FIB patterning
of
single-crystalline Quantum Materials

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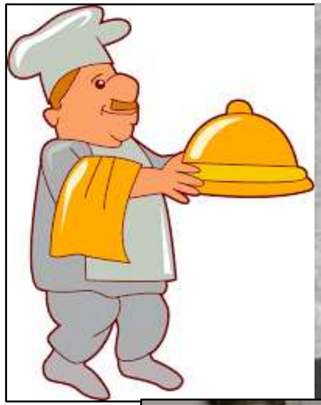

- Chemical Metal Science, Juri Grin
- Solid State Chemistry, Claudia Felser
- Physics of Correlated Matter, Liu Hao Tjeng
- Physics of Quantum Materials, Andrew Mackenzie

- Physics of unconventional metals and superconductors, Elena Hassinger
- **Physics of Microstructured Quantum Matter (MQM), Philip J. W. Moll**

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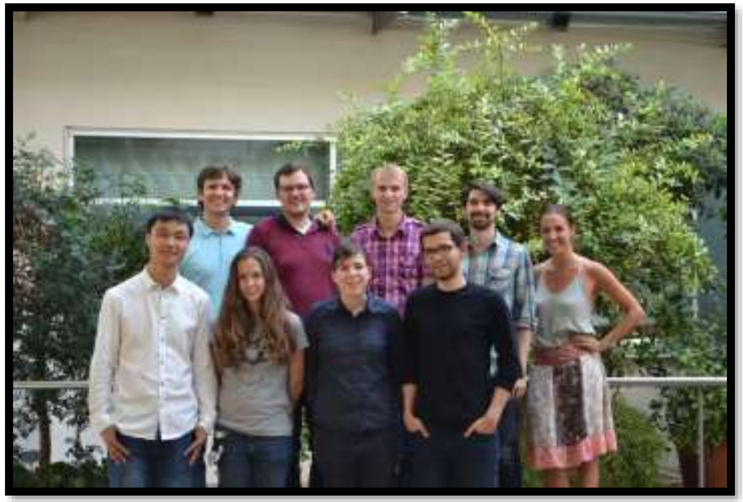


Collaborations

mqm

EPFL
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

UNIVERSITY OF CAMBRIDGE

UNIVERSITY OF JOHANNESBURG

Berkeley
UNIVERSITY OF CALIFORNIA

BERKELEY LAB

NATIONAL MAGLAB

EMFL
European Magnetic Field Laboratory

Los Alamos
NATIONAL LABORATORY
EST. 1943

HLD.

HELMHOLTZ
ZENTRUM DRESDEN
ROSSENDORF

WMI

TUM
TECHNISCHE UNIVERSITÄT MÜNCHEN

IFW

GOETHE UNIVERSITÄT
FRANKFURT AM MAIN

Outline

- Introduction to FIB patterning of Quantum Materials
- Focused Ion Beam (FIB) – Dual beam system
- Microscale experiments
- Example of current research in heavy Fermion superconductors

What are Quantum Materials?

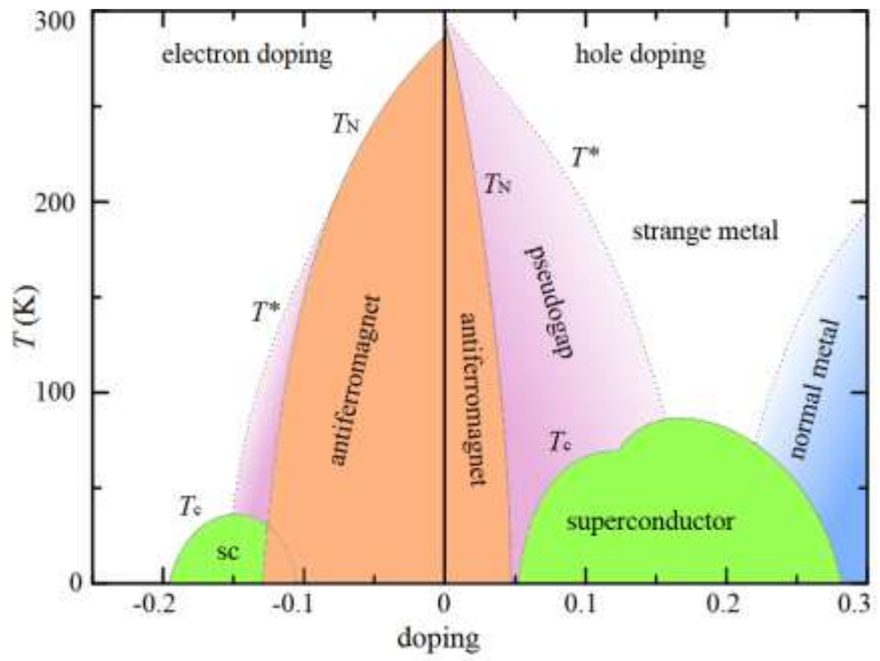
- states of matter [quantum many-body systems] with **emergent macroscopic properties that are intrinsically quantum mechanical.**
  e.g. Superconductivity: macroscopic quantum mechanical wave function
- concepts of topological order
  e.g. fractional quantum Hall effect and topological insulators, Dirac- and Weyl-Semimetals.
- bad metals, "quantum critical metals", and the "strange metal" in the Cuprates
- New states of Matter, such as Nematicity or Supersolids
- Quantum magnetism, frustrated systems, Spin liquids, metamagnetism

*"The notion of **quantum matter** is useful as a **unifying concept** for describing many of the common themes of interest in two culturally distinct research communities: those studying ultracold atomic gases and correlated electron materials."* [Prof. Ross L. Mckenzie]

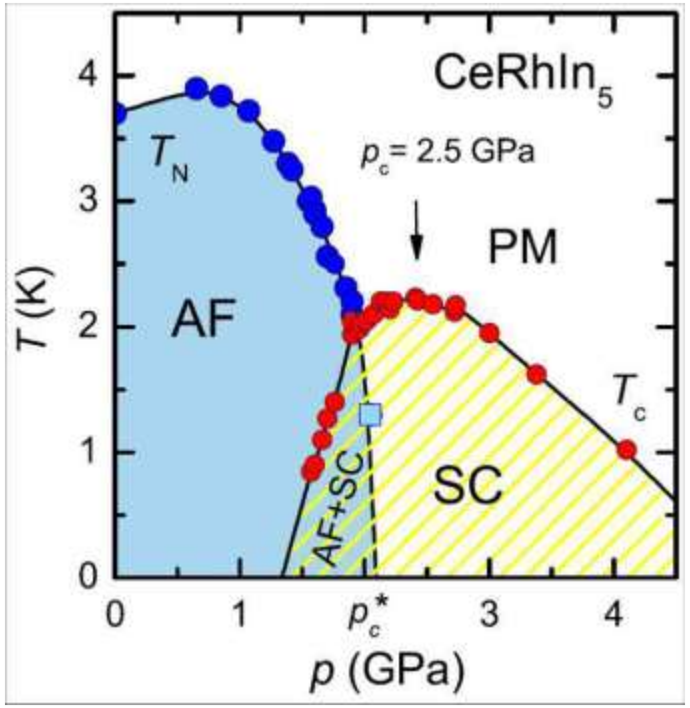
What are Quantum Materials?

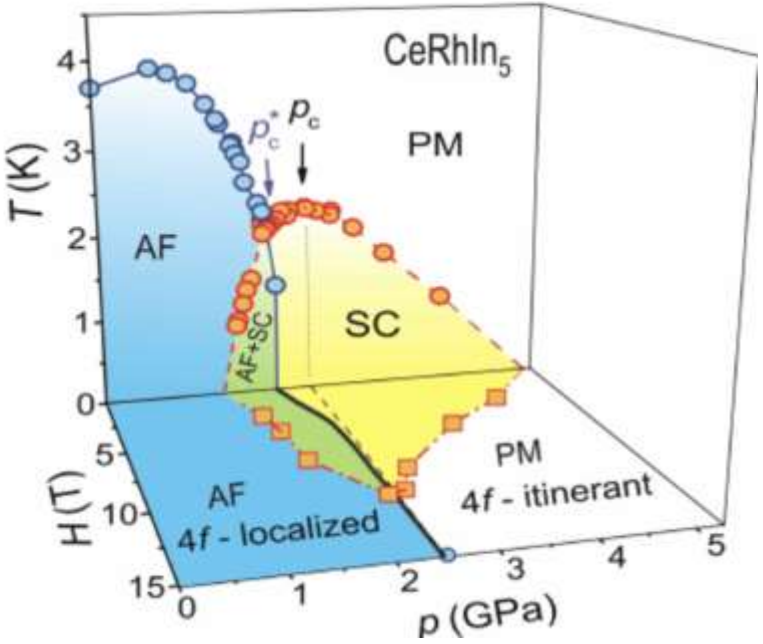
Unconventional Metals and Superconductors

Cuprate High-Temperature Superconductors



Heavy Fermion Superconductors

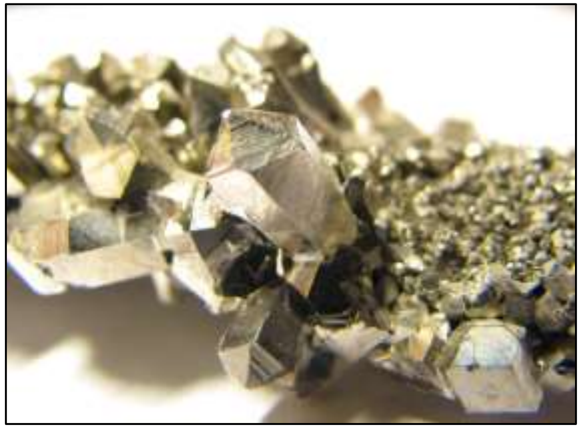




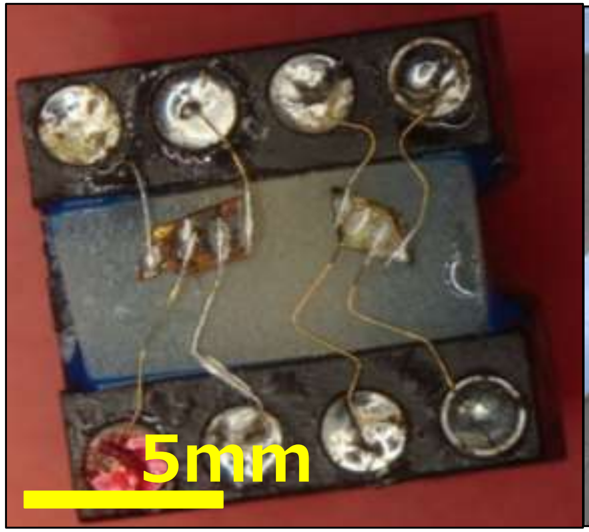
Tuning parameters: Chemical substitution Hydrostatic pressure Magnetic field

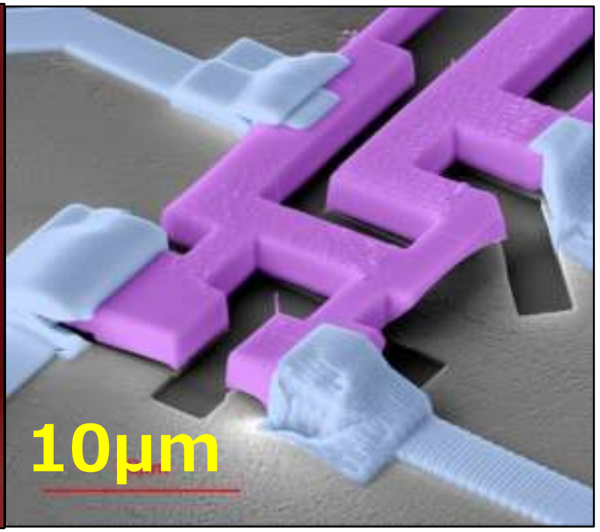
Main research philosophy of our group:

„Explore novel electronic materials on the microscale“



Start from bulk material or powder / polycrystals



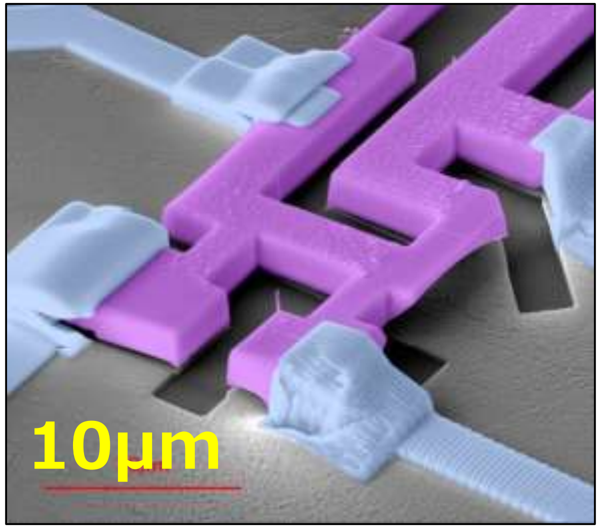


… and turn it into a microstructured devices

Main research philosophy of our group:

„Explore novel electronic materials on the microscale“

- Discover new physics of quantum matter
  „function follows form“
- Mesoscale effects / finite size
- Prototype devices of quantum matter electronics



··· and turn it into a microstructure

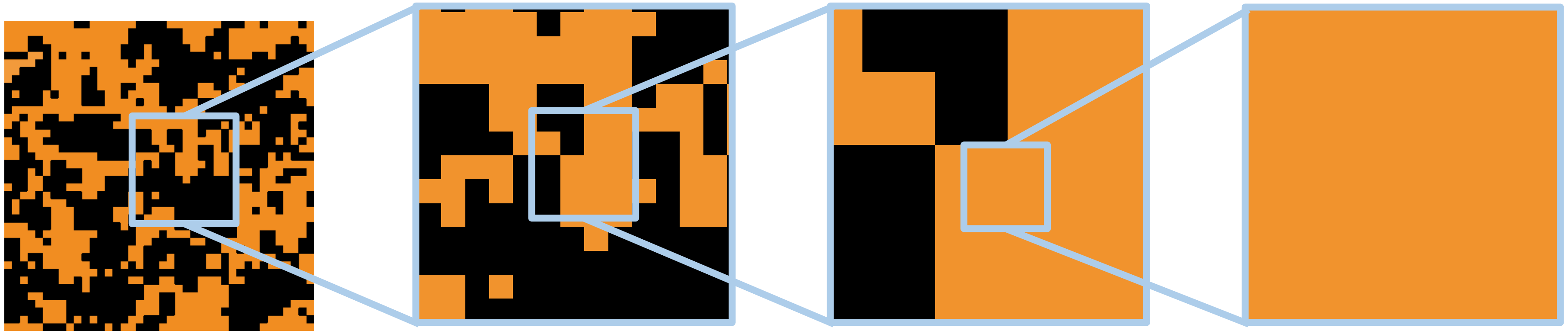
Why single crystals? → Quality/Purity

Why microstructures? – quantum effects at small scales

Qualitative change in quantum behavior when system size crosses relevant length scale L

L: Correlation length
- Magnetic
- Structural (CDW in high T_c)

Decreasing sample size / cutting smaller structures



Macroscopic (>L)
- Averaged resistivity
- resistivity isotropic

Mesoscopic (~L)
- Domain boundary scattering
- Domain dynamics

Microscopic (<L)
- Intrinsic scattering
- resistivity anisotropy

Why microstructures? – quantum effects at small scales

Qualitative change in quantum behavior when system size crosses relevant length scale L

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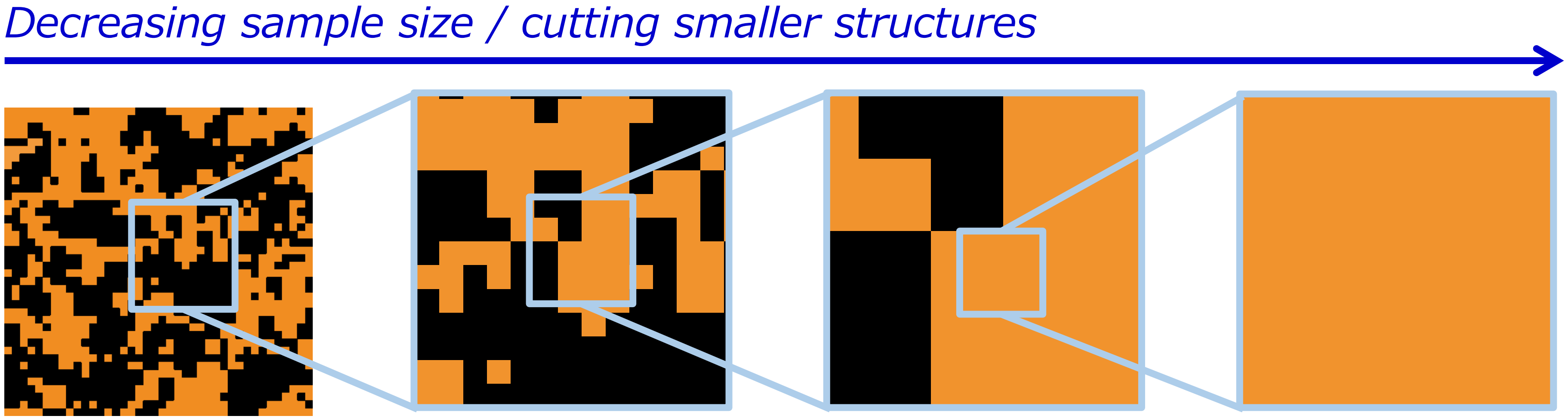
- Structural (CDW in high T_c)

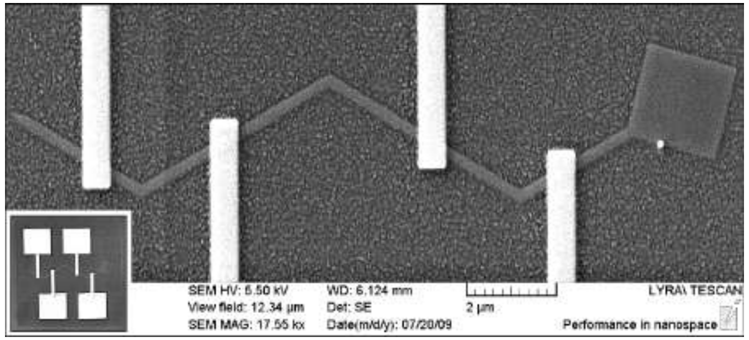


Mesoscopic (~L)

→ No rigid definition:
→ range between **a few nanometers** and **a few micrometers**

