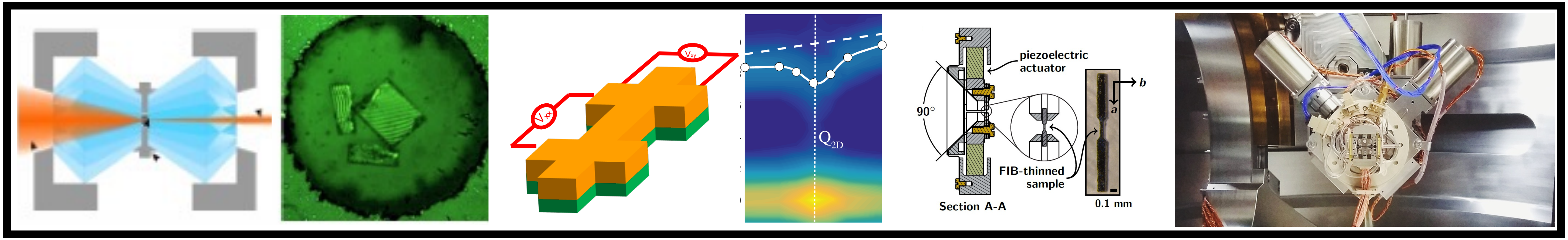
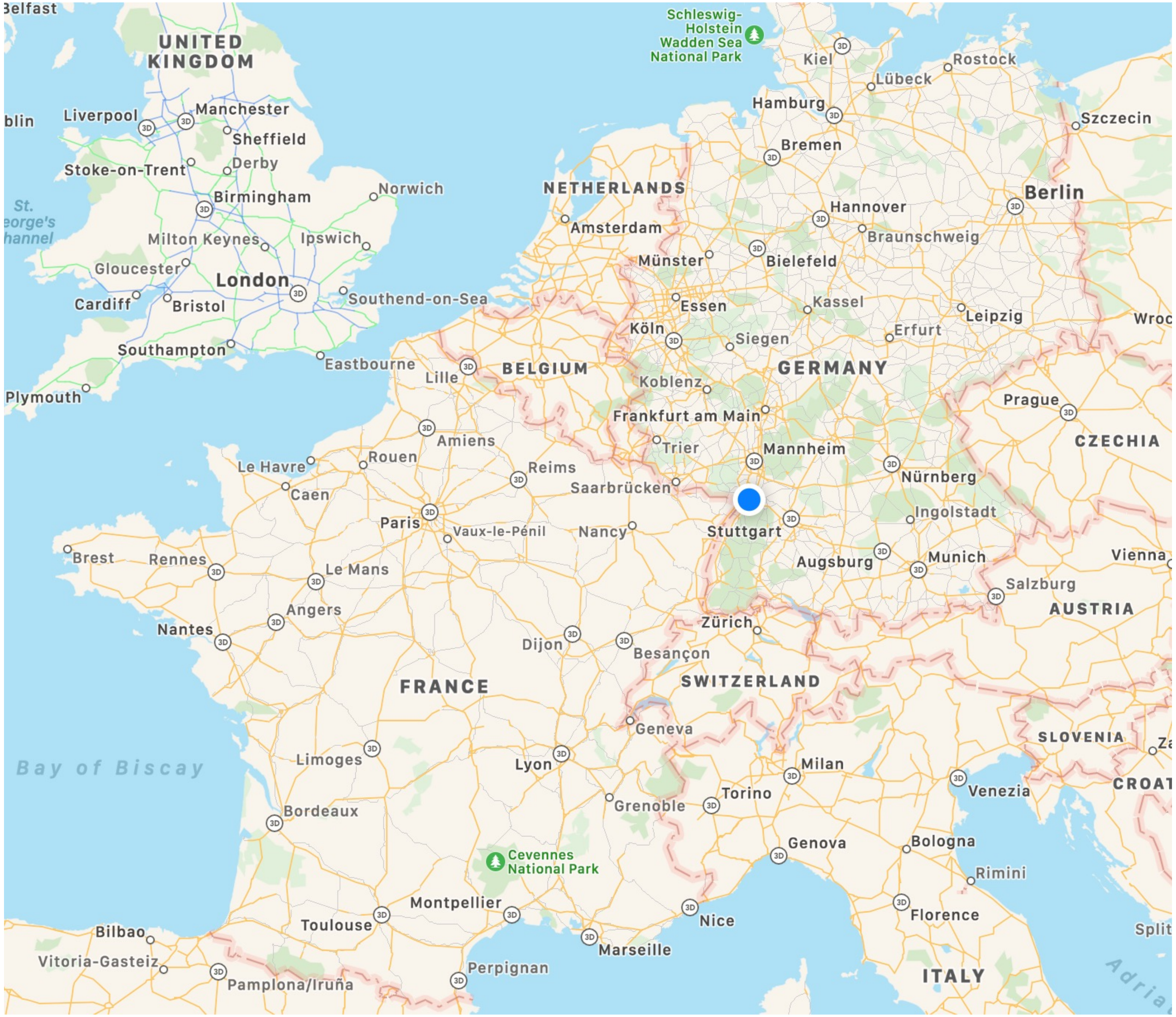
Tuning the electronic properties of Quantum Materials

