair potentials remain unchanged.
- Lattice particles become more localized translationally.
- Hydrogen and Helium become more harmonic in their translational motions.
- Compressibility is very large at low pressure and much smaller at high pressure.

Quantumness of a solid!

$$\lambda_{de-Boer} = \frac{\Lambda_{de-Broglie}}{\sigma} = \frac{h}{\sigma\sqrt{m\varepsilon}}$$

Lennard-Jones

Potential



$$H = \lambda^2 \times Kinetic.Energy + Potential.Energy$$

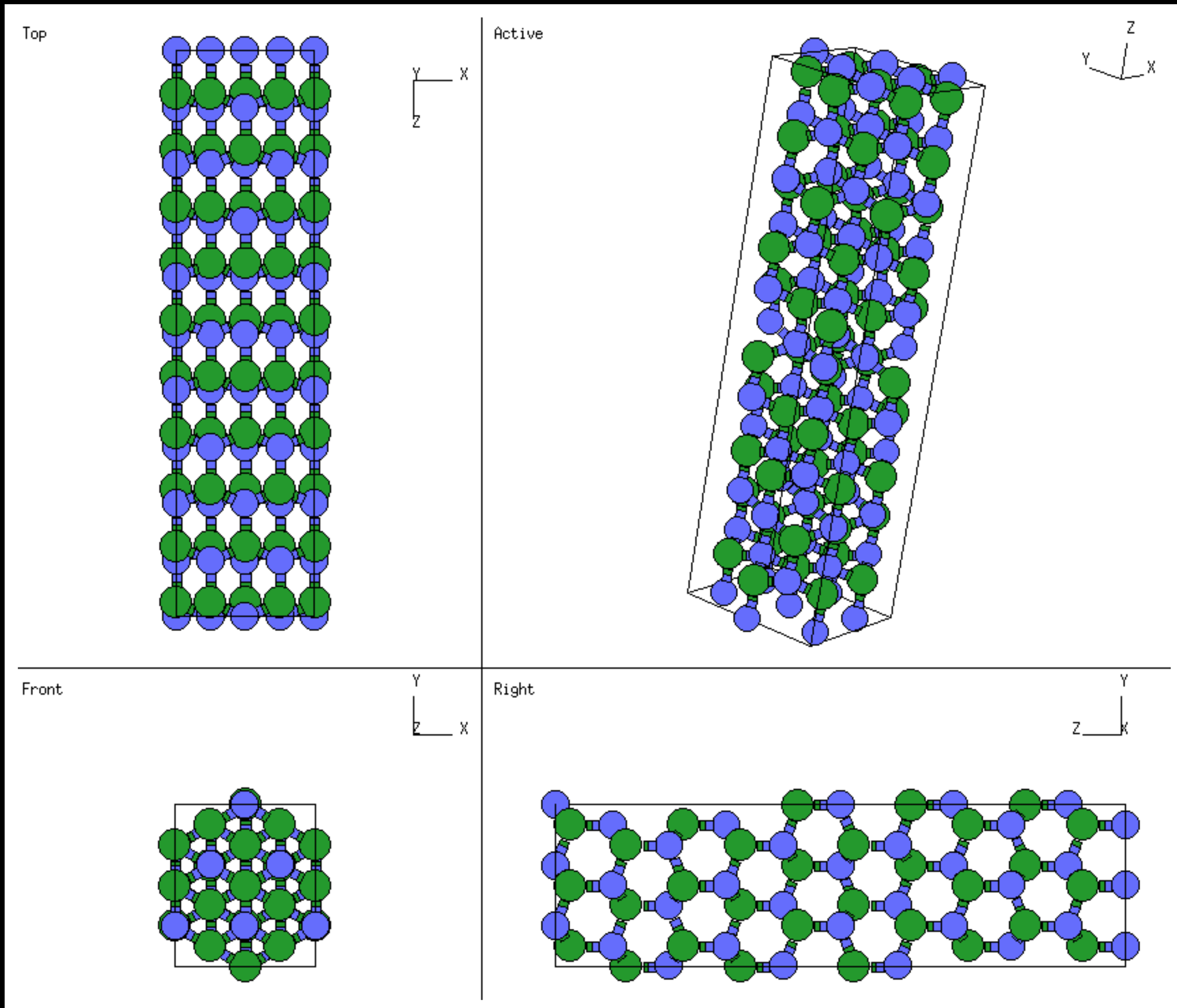
High pressure and superconductivity:

- Large magnitude of dT_c/dP is a good indication that higher values of T_c are possible at ambient pressure through chemical means.

- High pressure techniques can be used to vary the properties of a known superconductor.