Focused Ion Beam (FIB) Microfabrication

Domain motion in
thin film spintronic nanostructures



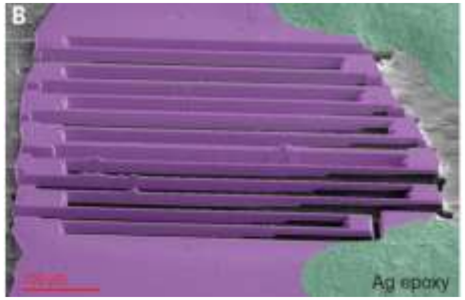
[Urbanek M. et al., Nanotechnology 21, 145304 (2010)]

Vortex physics in
SmFeAs(O,F)

~10 µm thin
platelets

[Moll P.J.W. et al. Nat. Mat. 12, 134-138 (2013)]

Hydrodynamic electron flow
in the Delafossite $PdCoO_2$

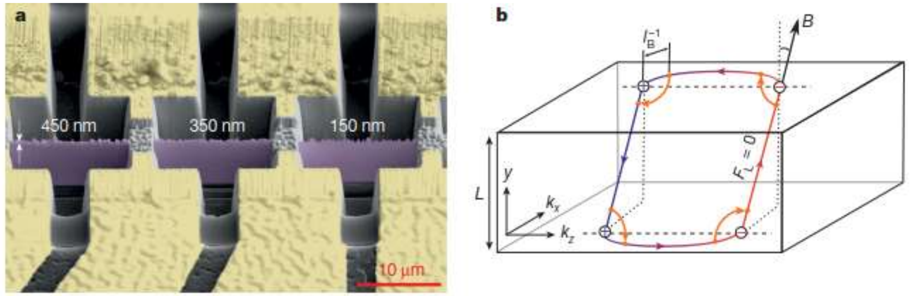


$\rho_0 \approx 10\, n\Omega cm$

→ 1/2 x ρ(Cu)

[Moll, P.J.W. et al. Science 351, 1061-1064 (2016)]

Topological surface states
in the Dirac semimetal Cd_3As_4



[Moll, P.J.W. et al. Nature 535, 266-270 (2016)]

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Focused Ion Beam (FIB) Microfabrication

Focused Ion Beam etching (FIB)

- Industrial application:

  investigation of defects in computer chips and materials

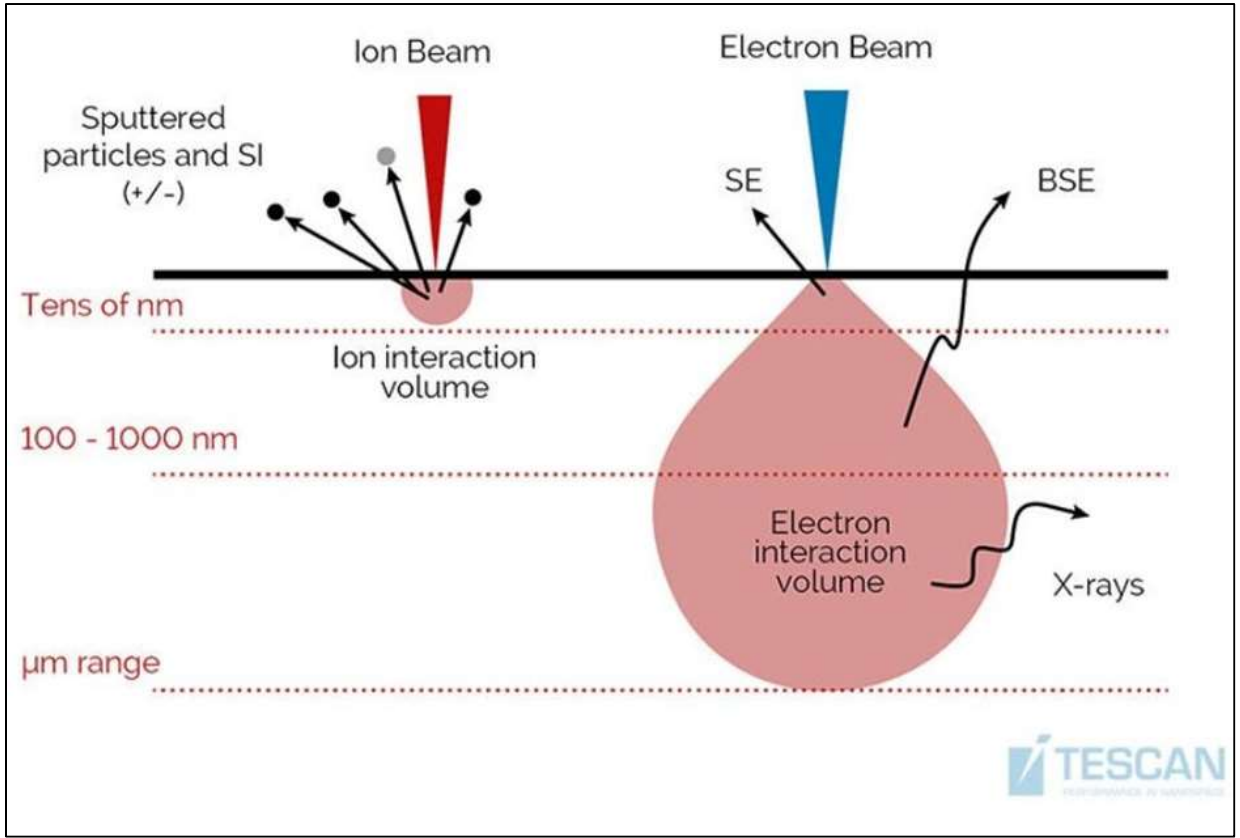
- Material science:

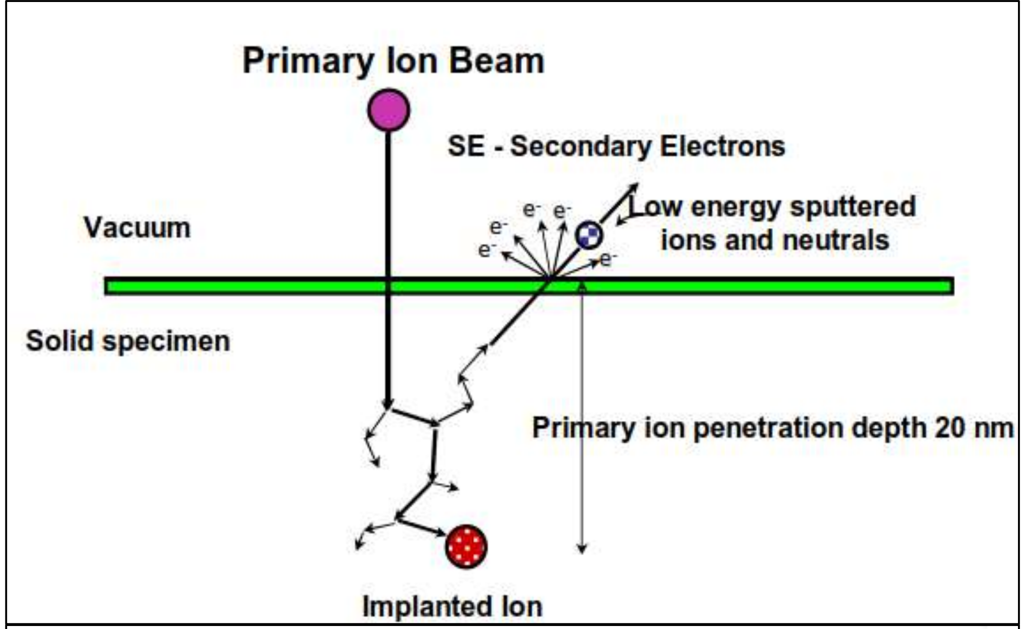
  Transmission Electron Microscopy (TEM) Lamella preparation

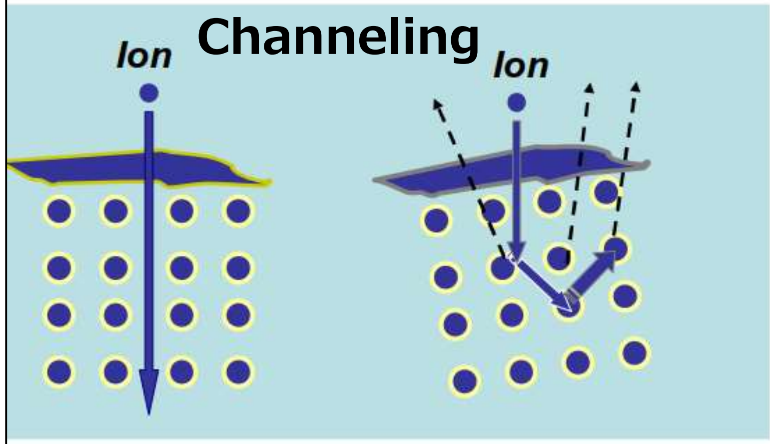
- Biology:

  Slicing organic specimens like cells and tissue

Focused Ion Beam (FIB)

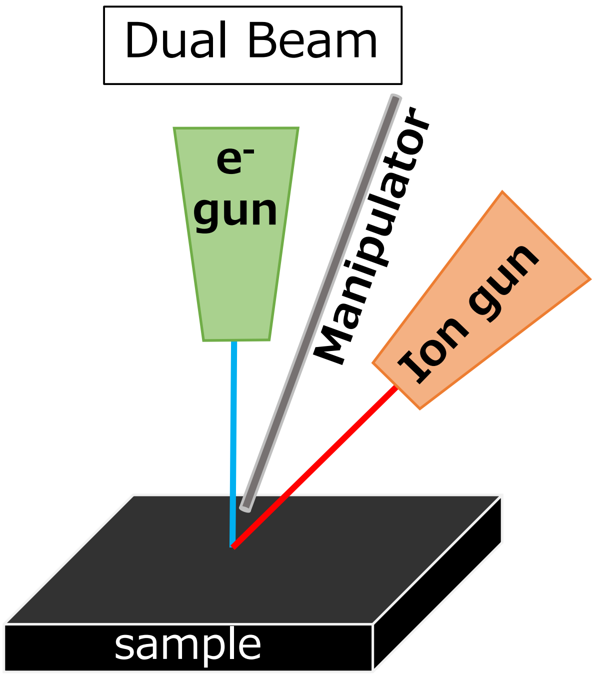


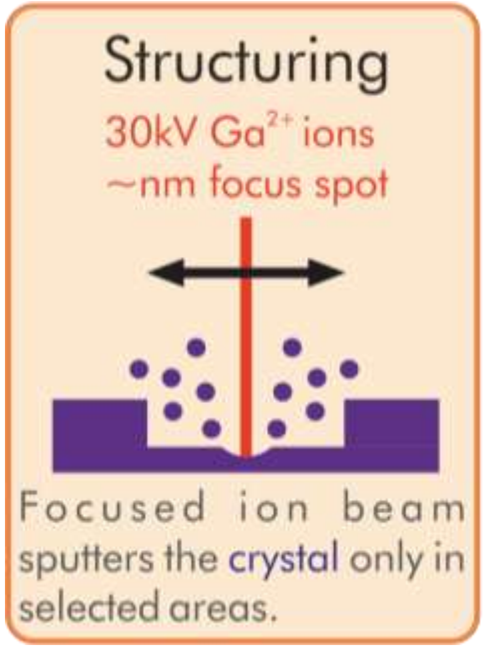




Secondary electrons escape & are detected

Focused Ion Beam (FIB)





- As-grown crystallites
- Feature size down to ~100nm
- 3D Structuring

Difference of FIB to SEM:

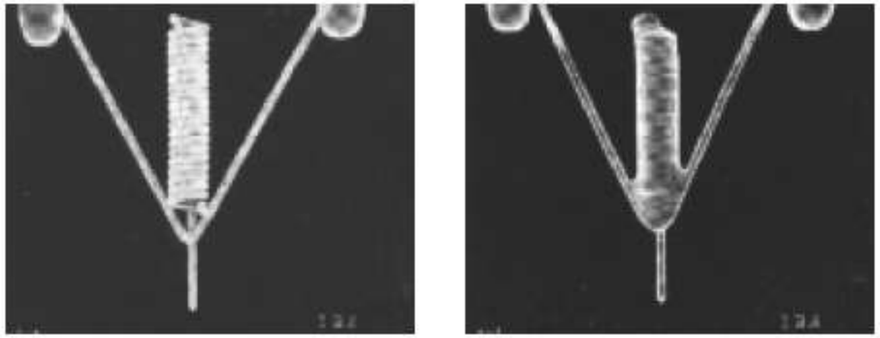
- Removes/Adds Material
- Secondary Ion imaging shows material contrast
- Channeling contrast
- In-situ sample preparation
- Combines high magnification imaging and sample modification
- Ion beam has smaller interaction volume at the target comparing with E-beam (~5-40nm for energies in the 30 keV range)

Focused Ion Beam (FIB)

most commonly used ion: **Gallium**

- longest liquid range of any metal (from 29.8°C to 2175°C)
- providing room temperature operation
- long lifetime source
- Spot size reaches below ∅ ≈ 10 nm
- highly vacuum compatible
- large ions for physical sputtering
- Below the melting point Ga is a soft, silver white metal, stable in both air and water.

Liquid Metal Ion Source (LMIS)



The tungsten is wetted with gallium which is held in the spiral by surface tension. The vapour pressure is about 10^{-7} mbar.

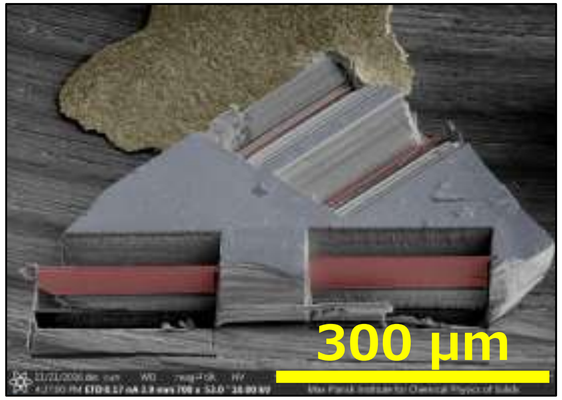
Frozen-in
-shape LMIS
showing 49° half angle. The field emission area is a 2-5nm across giving current densities $>10^{8}$ Acm^{-2}.

FEI

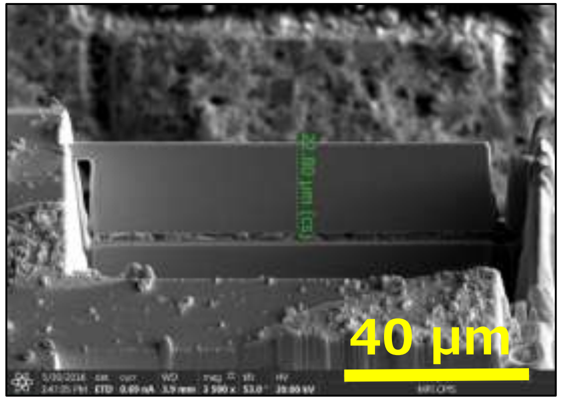
Focused Ion Beam (FIB)

Fabrication process steps

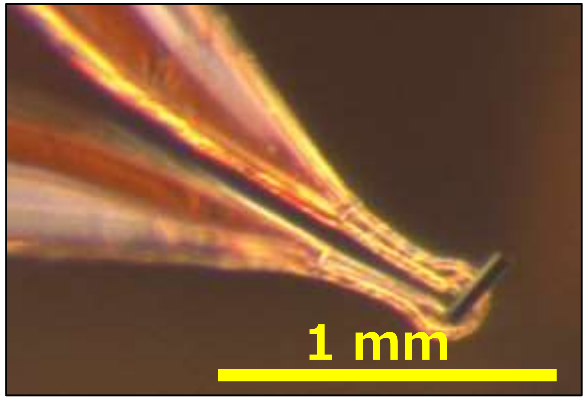
Lamella mining



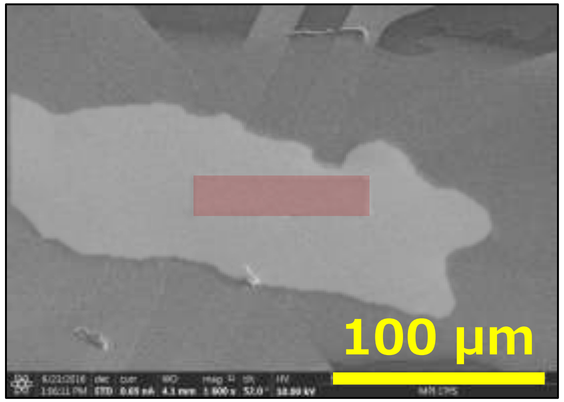
Lamella separation



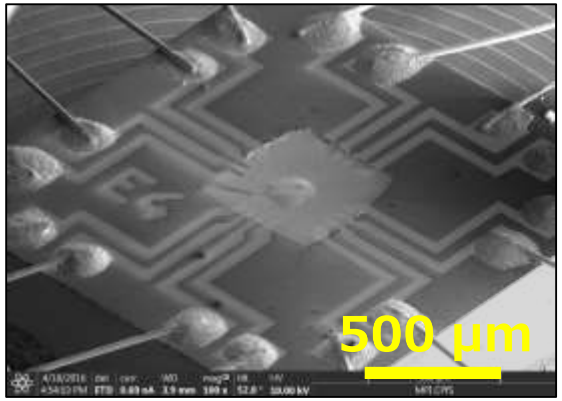
Lamella transfer



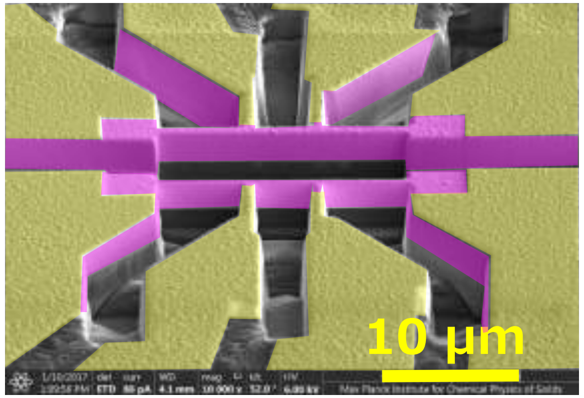
Lamella fixation



Contacting



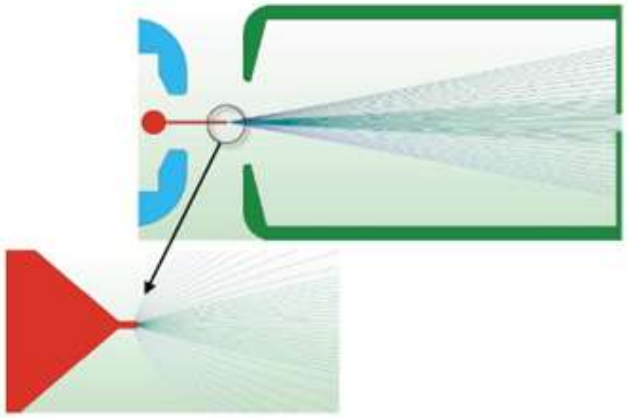
Microstructuring



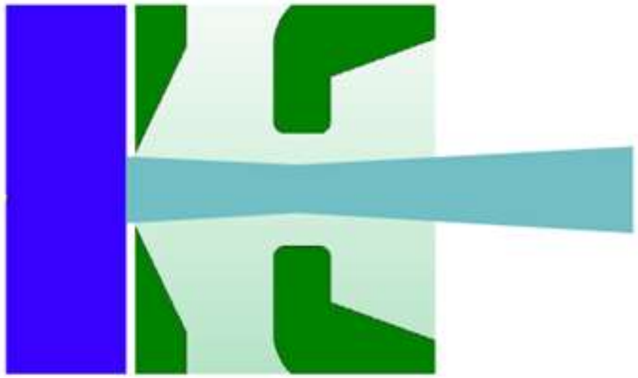
Focused Ion Beam (FIB) Microfabrication

Focused Ion Beam (FIB)