Accorder les propriétés électroniques des matériaux quantiques

Matthieu Le Tacon

Institute for Quantum Materials and Technologies (IQMT)



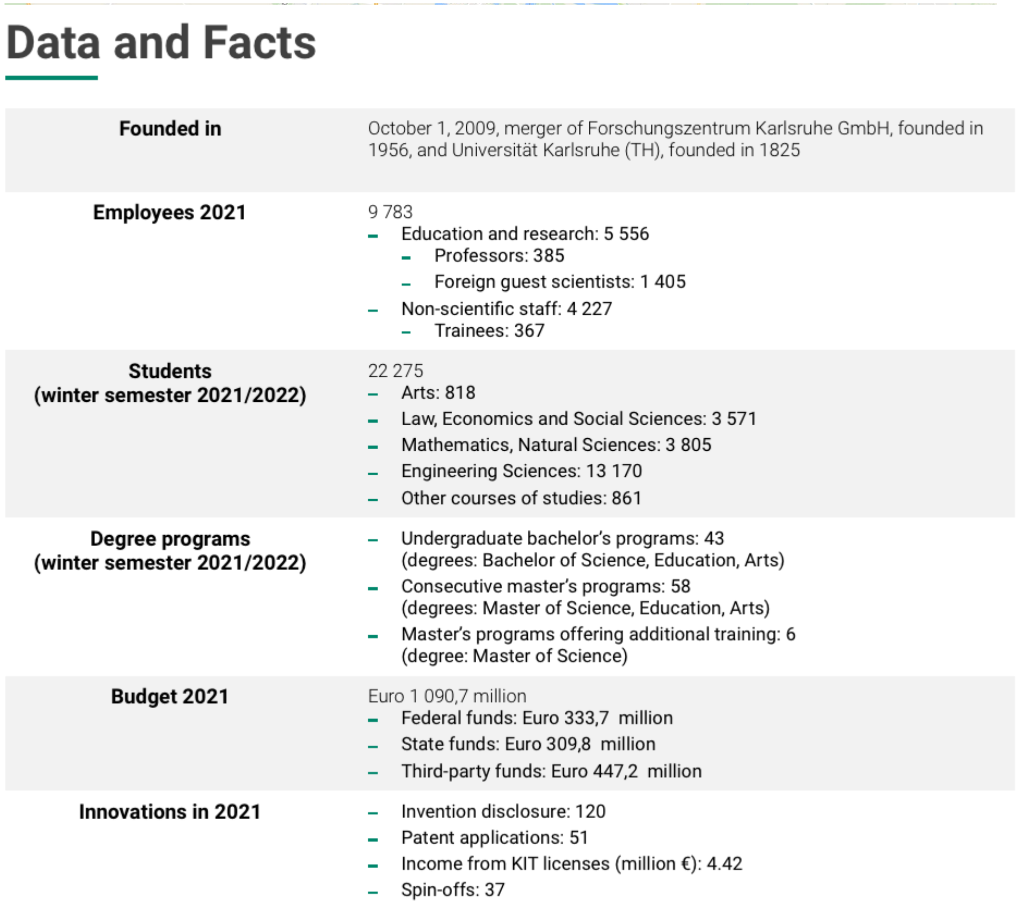


Heinrich Hertz (1857-1894)

Otto Lehmann (1855-1922)