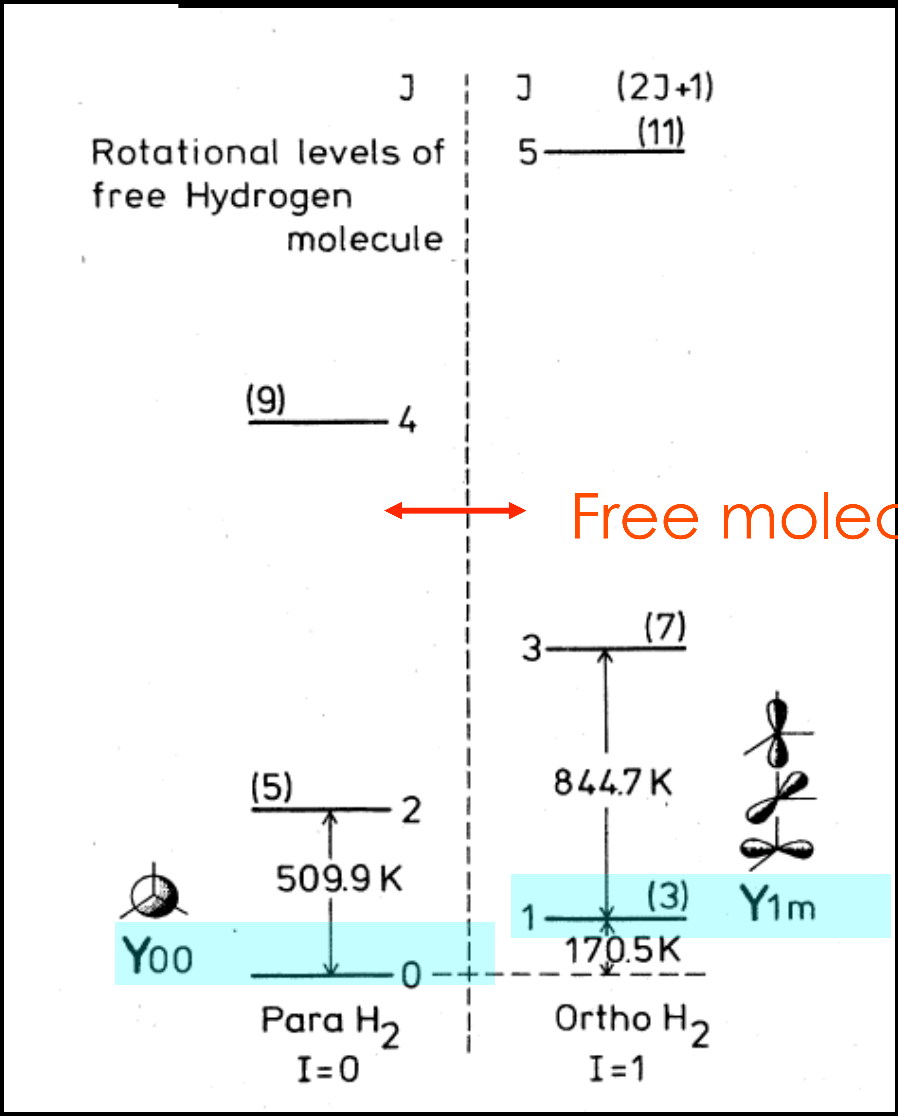
- Variations in the lattice parameters under pressure help us identify the pairing mechanism and critically test theoretical models.

9R (hR6)