Alternative Ion Source

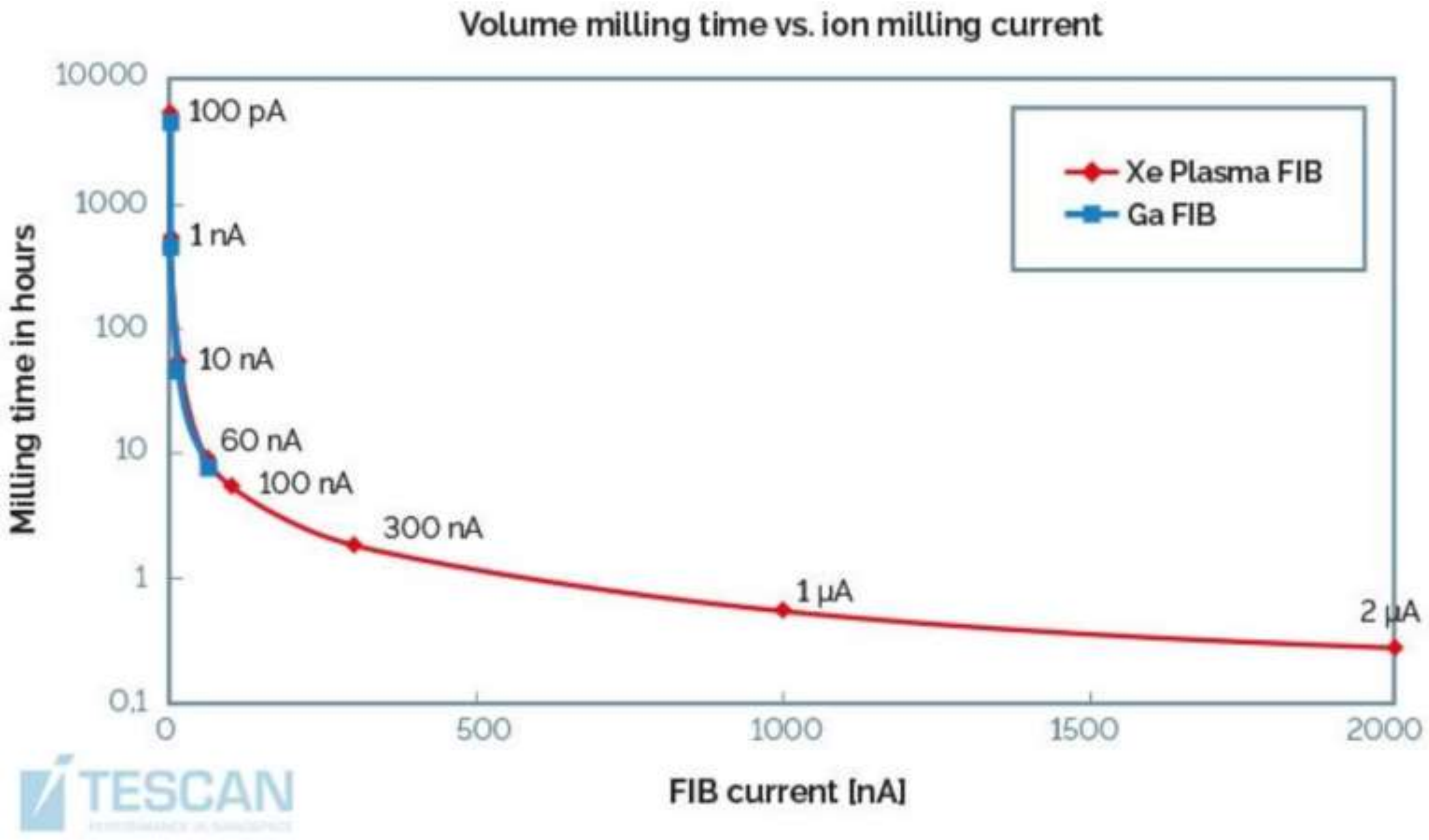


Liquid Metal Ion Source (Gallium)
Point source (50nm diameter)
Low angular intensity (15uA/sr)



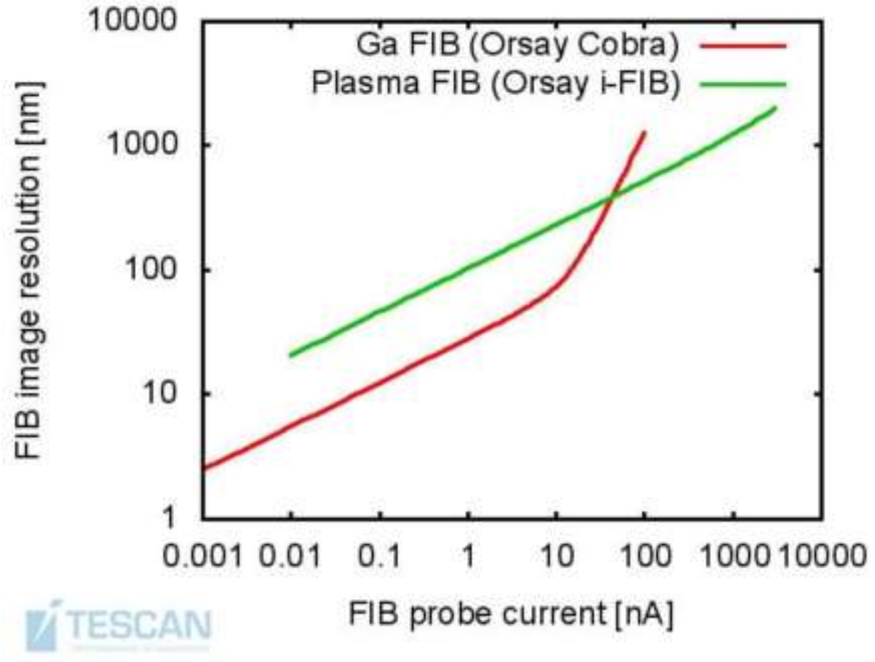
Plasma Ion Source
Broad Area Source (10-100um diameter)
High Angular Intensity (5-10mA/sr)

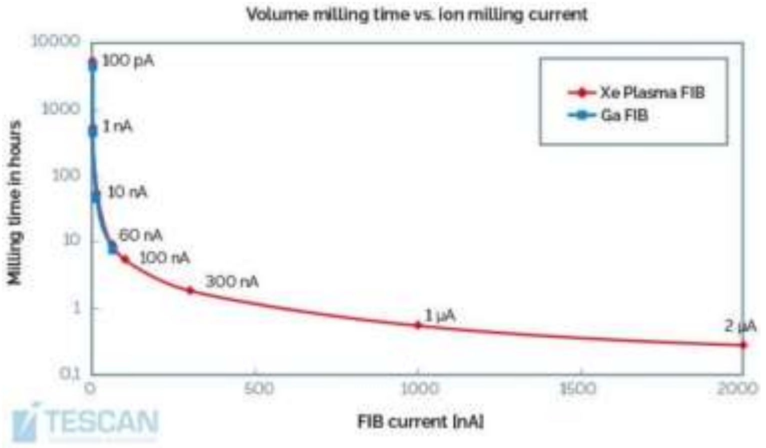
Focused Ion Beam (FIB)



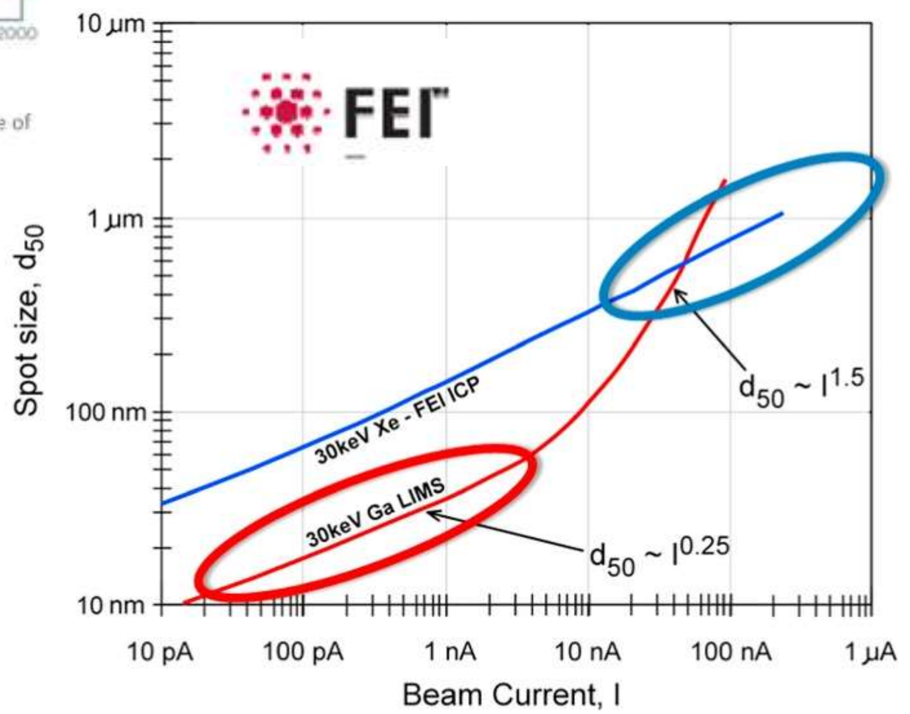
Milling time as a function of the FIB current on a Si sample with a volume of 100 x 100 x 100 μm^3

Focused Ion Beam (FIB) – Sputtering Rate





Milling time as a function of the FIB current on a Si sample with a volume of 100 x 100 x 100 μm³



Sputtering Rate

$$R = \frac{dA}{I\,t}.$$

$$R = \frac{1}{N_T\, q} Y_S\,(E,\Theta)$$

Focused Ion Beam (FIB) – Sputter Yield

P. Sigmund, Phys. Rev. 184, 383 (1969)

$$Y(E) = \frac{3}{4\pi^2 c_0} \frac{1}{U_0} \alpha\left(\frac{M_2}{M_1}\right) S_n(E) \frac{1}{\cos^n(\Theta)}$$

Mass-dependent fit parameter

$E \propto V$

Reducing V
reduces ion penetration-depth
AND sputtering rate

Screening constant

$$C_0 = \frac{1}{2} \pi \lambda_0 a^2$$

Surface binding energy

Numerical function
estimated from experimental data

$$\alpha(M_2/M_1) = 0.1694+0.04218(M_2/M_1)+0.0518(M_2/M_1)^2-0.00926(M_2/M_1)^3+0.00049(M_2/M_1)^4$$

Nuclear stopping cross section

$$S_n(E) = \frac{1}{\varepsilon_0} \frac{aZ_1Z_2eM_1}{M_1+M_2} s_n(\epsilon)$$

$$a = 0.8853\, a_0 (Z_1^{2/3} + Z_2^{2/3})^{-1/2}$$

$$a_0 = 0.529 \text{ Å (Bohr radius)}$$

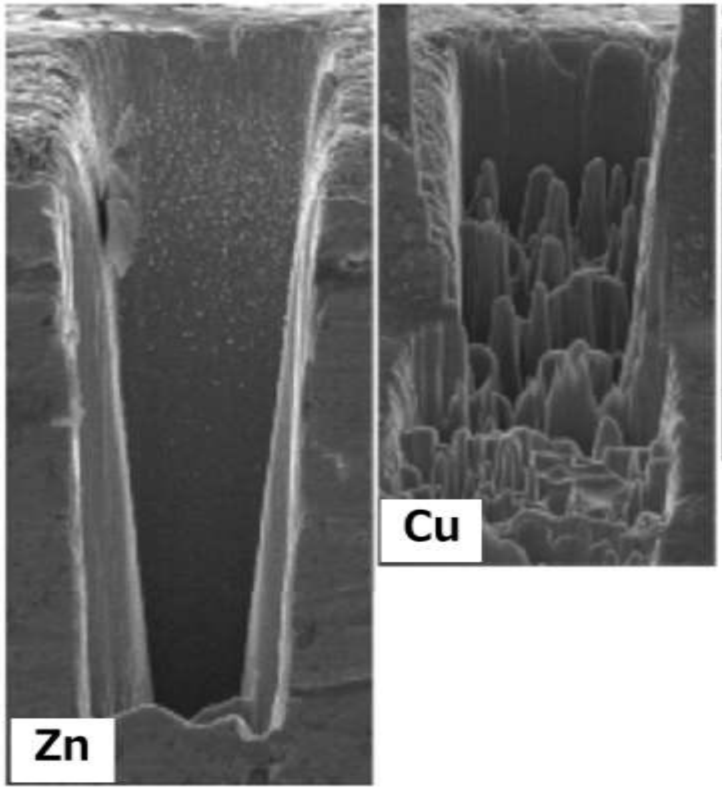
Thomas-Fermi interaction

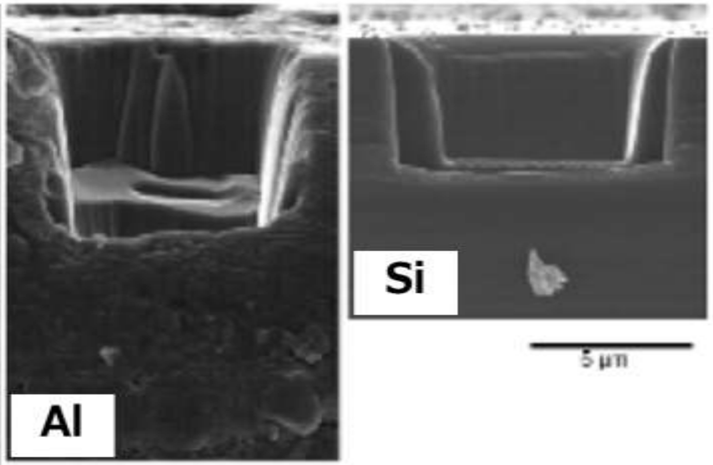
$$s_n(\epsilon) = \frac{3.441\sqrt{\epsilon}\ln(\epsilon + 2.718)}{1 + 6.355\sqrt{\epsilon} + \epsilon(6.882\sqrt{\epsilon} - 1.708)}$$

$$\epsilon = 4\pi\varepsilon_0 \frac{M_2}{M_1 + M_2} \frac{aE}{Z_1Z_2e}$$

Focused Ion Beam (FIB) – Sputter Yield

Different materials have different sputter yields

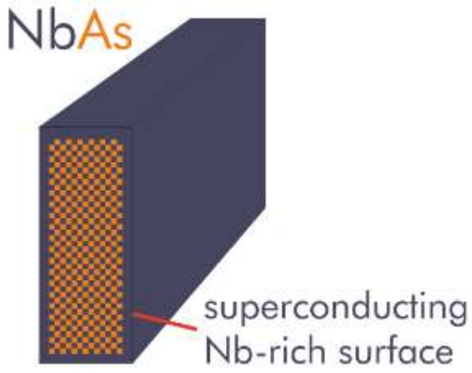




FEI

„Maja effect“

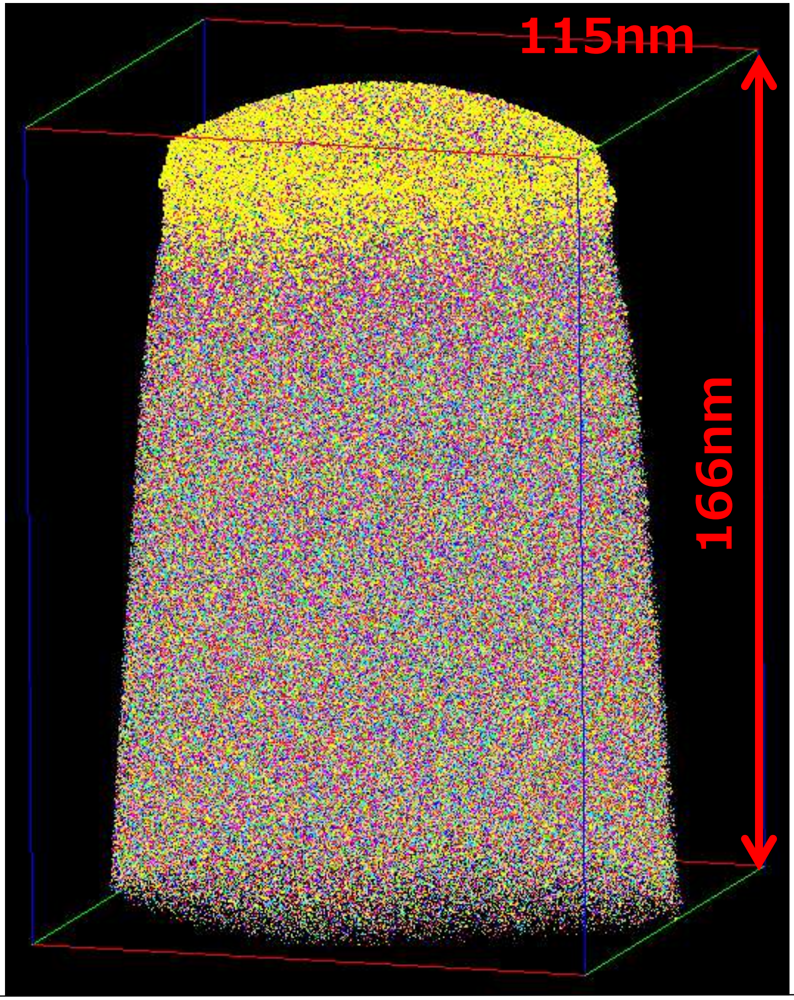
Ion-irradiation of a **NbAs/TaAs**
→ interface between the topological metal and the superconductor is formed within the material itself.