(Liquid Crystals)

Universität Karlsruhe (TH)
Forschungsuniversität • gegründet 1825



Data and Facts

Founded in	October 1, 2009, merger of Forschungszentrum Karlsruhe GmbH, founded in 1956, and Universität Karlsruhe (TH), founded in 1825

Employees 2021	9 783
	– Education and research: 5 556
	  – Professors: 385
	  – Foreign guest scientists: 1 405
	– Non-scientific staff: 4 227
	  – Trainees: 367

Students (winter semester 2021/2022)	22 275 – Arts: 818 – Law, Economics and Social Sciences: 3 571 – Mathematics, Natural Sciences: 3 805 – Engineering Sciences: 13 170 – Other courses of studies: 861
Degree programs (winter semester 2021/2022)	– Undergraduate bachelor's programs: 43 (degrees: Bachelor of Science, Education, Arts) – Consecutive master's programs: 58 (degrees: Master of Science, Education, Arts) – Master's programs offering additional training: 6 (degree: Master of Science)
Budget 2021	Euro 1 090,7 million – Federal funds: Euro 333,7 million – State funds: Euro 309,8 million – Third-party funds: Euro 447,2 million
Innovations in 2021	– Invention disclosure: 120 – Patent applications: 51 – Income from KIT licenses (million €): 4.42 – Spin-offs: 37

arlsruhe Institute of Technology

Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft

the Research University
in the Helmholtz Association

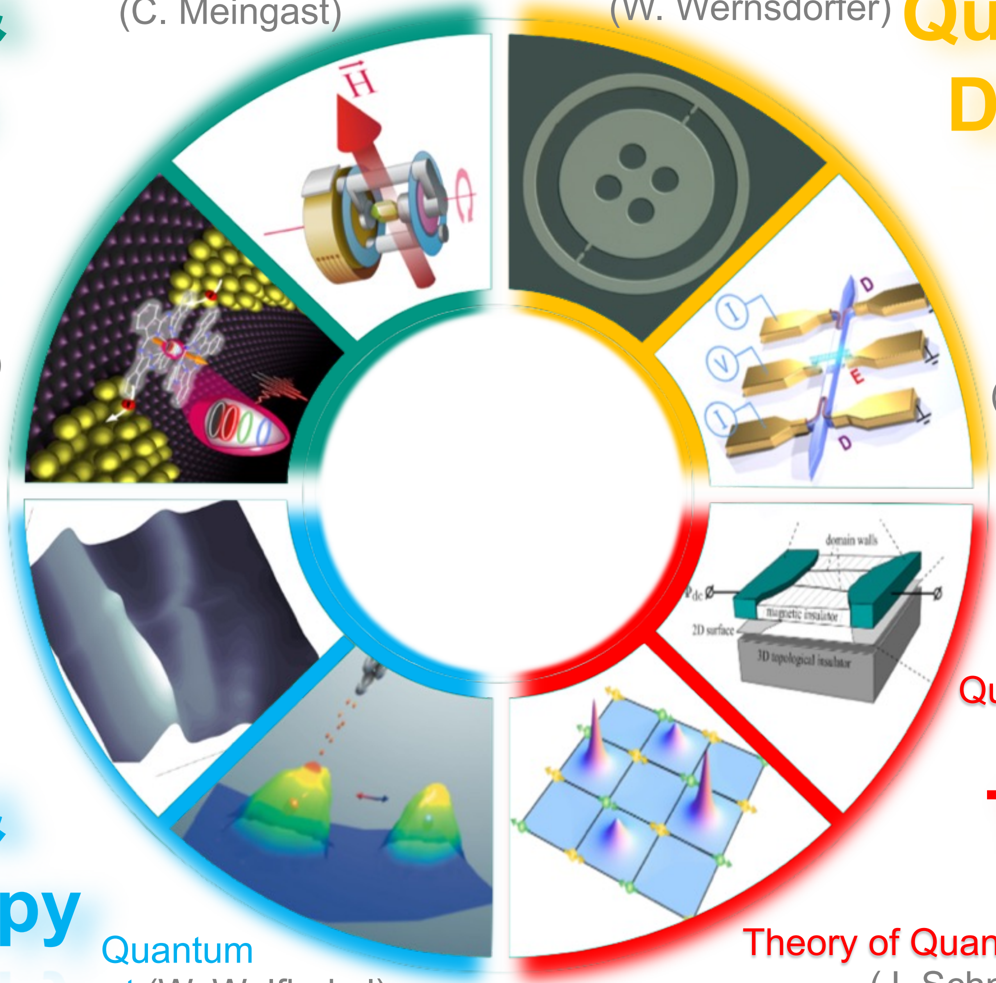
Karlsruher Institut für Technologie

1825
1956
2009

Exzellenzuniversität (2019)