Low Temperature Occupied States

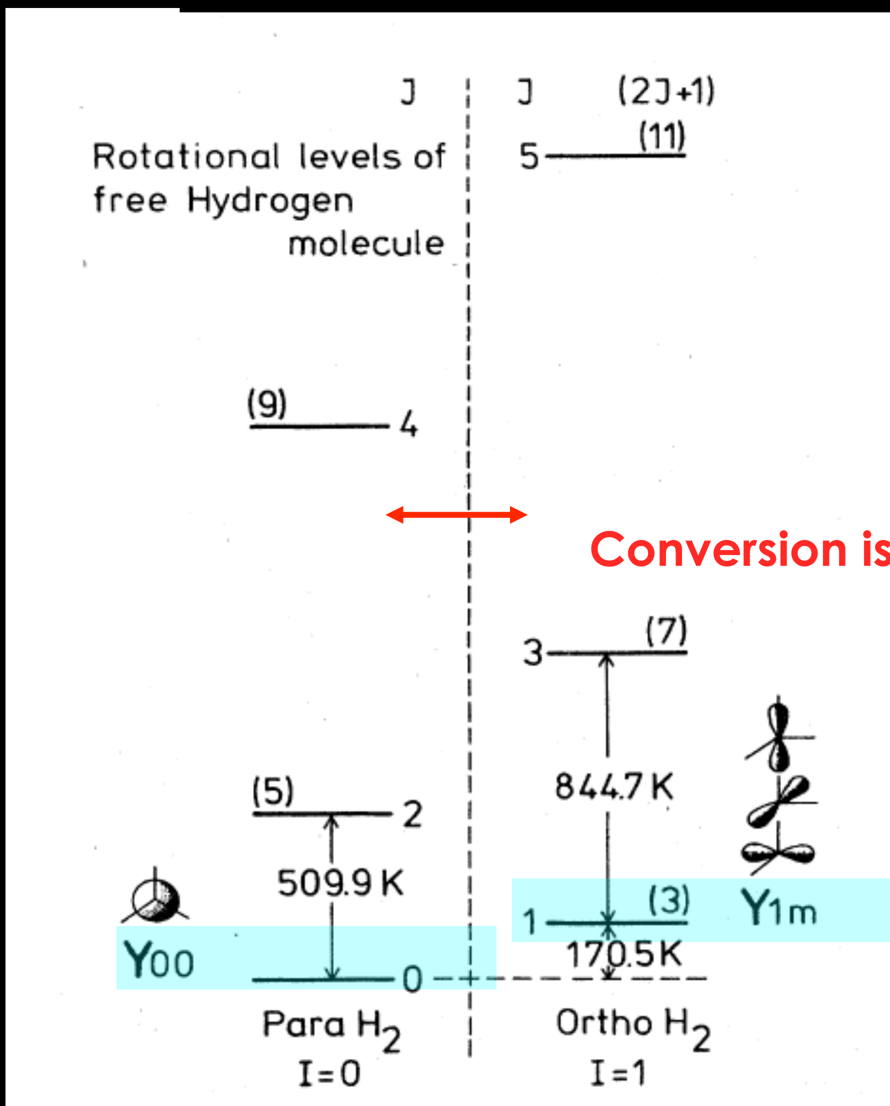
Only J=0 and J=1



Free molecule→ Forbidden transition

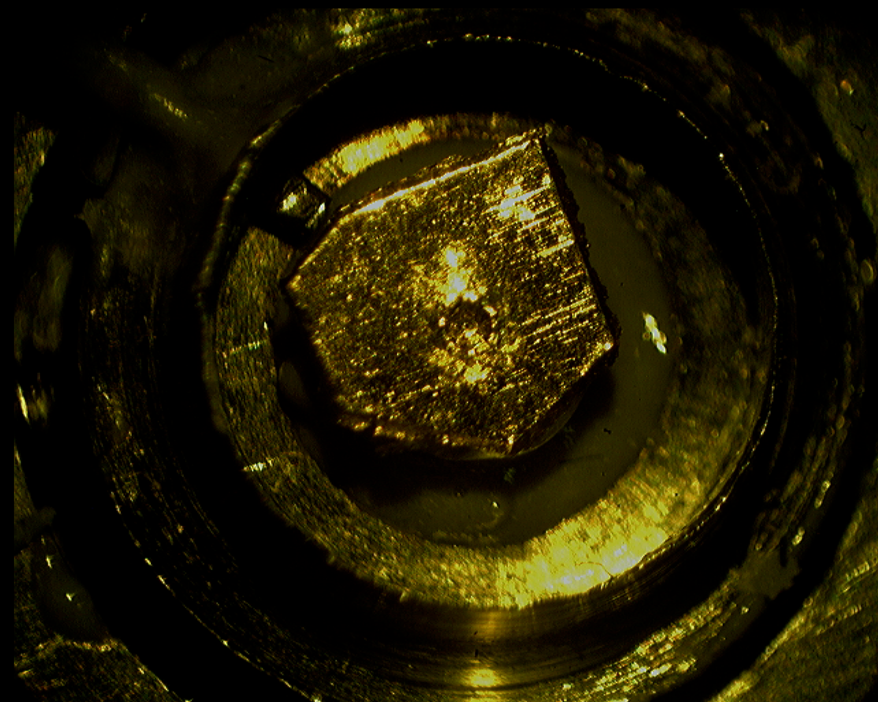
Low Temperature Occupied States

Only J=0 and J=1

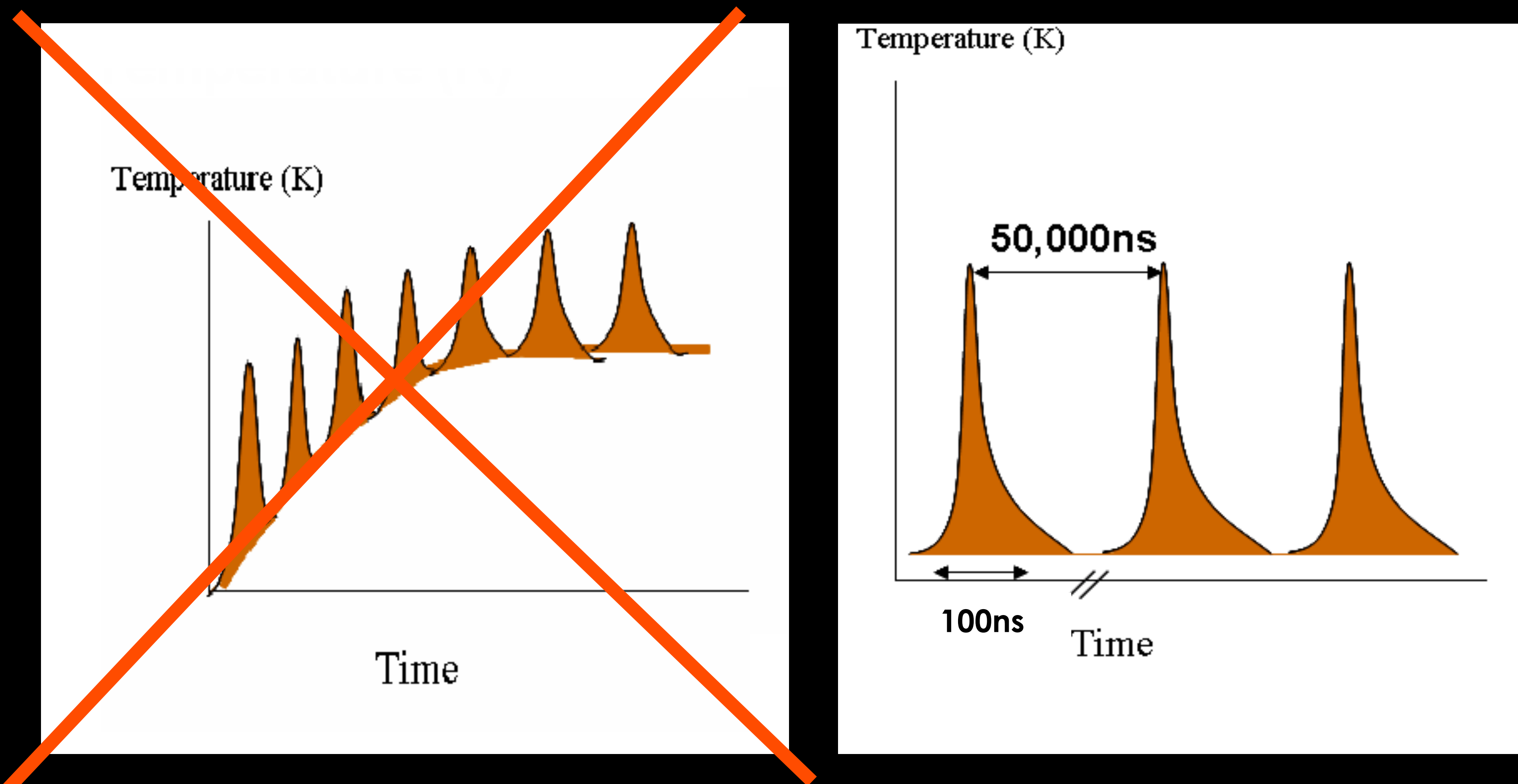


In the low pressure solid anisotropic interactions are small compared to rotational splitting so J is a good quantum number

This picture is valid to approximately 100 GPa for hydrogen

Pulsed Laser Heating

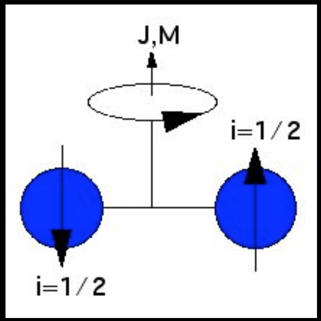


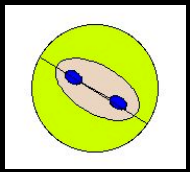
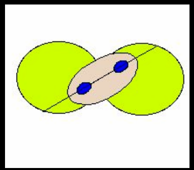
Rekhi et al. 2003
Deemyad et al. 2005

The Pauli Principle and Hydrogen Molecule: Ortho and Para Hydrogen

The hydrogen wavefunction must be antisymmetric under exchange of spin 1/2 protons=fermions

$$\Psi_{Antisymmetric} = \Psi_{rotational}\Psi_{nuclearspin}$$
$$= \Psi_{AS}\Psi_{S} \; or \; \Psi_{S}\Psi_{AS}$$



	J	I	Designation
	even	0	para
	odd	1	ortho

Generic Experimental High Pressure Phase Diagram for the Solid Hydrogens