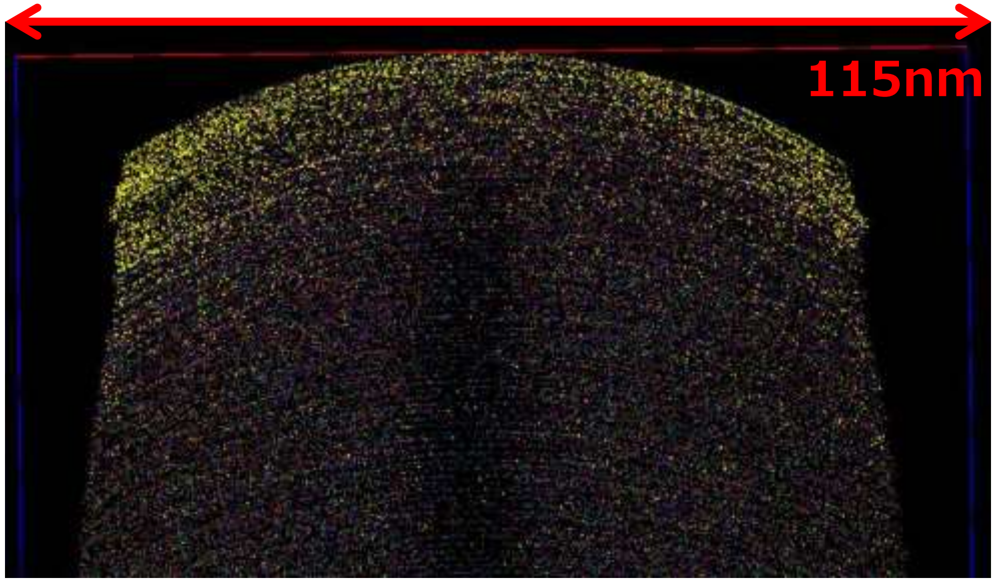


[Bachmann et al., Sci. Adv. Vol. 3, no. 5 (2017)]

Focused Ion Beam (FIB) – Ion Implantation

Real space atom imaging of Ga-FIB cut (30 keV) SmFeAs(O,F)





- Ga concentration decreases from 2% at the surface to 0% within 25nm (yellow)
- Crystal planes & lattice visible below 16 nm

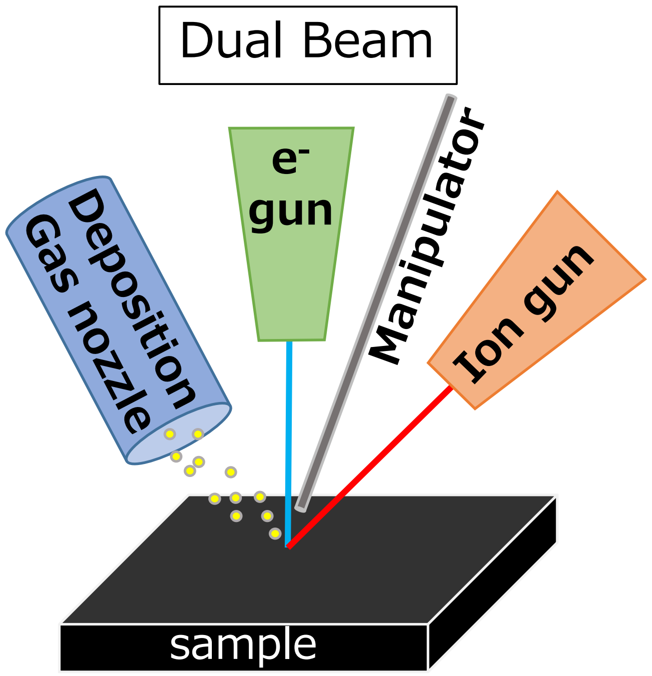
No evidence of material damage below 30 nm

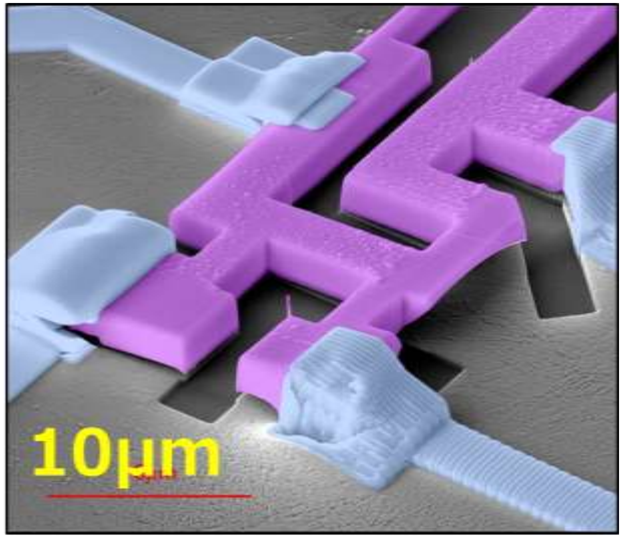
Focused Ion Beam (FIB)– Advantages / Disadvantages

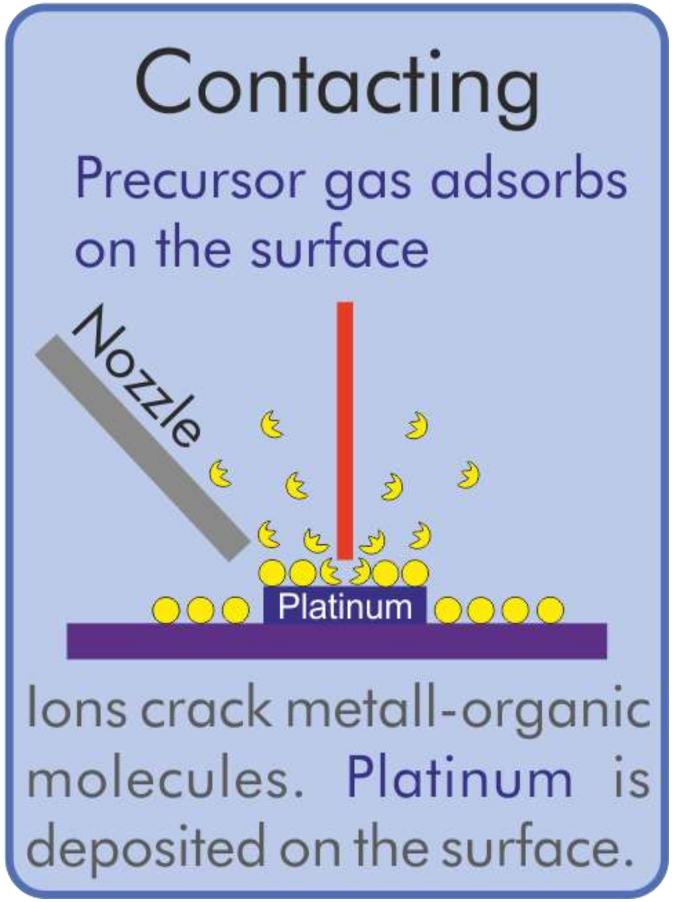
- Ga^{2+} Ion implentation
- Variance in the local angle of incidence effects

  impact of Ions
- Channeling (poly-crystals, impurities, defects)
- Ion-induced grain growth (recrystallization)
- Redeposition
- Local heating effects

FIB-assisted deposition







FIB-assisted deposition

- delicate balance between decomposing the adsorbed gas and sputtering.
- Pt, W, C or insulators

Example Platinum: $C_9H_{16}Pt$, trimethyl(methylcyclopentadienyl)platinum

- Solid at room temperature (Operating Temperature 38-42 °C)
- Very hard, and therefore stable against thermal cycling
- Chemically resistant

- For metal deposition, the effect of Ga^+ implantation is not so critical: deposited Pt consists of **~46% Pt, ~24% C, ~28% Ga, ~2% O**

[J. Vac. Sci. Technol. B **19**, 6 (2001)]

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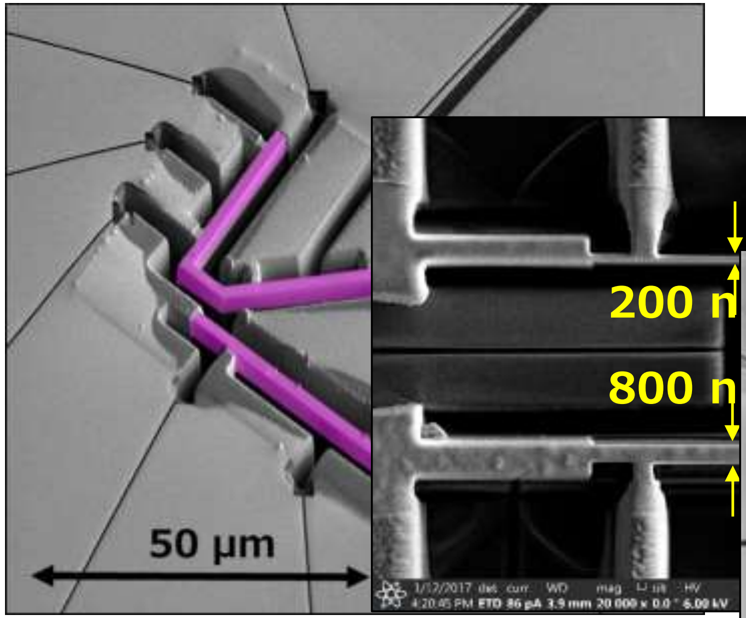
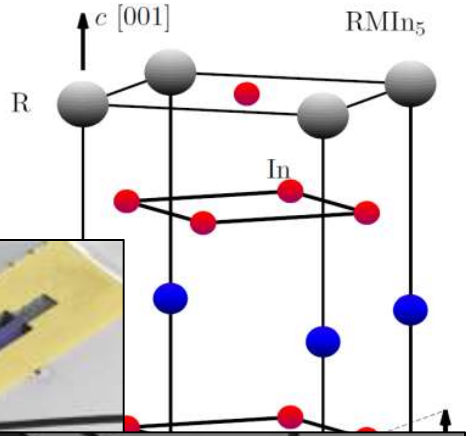
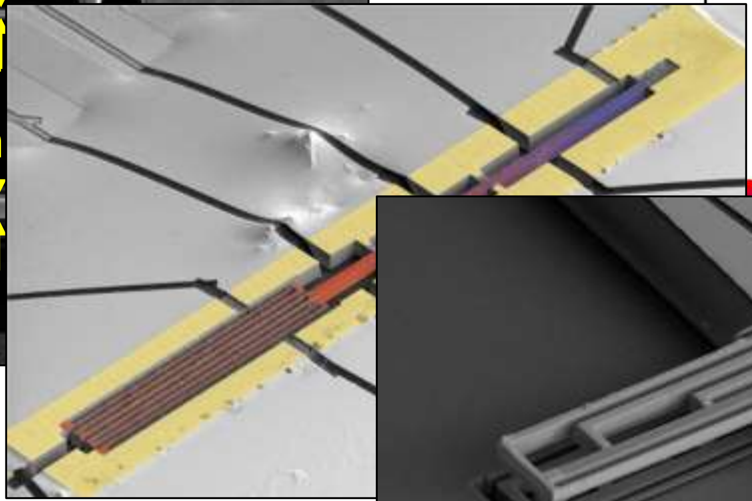
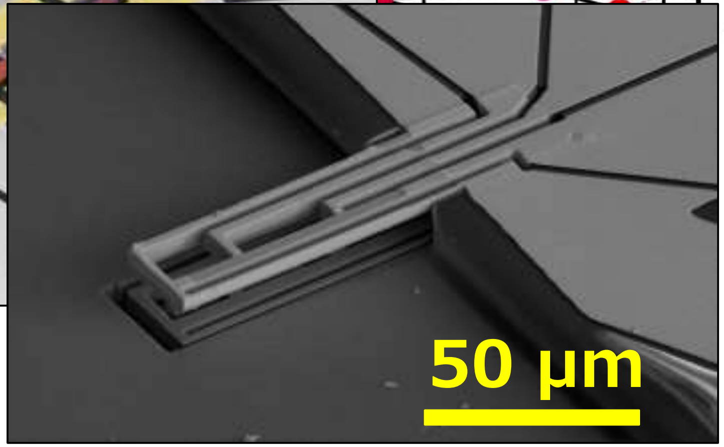
- Example of current research in heavy Fermion superconductors

Microscale Experiments





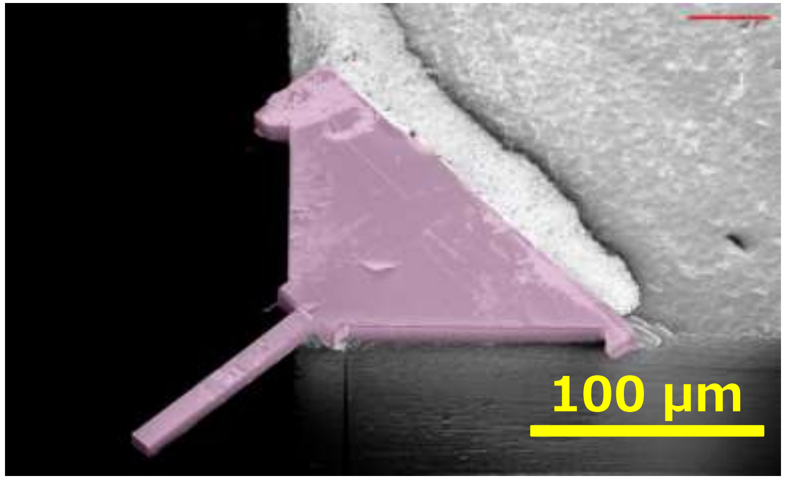




- **Electrical-transport anisotropy**
- **Finite size effects**
- **Thermoelectrical transport**
- **Free standing structures**

Microscale experiments

Thermodynamic properties from crystalline micromechanical oscillators



Elastic modulus measurement

Measure mechanical resonances

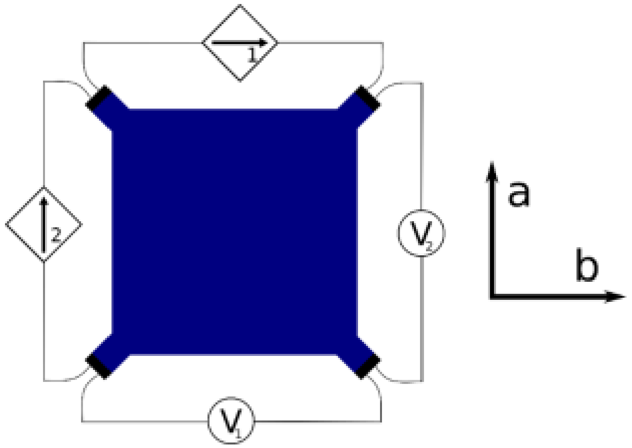
elastic constants

Spring constant

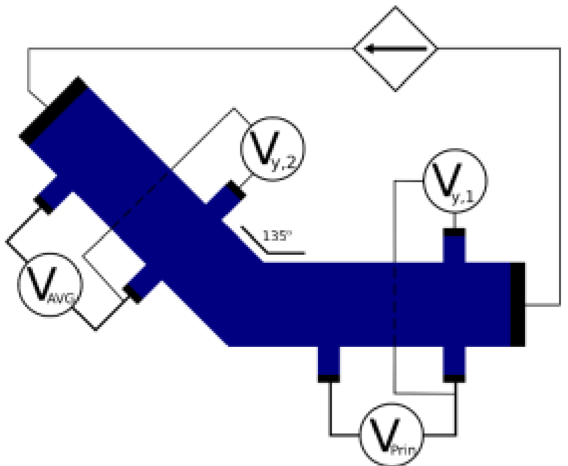
$$k = \frac{wt^3}{4L^3} E$$

Youngs modu

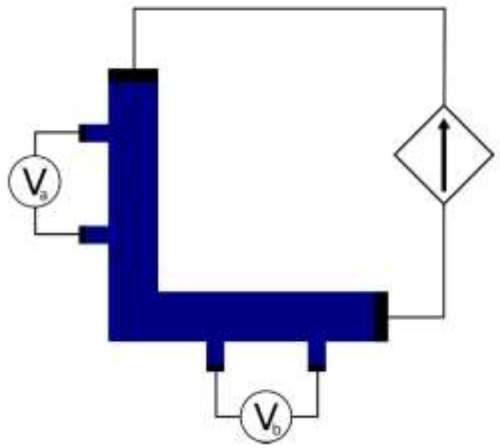
Microscale experiments – Transport anisotropy

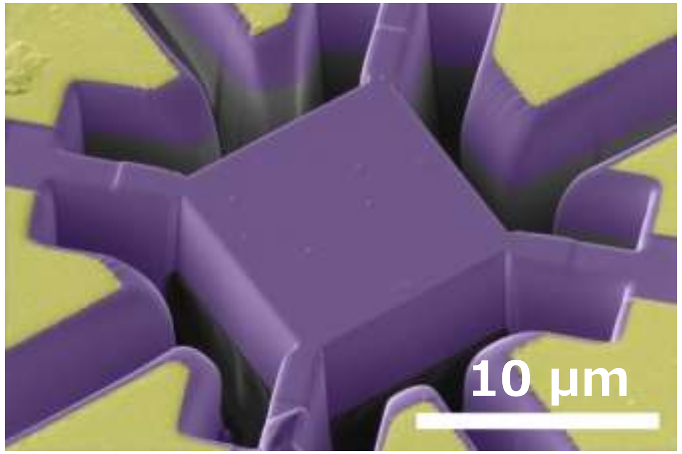


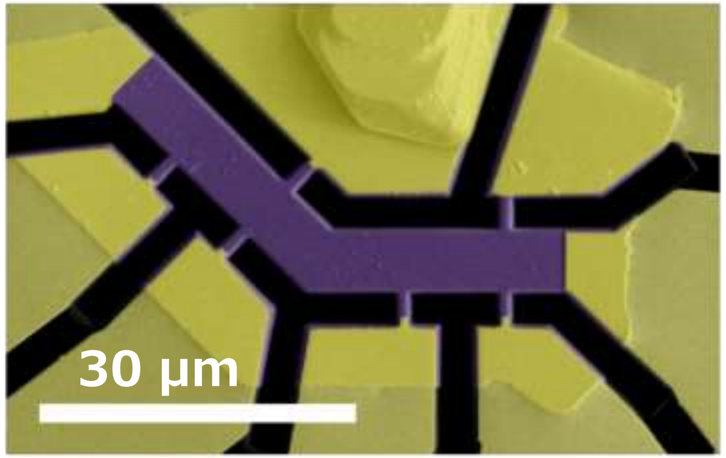
H. C. Montgomery (1971),
J. Appl. Phys. **42,** 2971