Institute for **Quantum** **Materials** & **Technologies** (IQMT)

Karlsruhe Institute of Technology



Materials & Molecules

New Quantum materials (C. Meingast)

Quantum Molecular Systems (M. Ruben)

Quantum Devices

Quantum Circuits (W. Wernsdorfer)

Quantum Optical Devices (R. Krupke)

Transport & Spectroscopy

Spectroscopy of Quantum Materials (M. Le Tacon)

Quantum Transport (W. Wulfhekel)

Theory

Mesoscopic Quantum Systems (A. Mirlin)

Theory of Quantum Materials (J. Schmalian)

- ~~8~~ 9 Departments

ca. 120 staff (2022)

- Close Theory-Experiment Interactions
- Synthesis of new Quantum Materials
- Functionalisation
- Devices for Quantum technologies
- Building blocs for Quantum computer

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

What are quantum materials?

- Materials which electronic properties cannot be described as an assembly or essentially independent charge carriers (~ “electrons”)
- Semiconductors, band insulators or ‘simple metals’ on which most of our technology relies do generally not fall into the ‘quantum materials’ category

Copper
(Cu)

Silicium
(Si)

Quartz
(SiO_2)

- Superconductors in which the electrons condense into a macroscopic wavefunction, are.

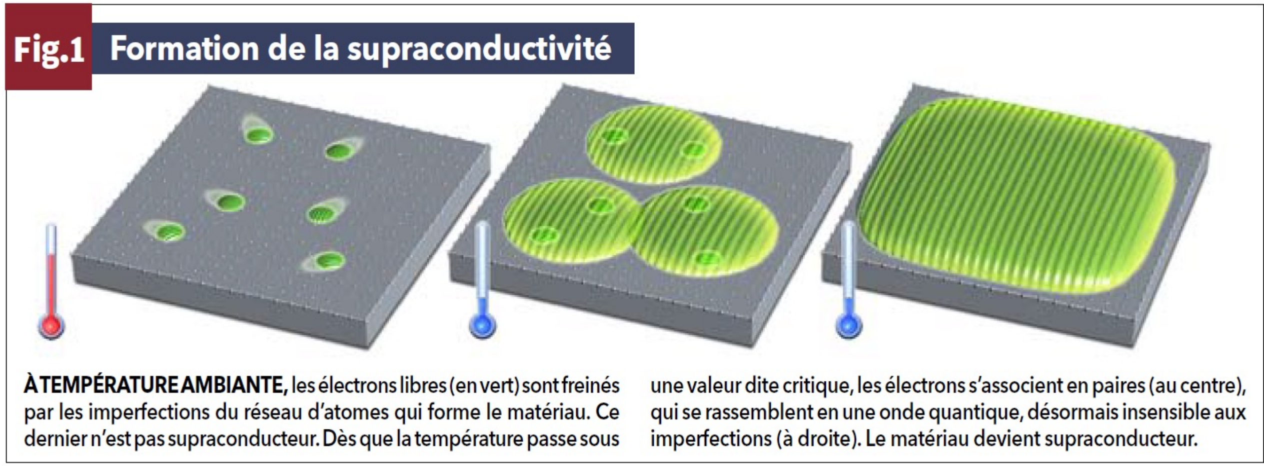


Fig.1 **Formation de la supraconductivité**

À TEMPÉRATURE AMBIANTE, les électrons libres (en vert) sont freinés par les imperfections du réseau d’atomes qui forme le matériau. Ce dernier n’est pas supraconducteur. Dès que la température passe sous une valeur dite critique, les électrons s’associent en paires (au centre), qui se rassemblent en une onde quantique, désormais insensible aux imperfections (à droite). Le matériau devient supraconducteur.