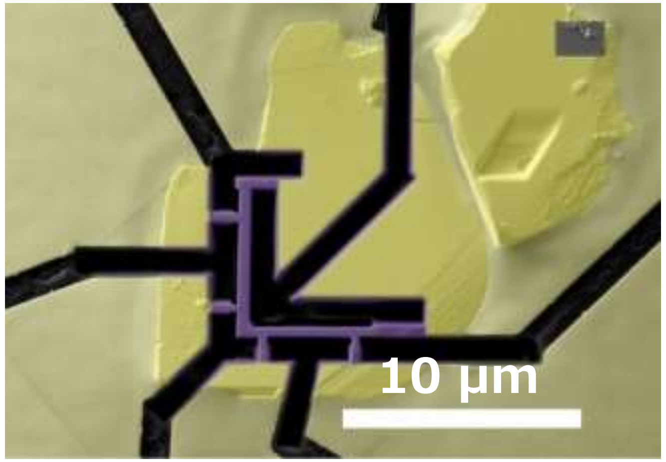


P. Walmsley and I. R. Fisher (2017),
Rev. Sci. Instr., **88,** 043901









[R. Fermin, „Transportanisotropy of SmFeAsO“ Master thesis 2018]

Microscale experiments

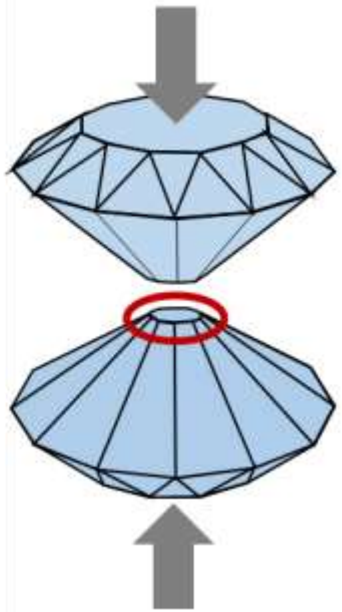
Electrical transport under extreme conditions:

at **high pressure** $p \leq 100$ kbar

Under water:

ears	4m	0.03 bar
submarine	600m	5 bar
ocean floor	3600m	30 bar

Diamond Anvil Pressure Cells



Outline

- Introduction to FIB patterning of Quantum Materials
- Focused Ion Beam (FIB) – Dual beam system
- Microscale experiments
- Example of current research in heavy Fermion superconductors

News in heavy Fermion Matter

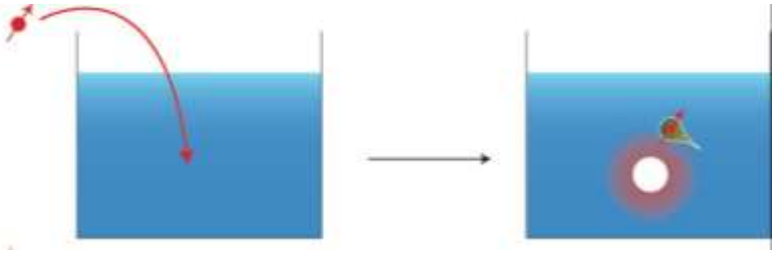
FIB microstructure

Electronic in-plane symmetry breaking at field-tuned quantum criticality in $CeRhIn_5$
F. Ronning, T. Helm, K. R. Shirer, M. D. Bachmann, L. Balicas, M. Chan, B. J. Ramshaw, R. McDonald, F. Balakirev, E. Bauer, and P. J. W. Moll
Nature **315**, 214-7 (2017)

[F. Ronning Nature **315**, 214-7 (2017)]

Heavy electrons

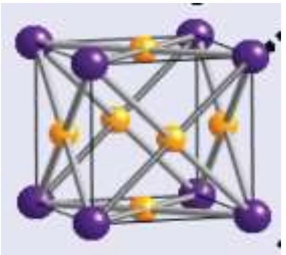
Kondo effect:



[P. Coleman, Book „Many-Body Physics: From Kondo to Hubbard“ (2015)]

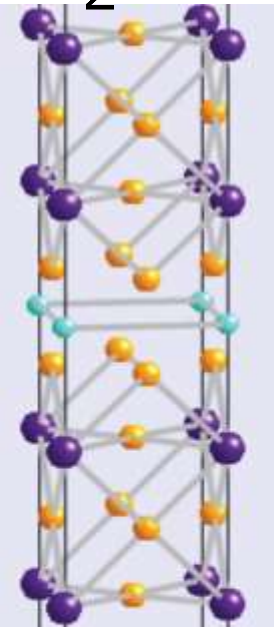
115 Superconductors

$CeIn_3$



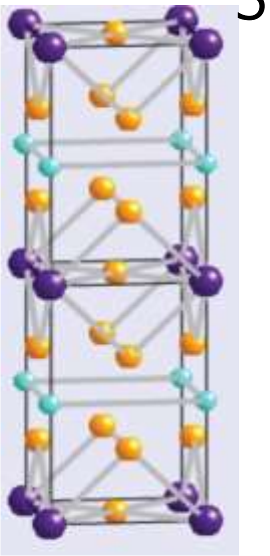
$T_c = 0.2$ K

Ce_2MIn_8



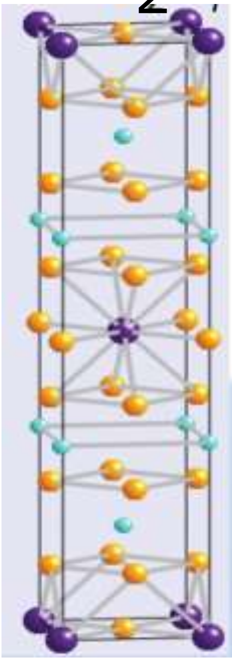
$T_c = 2.1$ K

$CeMIn_5$

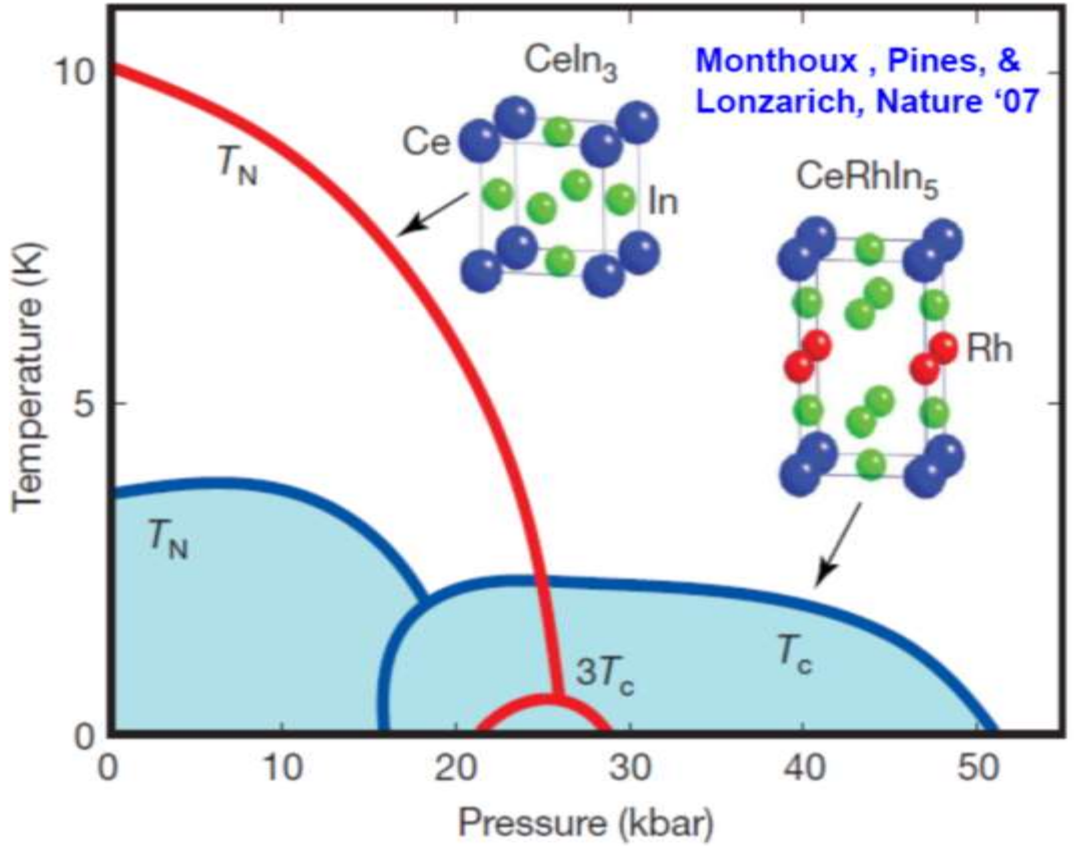


$T_c = 2.3$ K

CeM_2In_7

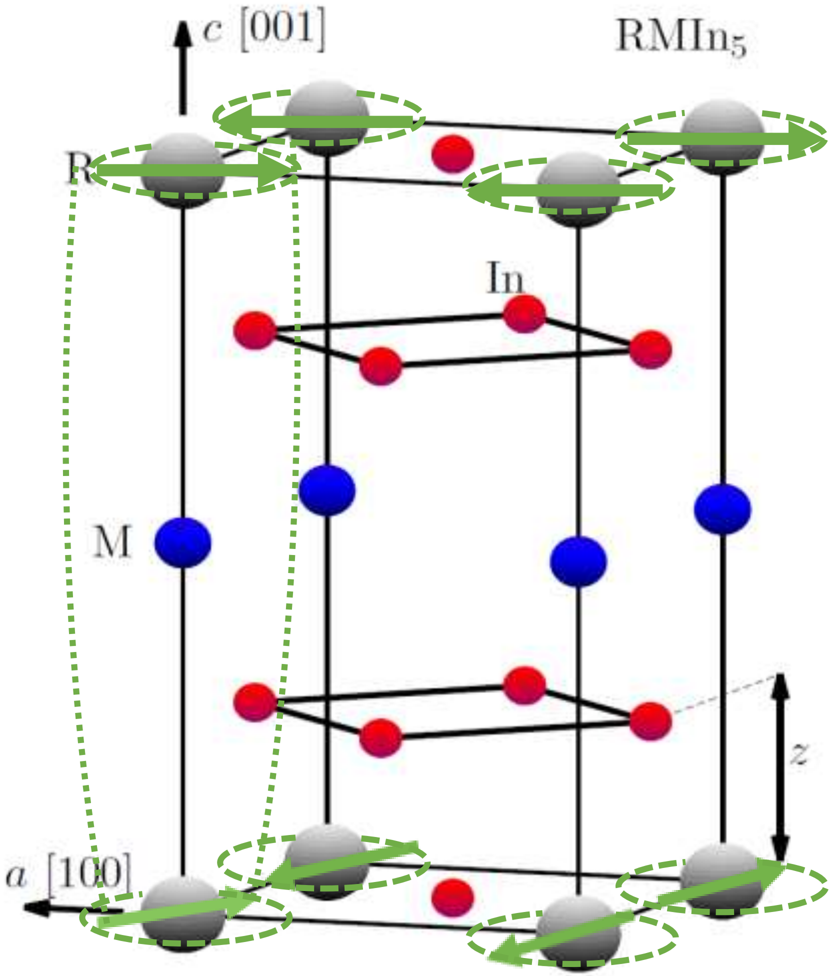


Dimensionality: 3D 2D 1D



$CeRhIn_5$

0.26μ_B/Ce

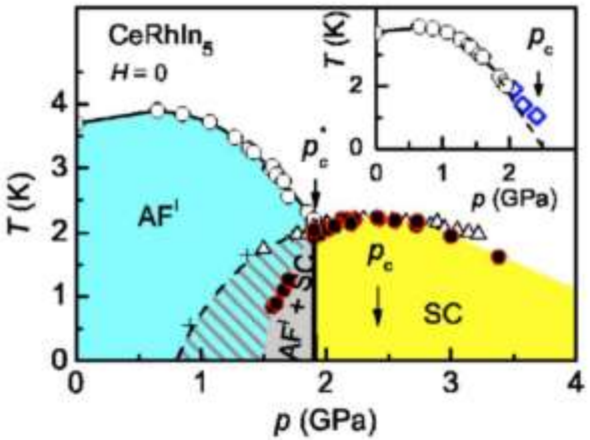


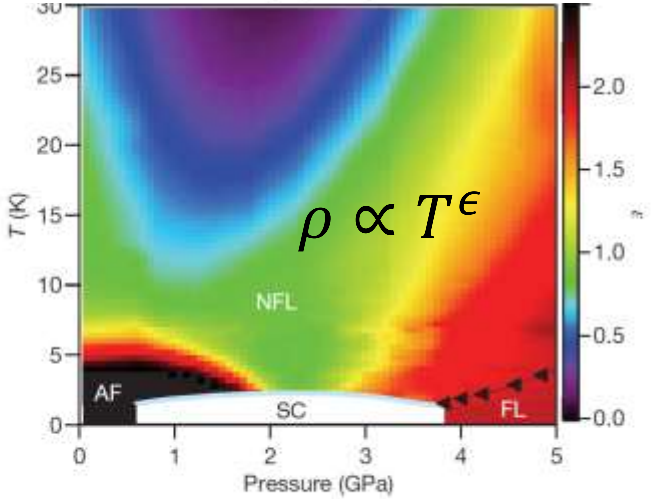
$CeRhIn_5$ is an anti-ferromagnet (AFM)

- Local moments on the Ce sites (**$4f^1$** configuration)
- f-electrons not completely localized **$\gamma \sim 70$ mJ mol^{-1}K^{-2}**
- Anti-ferromagnetic ordering at **T_N = 3.85K**
- In-plane spins anti-parallel, incommensurate spin-spiral along ***c*** direction **q = (1/2,1/2,0.297)**

Quantum critical superconductivity under pressure

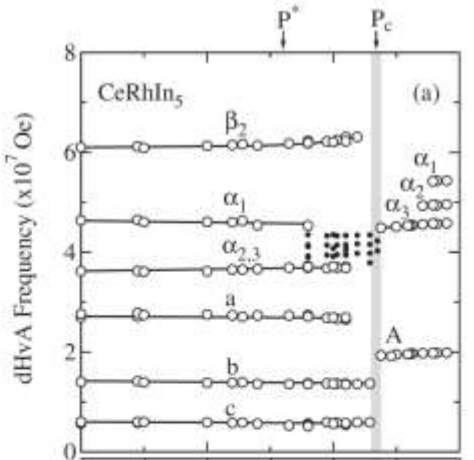
Knebel et al., PRB **74**, 020501(R) (2006)

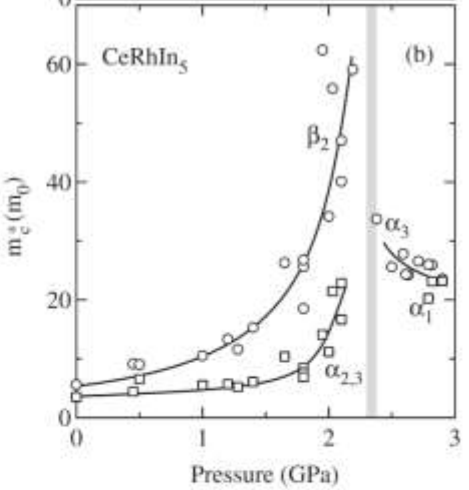




Park et al., Nature **456**, 336 (2008)

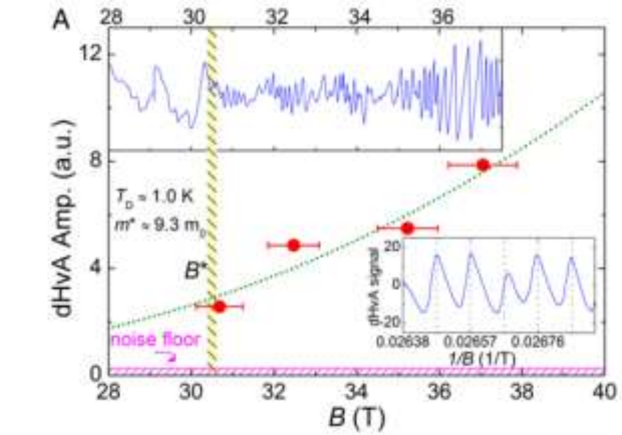
Hegger et al., PRL **84**, 4986-9 (2000)

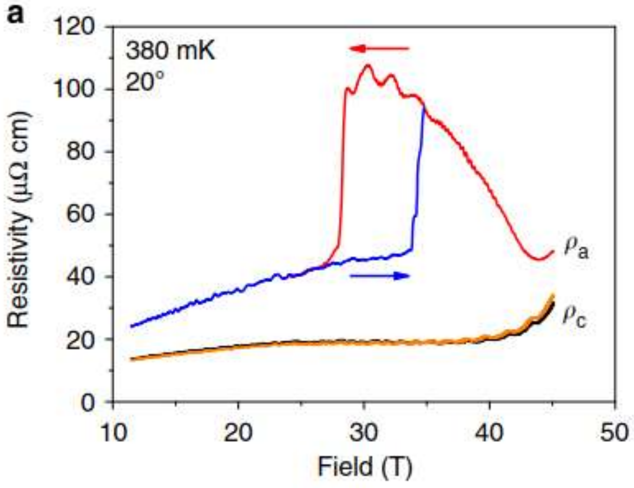




Shishido et al., JPSJ **74**, 1103-6 (2005)

Jiao et al., PNAS **112**, 673-678 (2015)



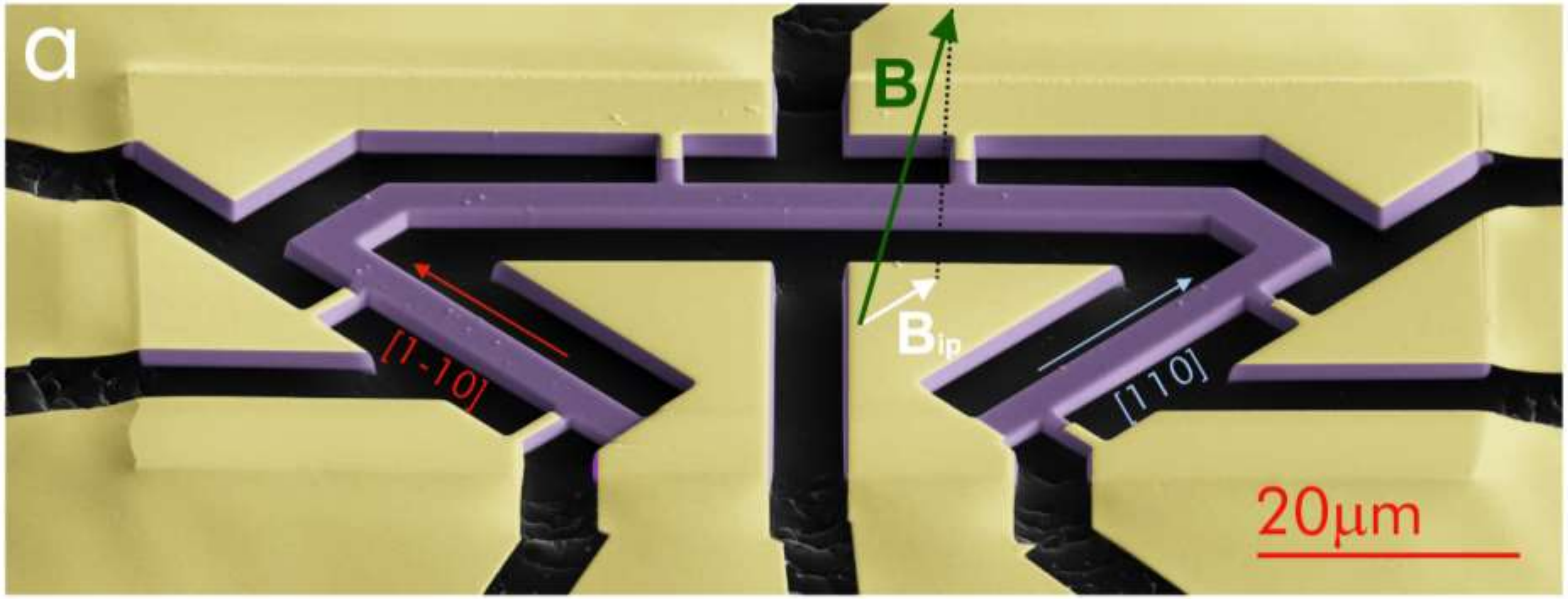


Moll et al., Nat. Commun. **6**, 6663 (2015)