56 • La Recherche | OCTOBRE 2011 • N° 456

Quantum Materials

Emergence: ‚more is different‘

new properties or structures of a system as a result of the interaction of its elements

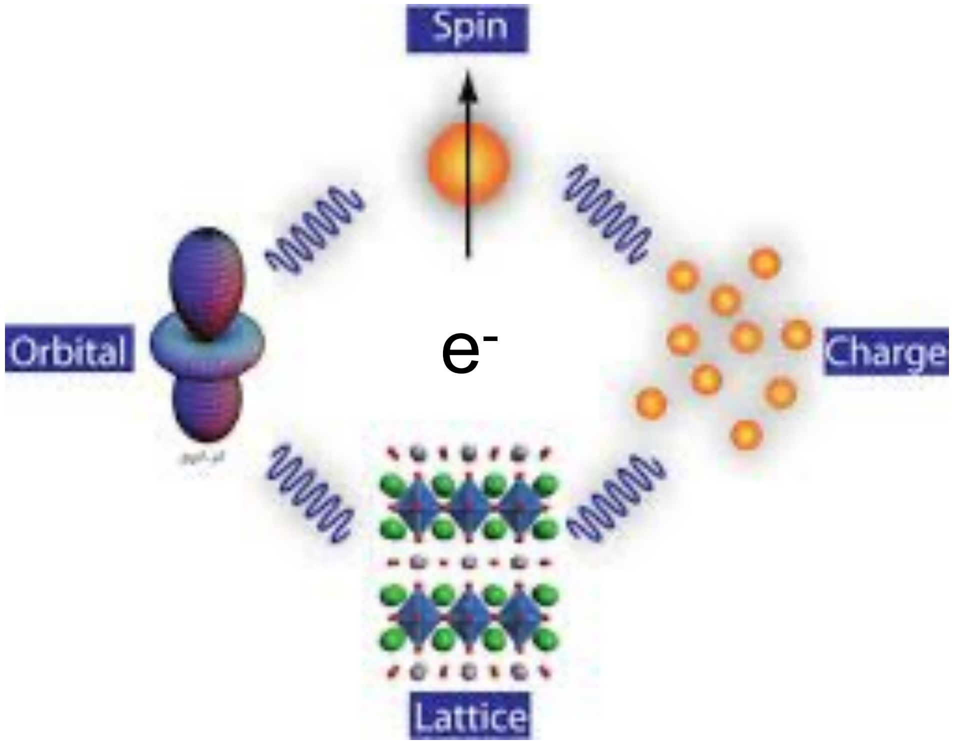
Topology: ‚not that different‘

Properties of mathematical structures that are preserved under continuous deformations.

Quantum Materials: a matter of energy scales

exchange interactions (J)