News in heavy Fermion Matter

Microstructured $CeRhIn_5$

FIB microstructure



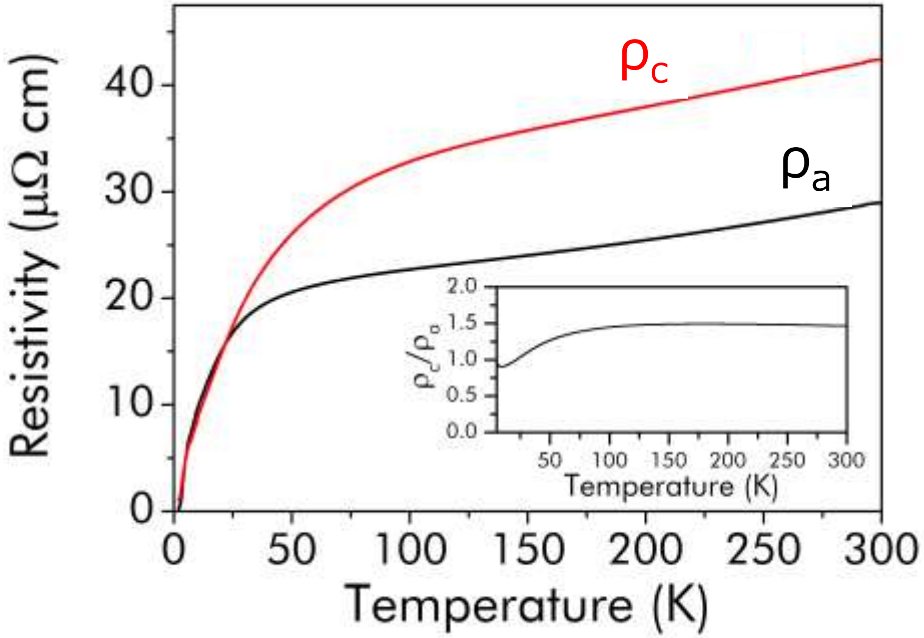
Fabricate crystal microstructures for high field measurements of resistivity along arbitrary crystal directions

[F. Ronning Nature **315**, 214-7 (2017)]

FIB microstructuring : Evidence for high sample quality

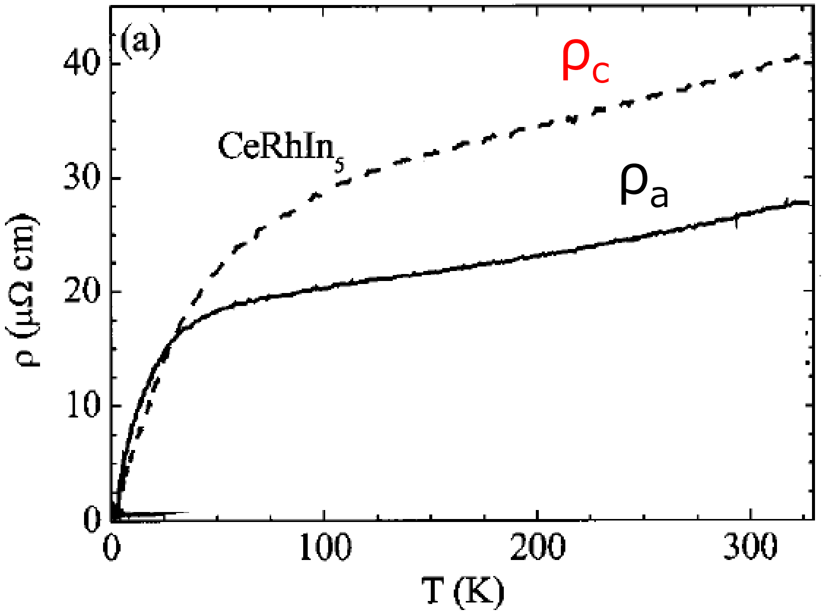
Microstructure

P.J.W.M. et al., Nat. Comm. 6:6663 (2015)



Bulk crystal

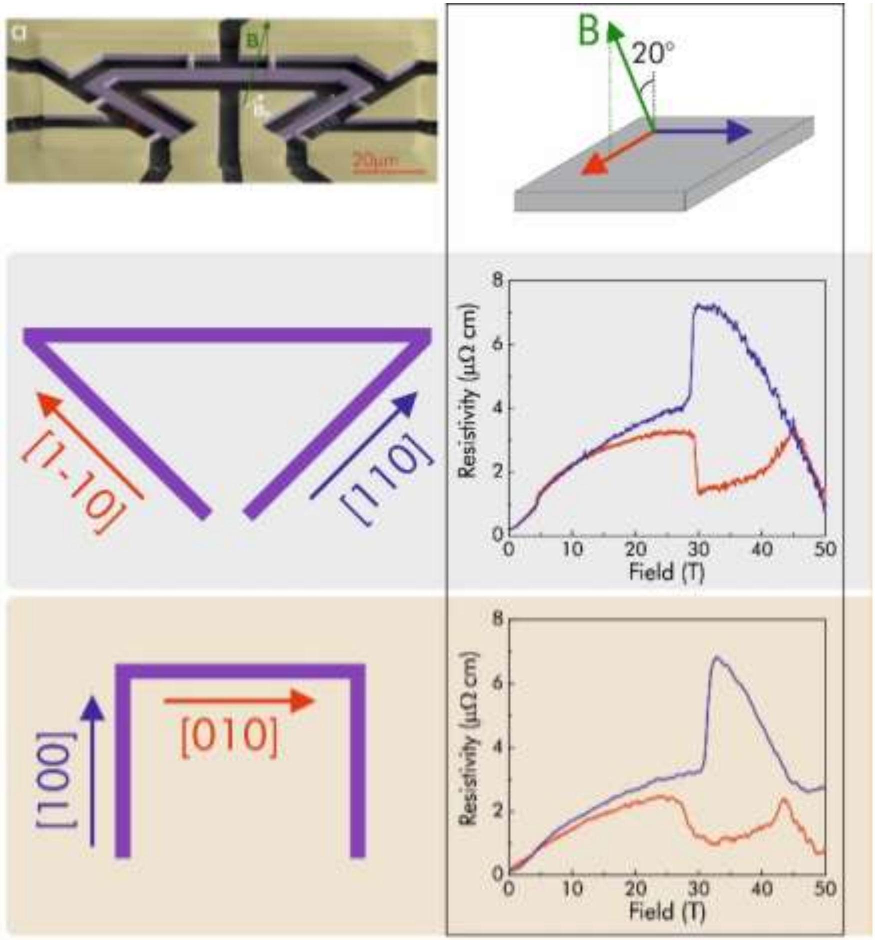
A.D. Christianson et al., PRB 66, 054410 (2002)



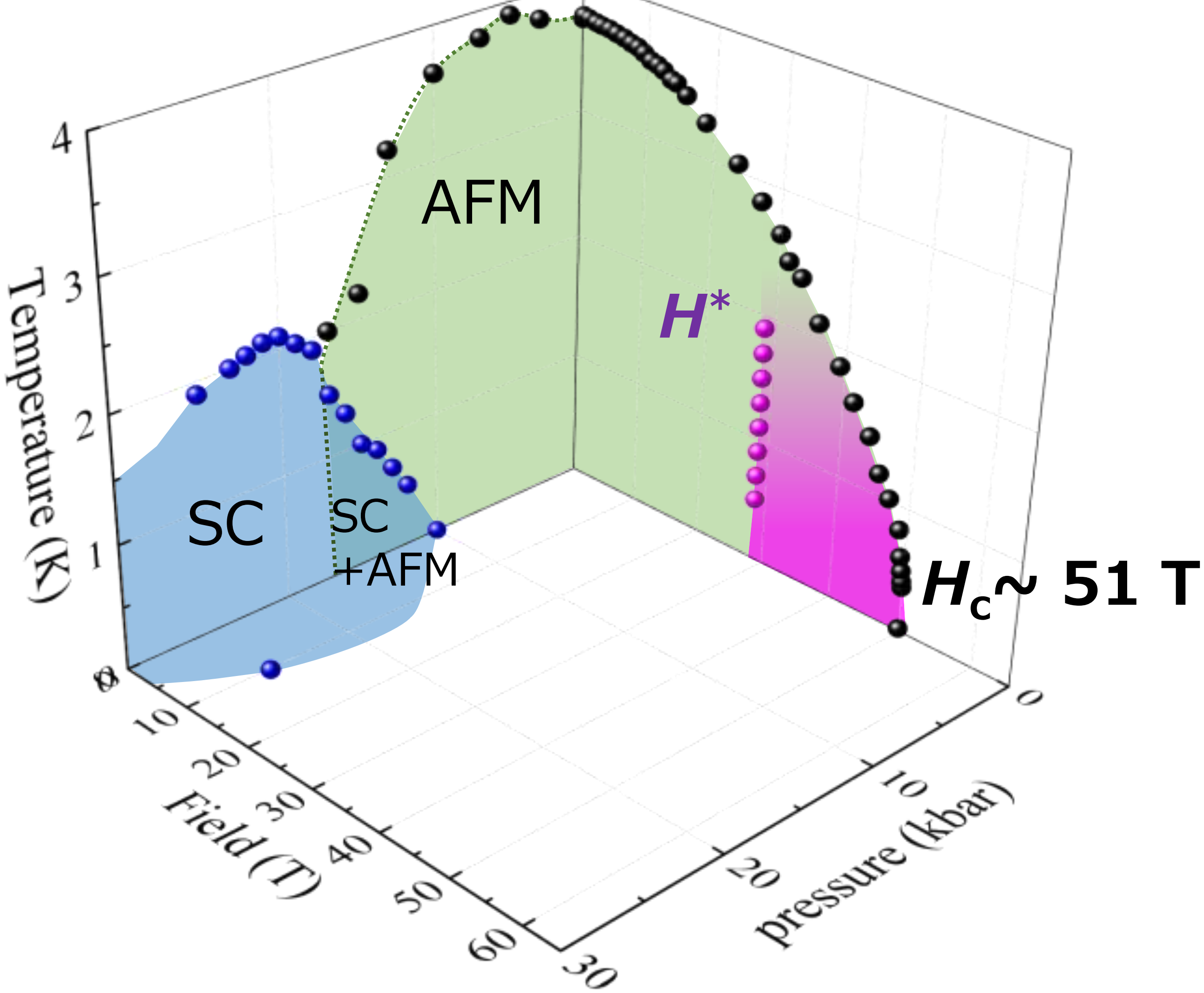
- Quantitative agreement with bulk crystal resistivity measurements
- Large RRR (>100)
- Large quantum oscillations in resistivity (SdH)

High-field Magnetortransport anisotropy of $CeRhIn_5$

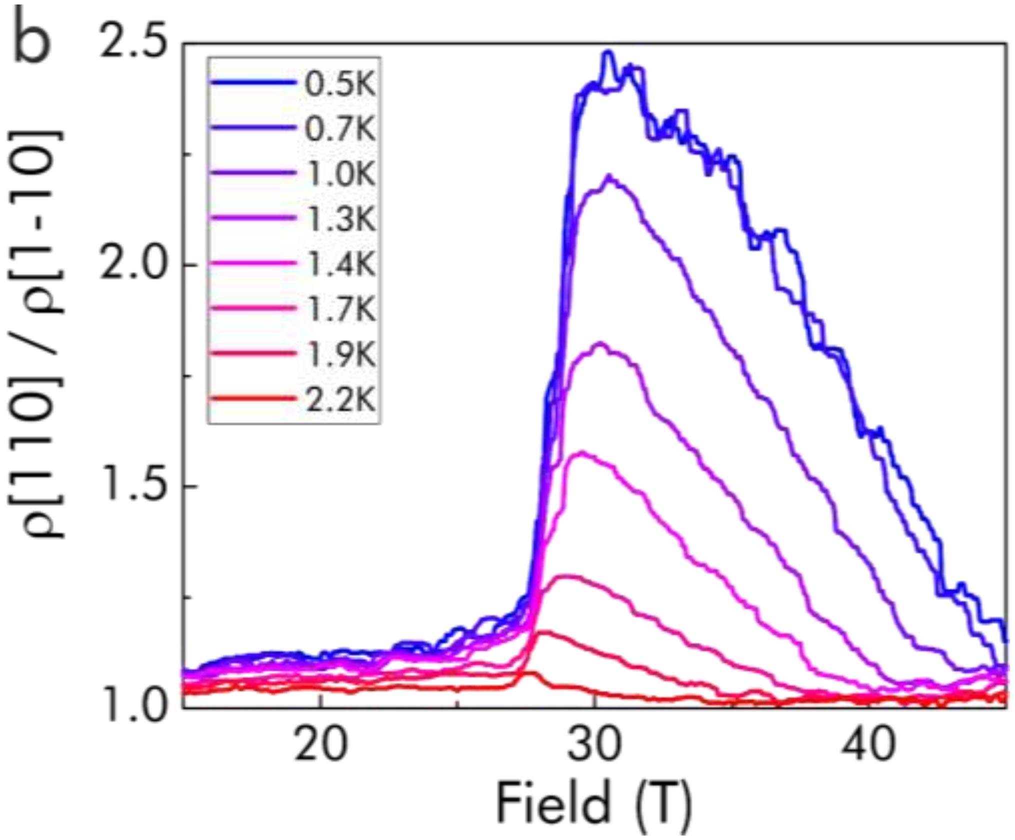
$CeRhIn_5$: A new high-field state



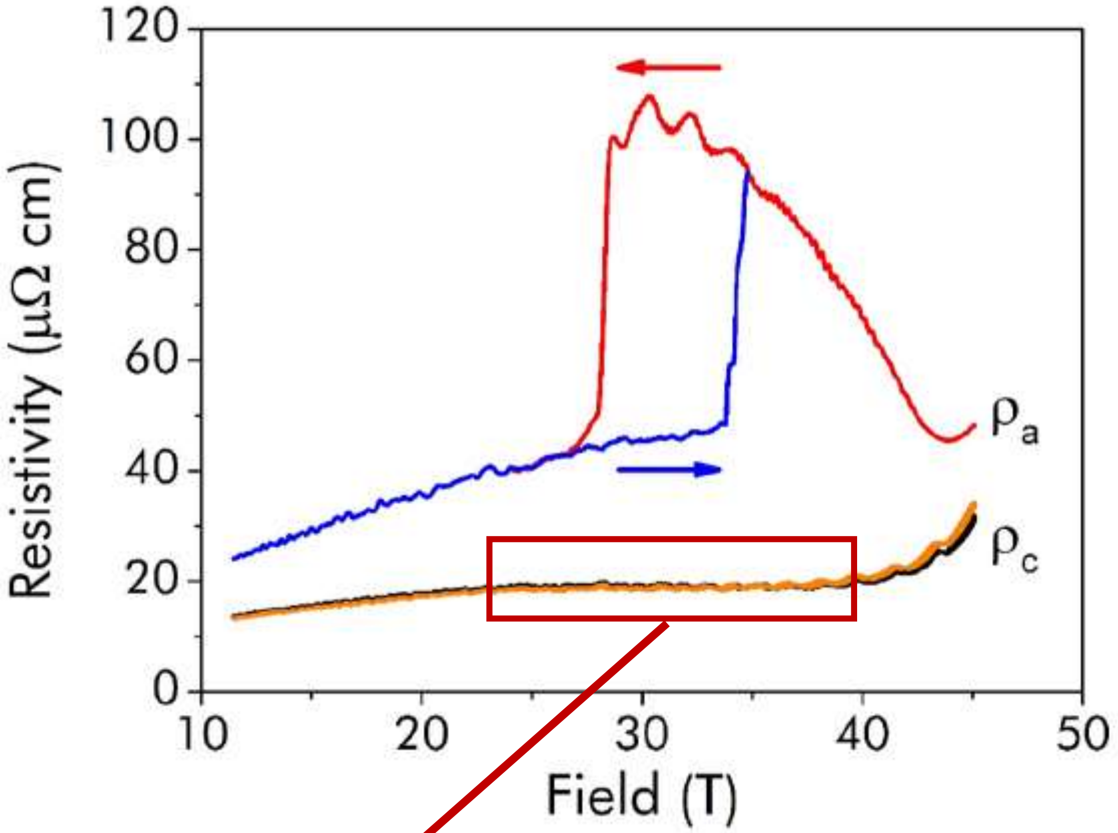
[F. Ronning Nature **315**, 214-7 (2017)]



High-field Magnetortransport anisotropy of $CeRhIn_5$



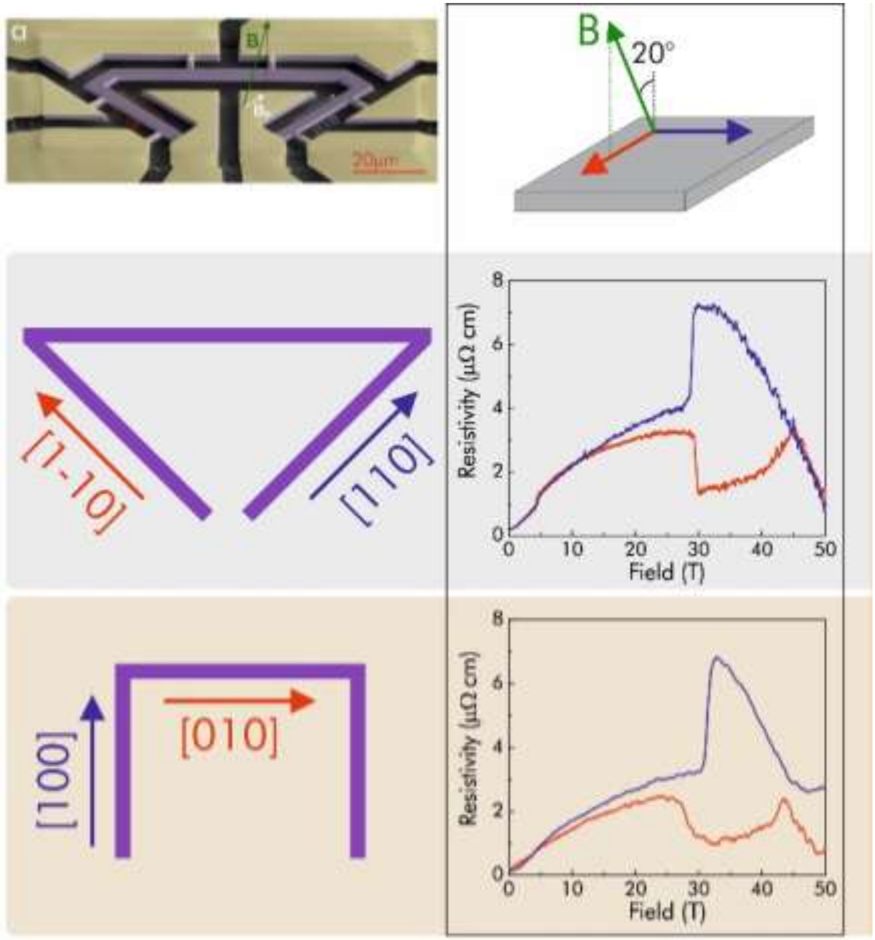
[F. Ronning Nature 315, 214-7 (2017)]



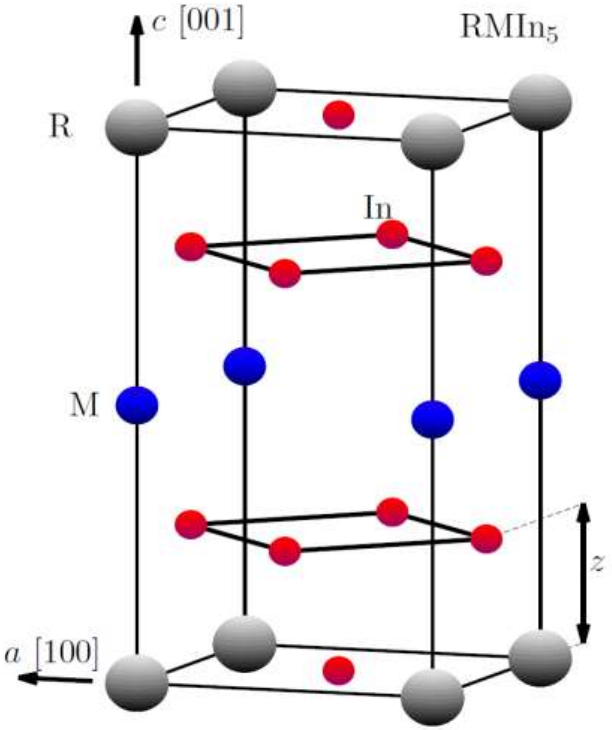
Nothing in ***c***

High-field Magnetortransport anisotropy of $CeRhIn_5$

$CeRhIn_5$: A new high-field state

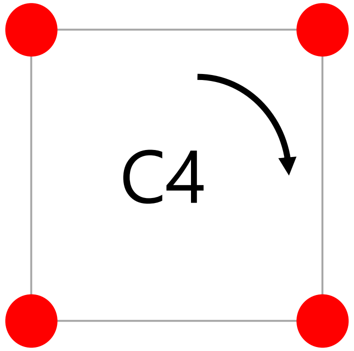


[F. Ronning Nature **315**, 214-7 (2017)]

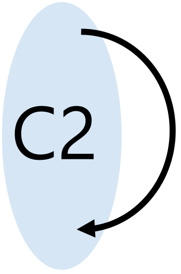


Electronic nematic

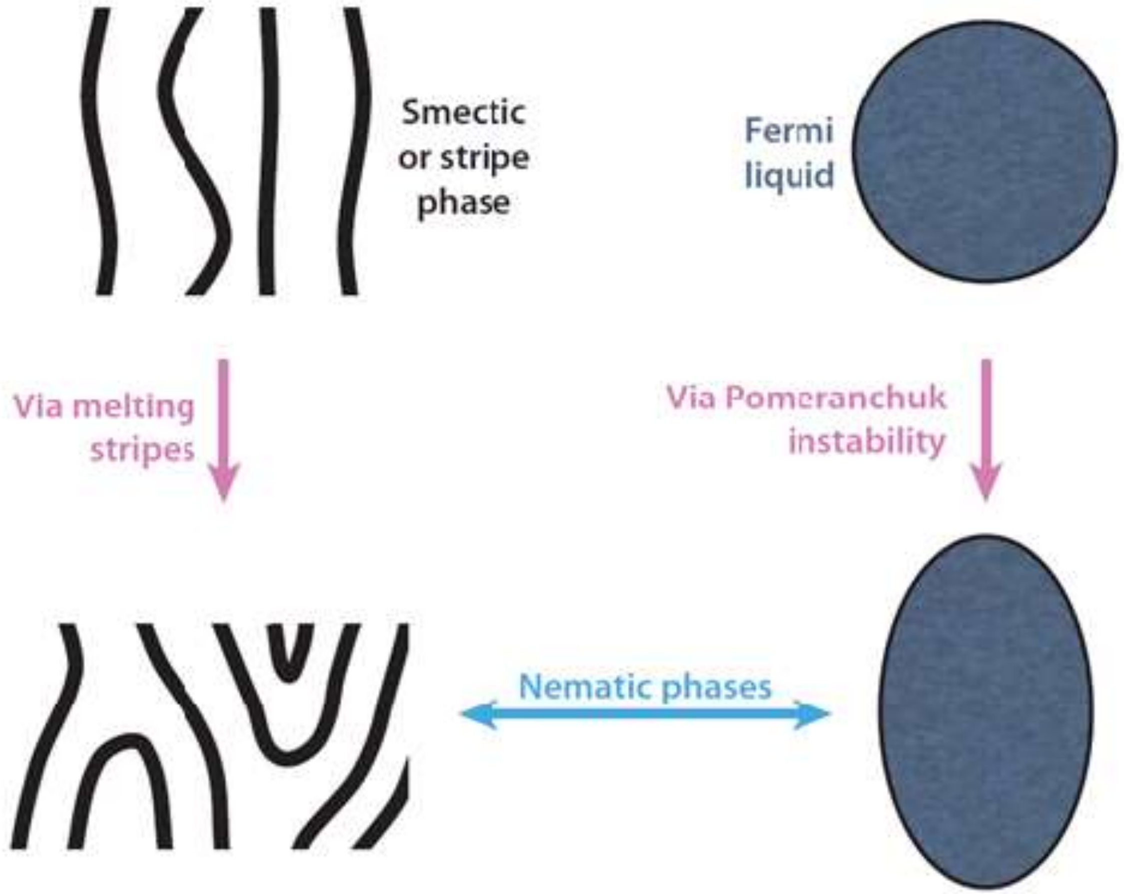
Tetragonal crystal
P4/mmm



Fermi surface
C2 symmetric



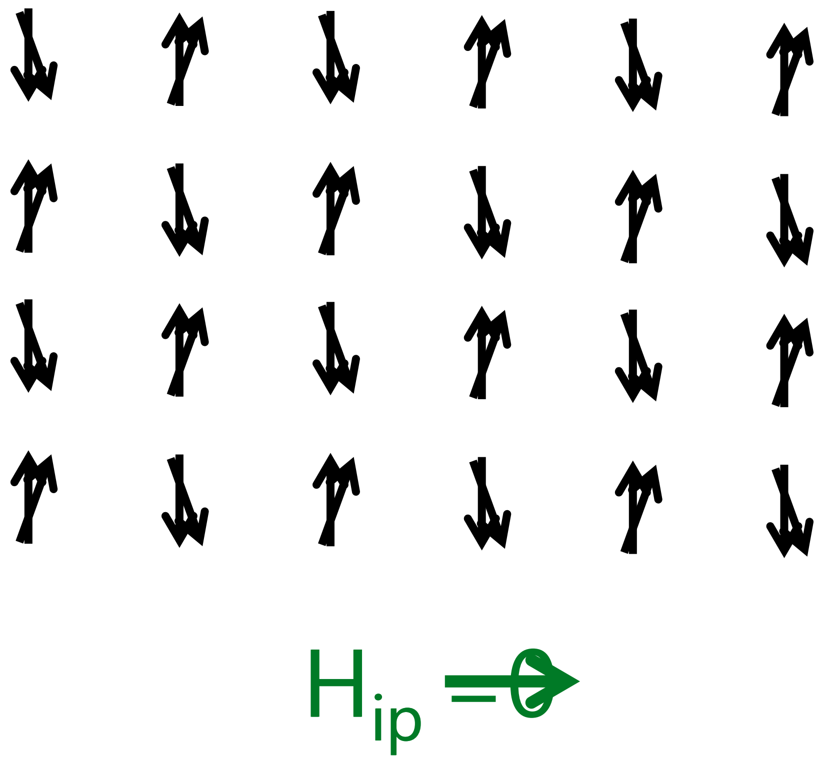
Electronic nematics

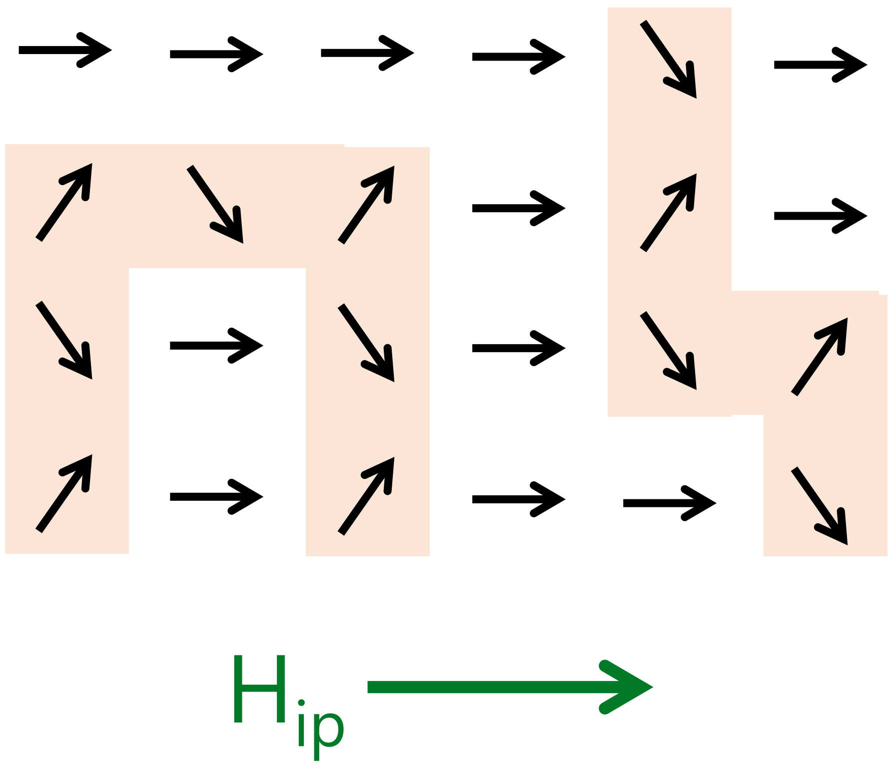


Kivelson et al., Nature 393, 550 (1998)

Electronic nematics

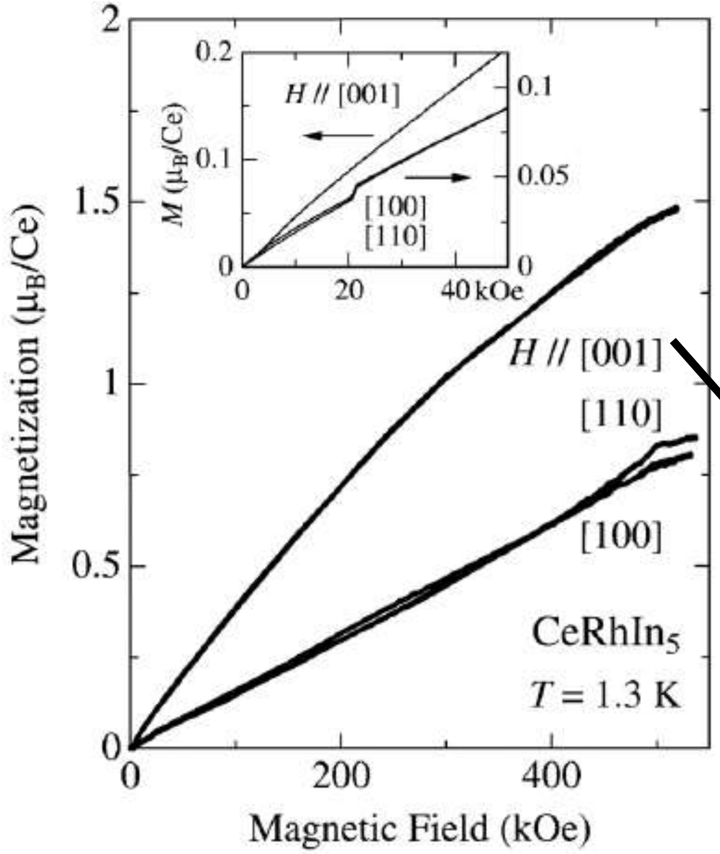
Nematic orders:
direction but no orientation



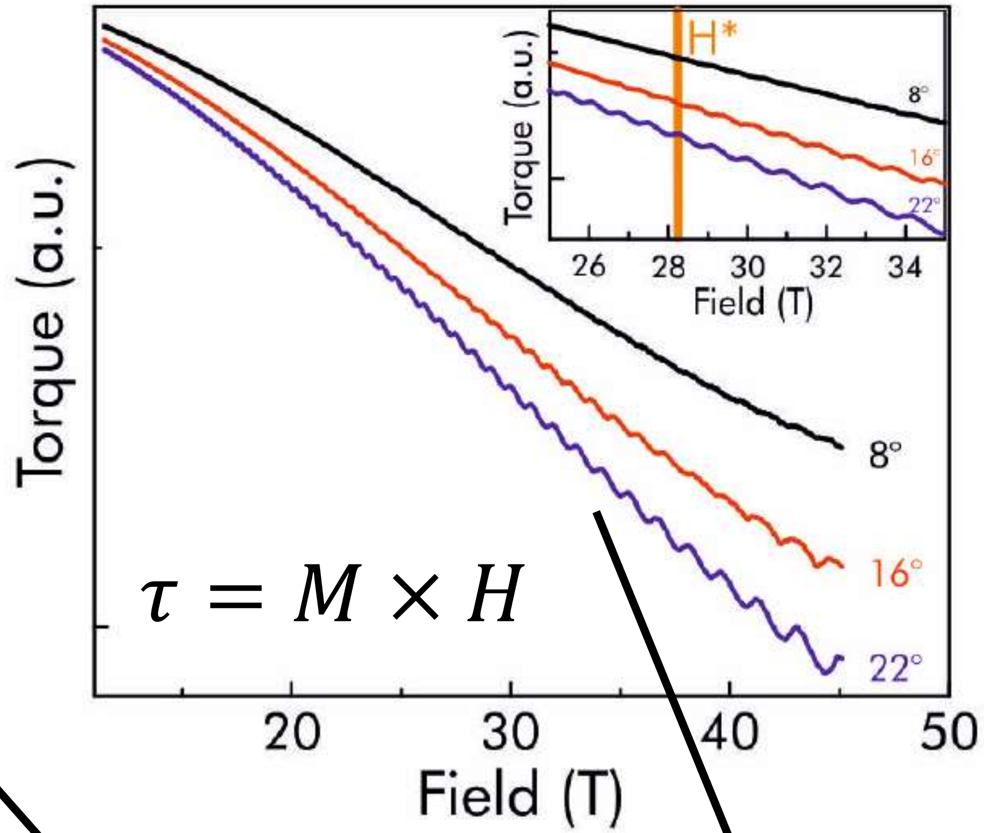


Electronic system breaks C4 rotational symmetry <u>but persives</u> translational symmetry.
(q = 0 order)

A new high-field state in $CeRhIn_5$



T. Takeuchi et al., JPSJ 70, 877-883 (2001)



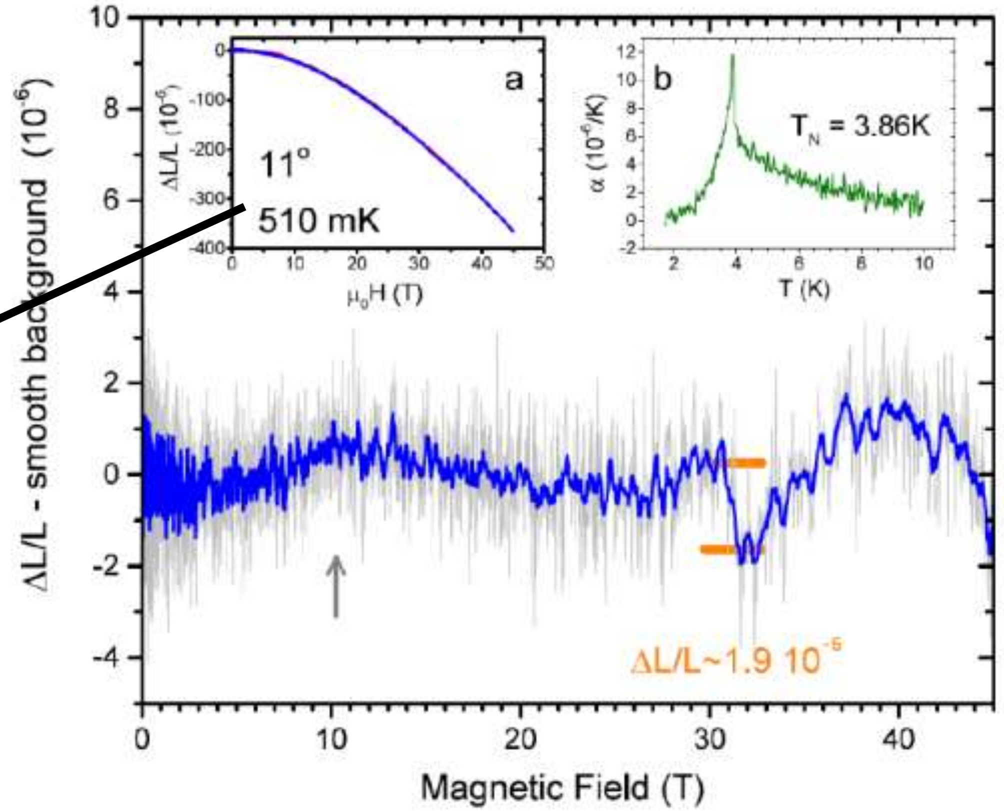
Metamagnetism? No feature in Magnetization nor in Torque

A new high-field state in $CeRhIn_5$

Structural Transition?