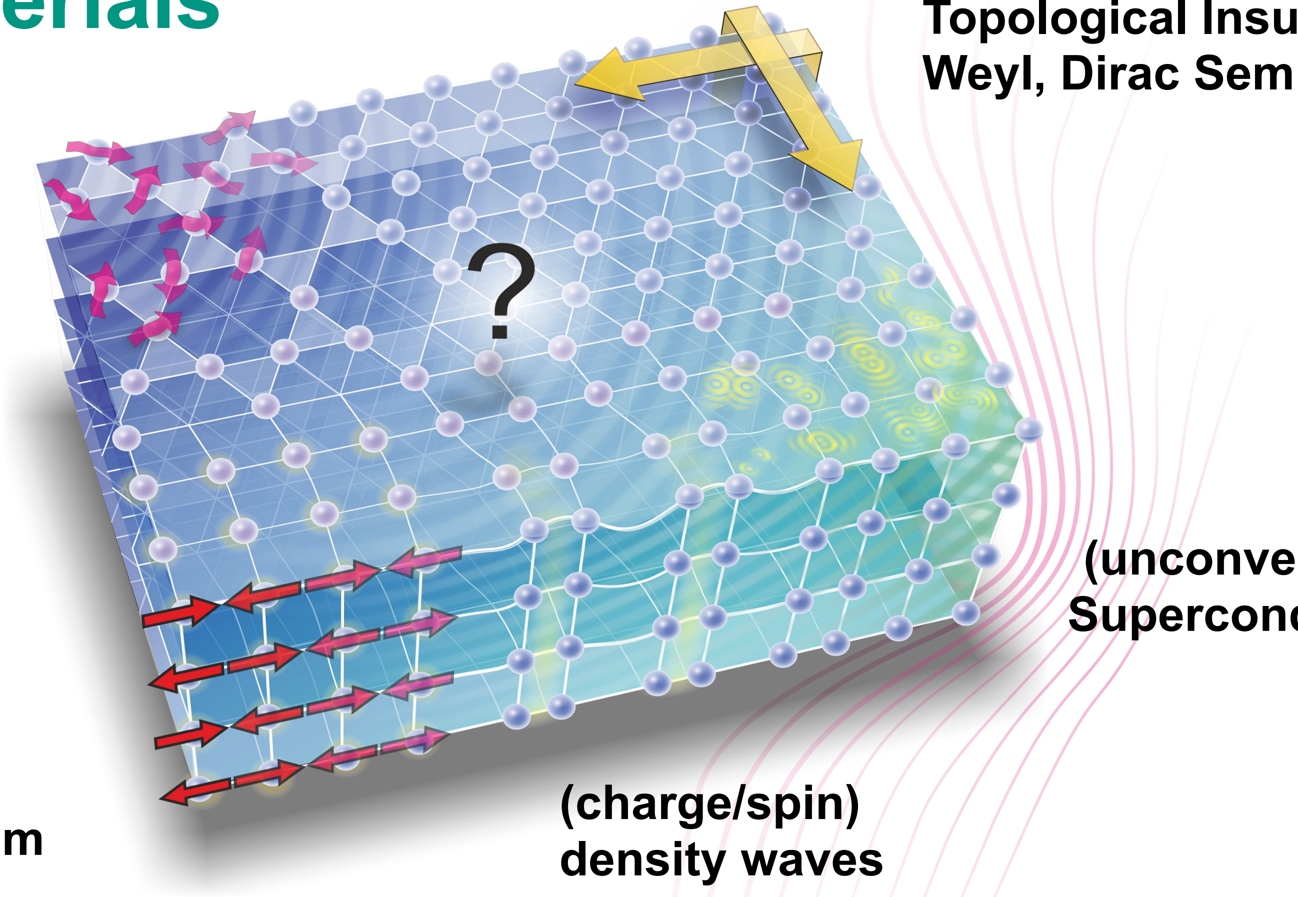
Spin-orbit coupling (λ)



hopping (t)

Coulomb Repulsion (U)

Quantum Materials



Topological Insulators
Weyl, Dirac Semimetals

Quantum Spin
Liquids

(unconventional)
Superconductivity

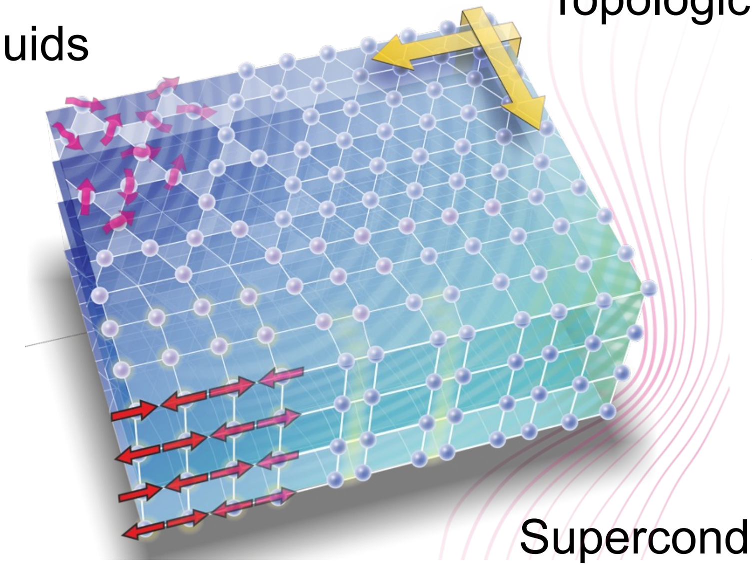
quantum
Magnetism

(charge/spin)
density waves

- Wide variety of ‘emergent’ physical phenomena
- Highly tunable materials: chemical composition, external stimuli (Pressure, Field etc..)
- **Goal: understand the interplay between electronic orders**