Very weak response in magnetorstiction

$$\frac{\Delta L}{L} \approx 1.9 \times 10^{-6}$$



[F. Ronning Nature **315**, 214-7 (2017)]
[P. F. S. Rosa arxiv:1803.01748 (2018)]

$CeRhIn_5$: A new high-field state

- Strong anisotropy feature in the **inplane transport** above ***H**** **~ 30 T**

- No anomaly in **c-direction Resistivity**

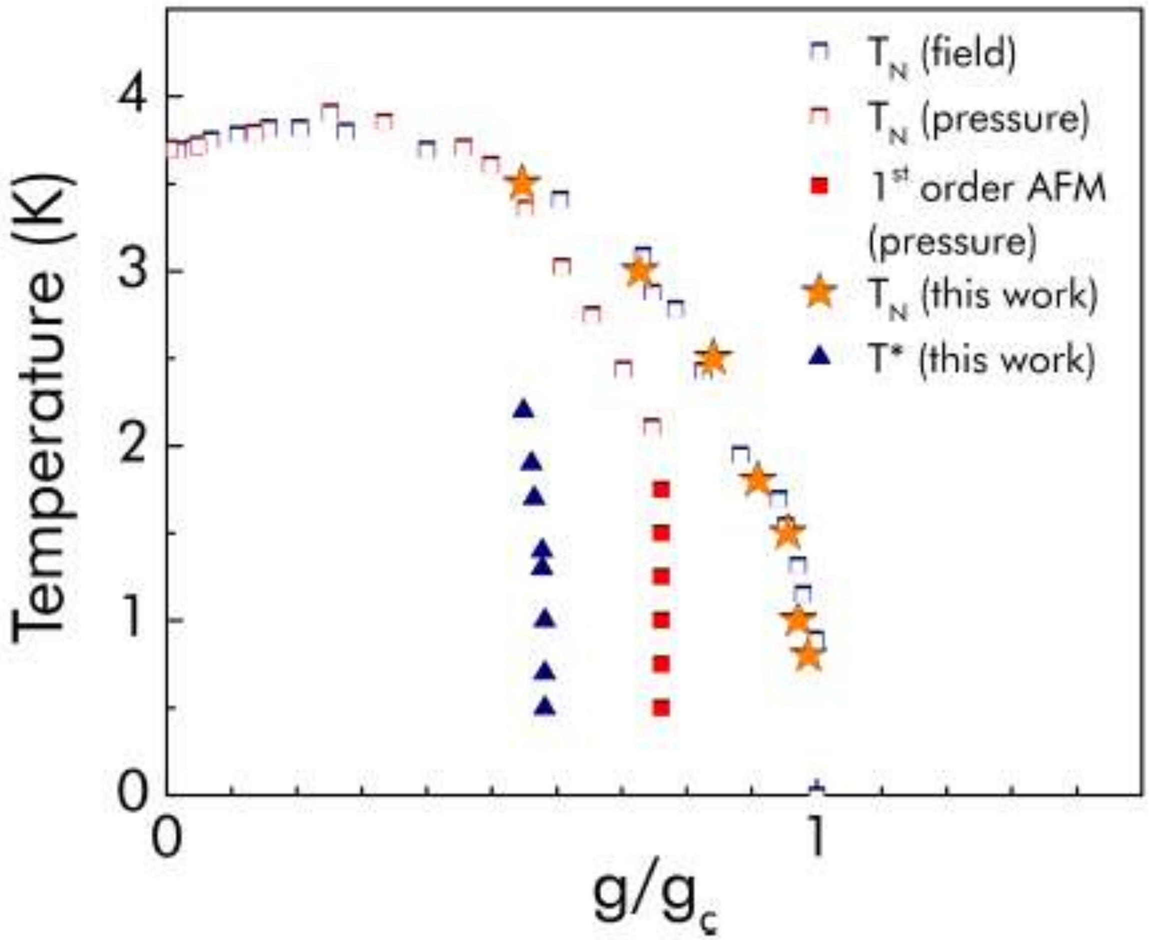
- No evidence for metamagnetism from **Magnetization** and **Torque**

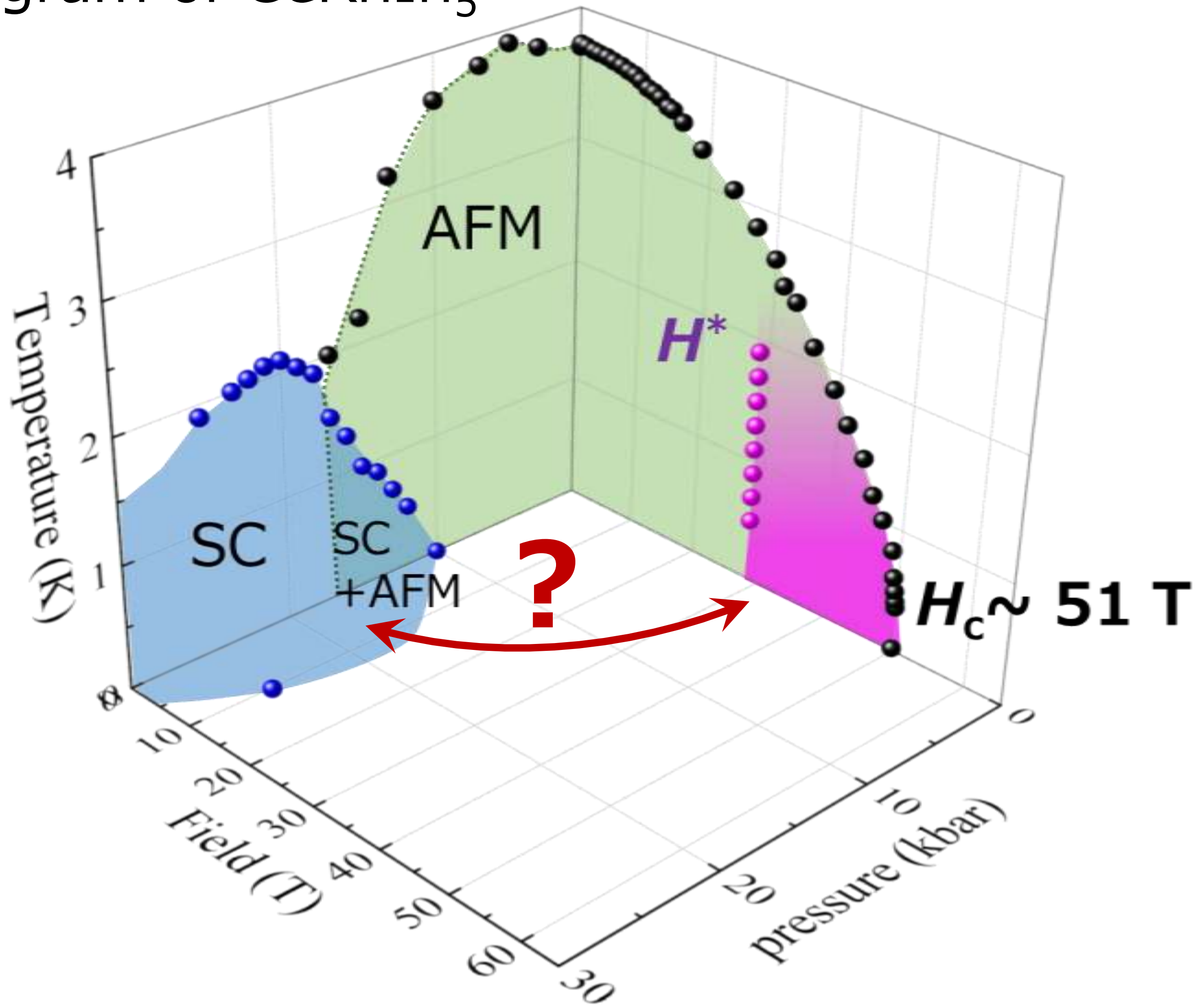
- Very weak lattice response in **Magnetostriction**

Electronic Nematic high-field phase

- Breaks rotational symmetry but sustains translational symmetry

(p,B) Phase diagram of $CeRhIn_5$

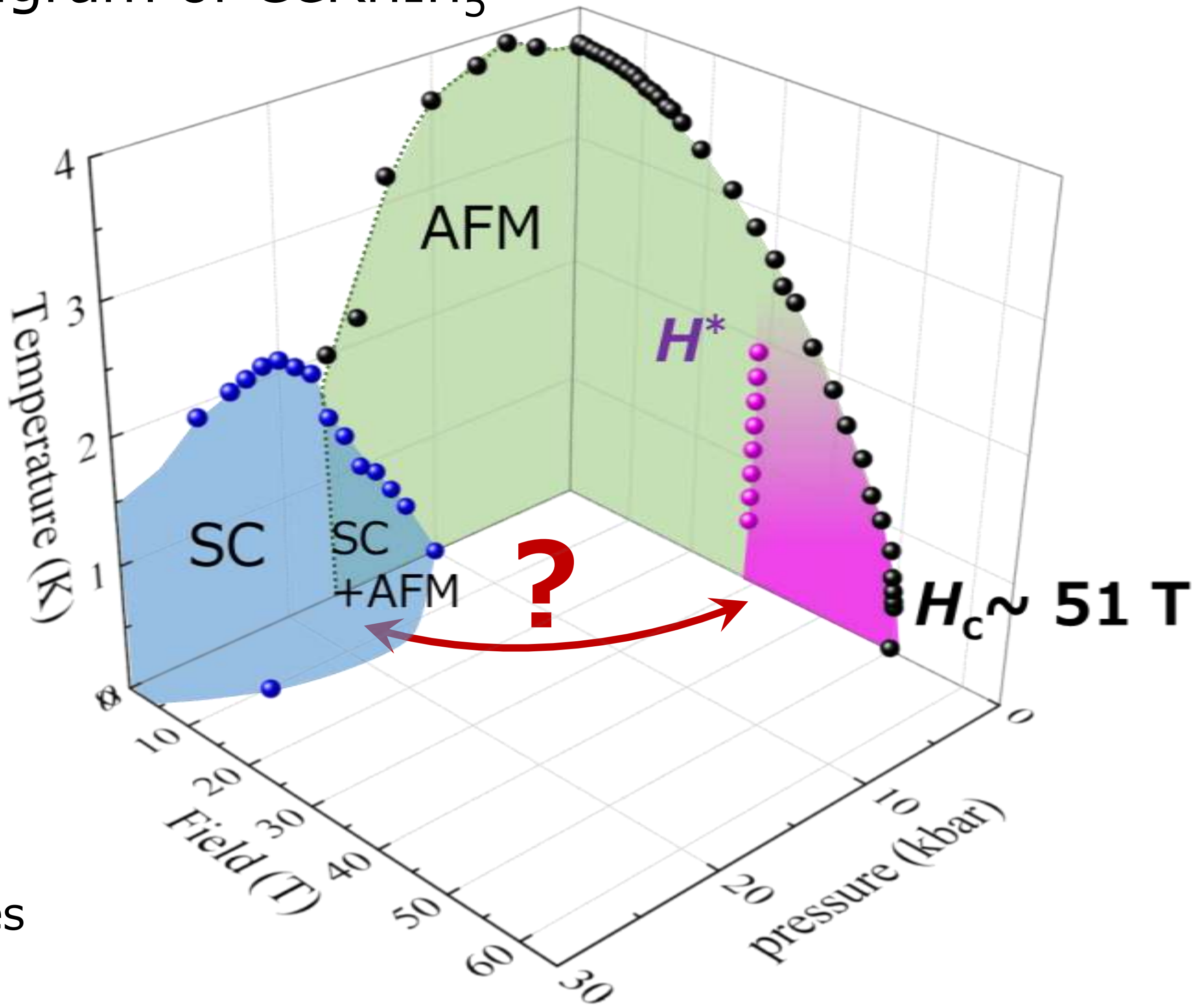




(p,B) phase diagram of $CeRhIn_5$

Experimental challenges:

- High conductivity $\rho_0 \approx 0.5\ \mu\Omega cm$
  - → Low signal/noise ratio
- Fast changing field $\frac{dB}{dt} \approx$ **10000 T/sec**
  - → Eddy current heating
- limited space
  - → VTI space **~ 8 mm**
  - → pressure cell sample space Ø **~ 100 µm**
- Strong friction forces
  - → Low success rate for **multiterminal** devices



Joint experiment

MPI CPFS, Dresden

www.miquamat.de

NHMFL Tallahassee

A. Grockowiak

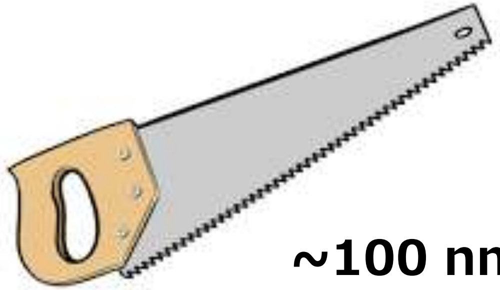
S. Tozer

NHMFL Los Alamos

F. Balakirev

J. B. Betts

FIB Micromachining



~100 nm

Moll et al.,
Ann. Rev. Cond. Mat. Phys. **9**, 147-162 (2018)

Hydrostatic pressure

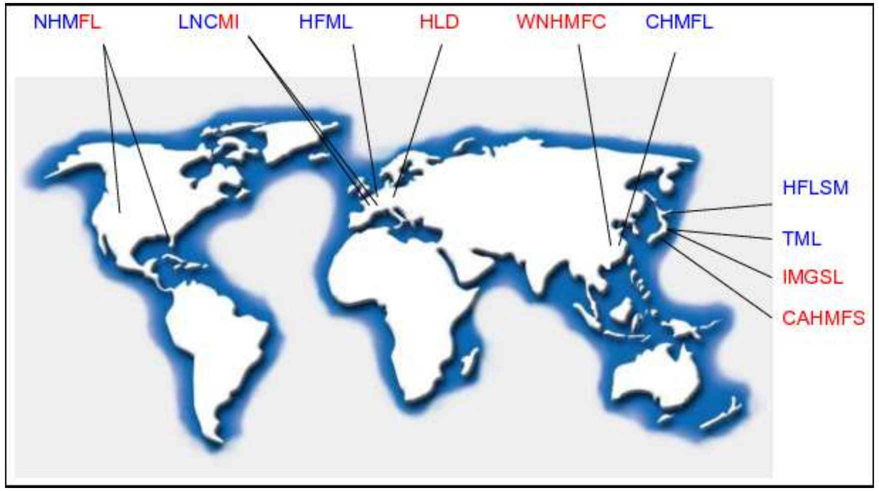
[Coniglio et al.,
High Pressure Research **33**, 425 (2013)]

High magnetic fields

The world's highest magnetic fields

NATIONAL MAGLAB

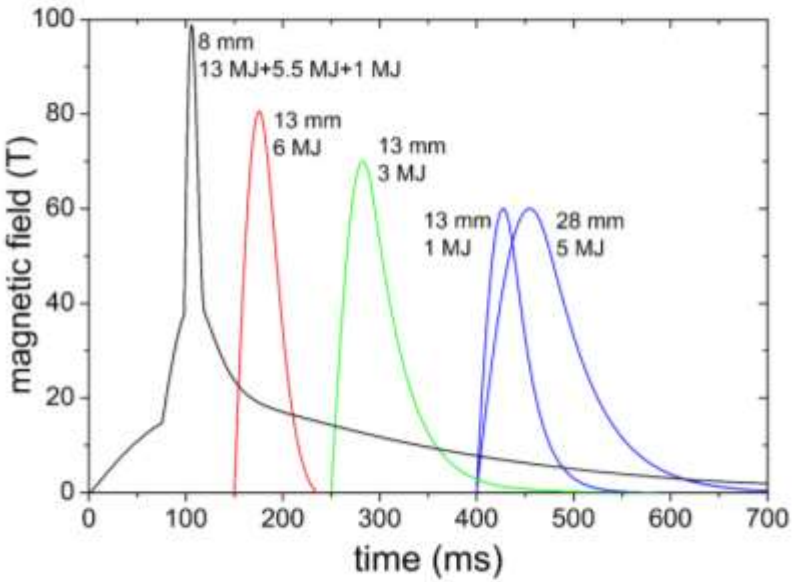
Los Alamos
(NM, USA)



EMFL
European Magnetic Field Laboratory

Dresden
(Germany)

1 Mega Joule Generator



50 Mega Joule Capacitor Bank

(p,B) Phase diagram of $CeRhIn_5$

Experimental challenges:

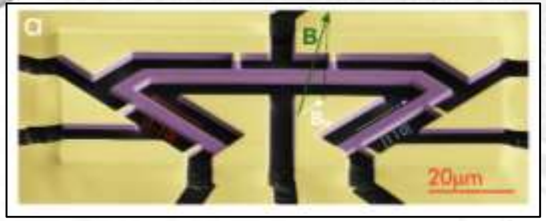
- High conductivity $\rho_0 \approx 0.5\mu\Omega cm$
  → Low signal/noise ratio
- Fast changing field $\frac{dB}{dt} \approx 10000\text{T/sec}$
  → Strong eddy current heating
- limited space for cryostat + pressure cell
  → VTI sample space **~ 8 mm**
  → pressure cell sample space Ø **~ 100 µm**
- Strong friction forces
  → Low success rate for multiterminal devices

Solutions:

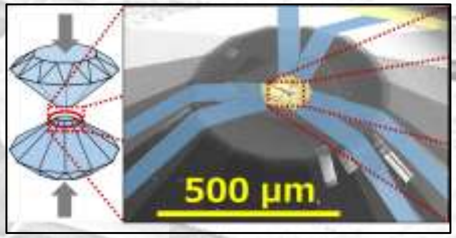
- Focused Ion beam (FIB) microstructuring
  → small cross sections ~ 1 μm^2
  → Optimized current paths
- **Plastic ^{3}He cryostats**
- Minaturized **Plastic Diamond-anvil pressure cells**
- Extremely robust FIB-Platinum leads

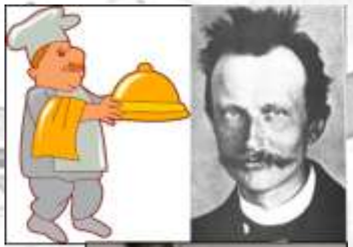
Summary

- Basics of FIB microfabrication



- New possibilities for studying quantum materials, such as unconventional superconductors





- Nematic high-field state in $CeRhIn_5$

Thank you for your attention

www.miquamat.de