From quantum materials to quantum devices

- **A wealth of macroscopic quantum states in quantum materials**

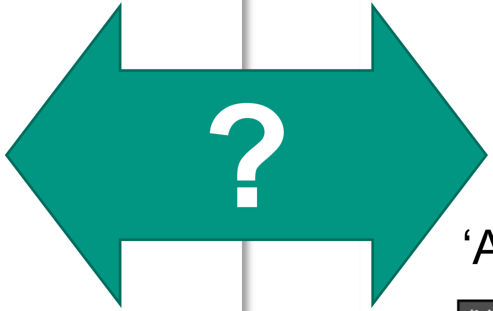


Topological states

Spin liquids

Superconductivity

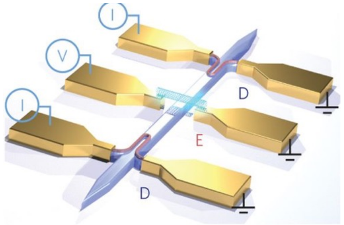
Magnetism



?

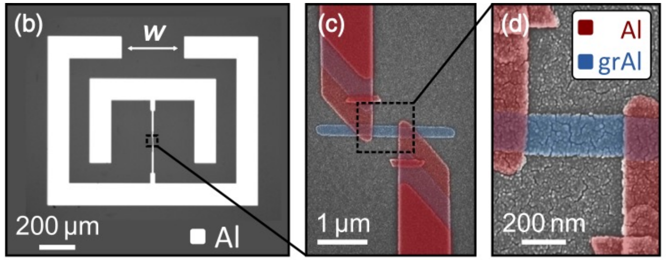
- **Need for functional quantum devices**

Single/entangled photon sources as quantum emitters



He et al. **Nature Materials** 2018

'Artificial atoms': superconducting circuits



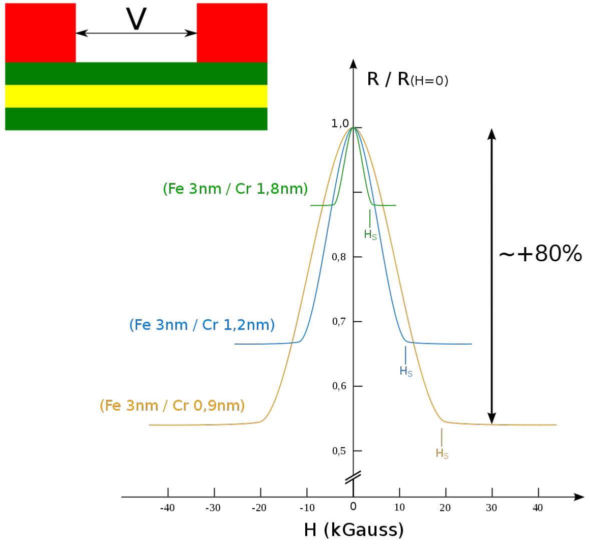
Winkel et al.
PRX 2020

- Quantum materials are generally relevant for (quantum) technology
- Quantum technology can accelerate the research on quantum materials

‘Was kann man damit bauen?’

‘A deeply original behavior always results – at some point – on an economically viable application’

(H. Alloul & H. J. Schulz – Physique des électrons dans les solides)



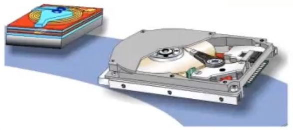
Fert, Grünberg (1987)

Spintronic technologies evolution

HDD Spin Valve & MTJ read heads

1988-1991
GMR
Spin Engineering
- Oscillatory interlayer coupling
- Co/Cu
- Interface spin-dependent scattering
- Dusting layers

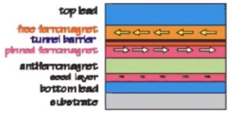
1997
Spin-valve recording heads (mass-production)



2007
Magnetic Tunnel Junction recording heads (mass production)

2015
Slow-down of increased HDD capacity

MRAM



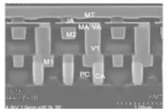
1995
MTJ based MRAM proposal

1996
Spin transfer torque (STT) switching

1999
1 kbit array
High MR
Low RA
0.25 μm
2.3 ns R/W

2001
Giant TMR using MgO

2005
16 Mbit demonstrator (180nm CMOS)
Field switched



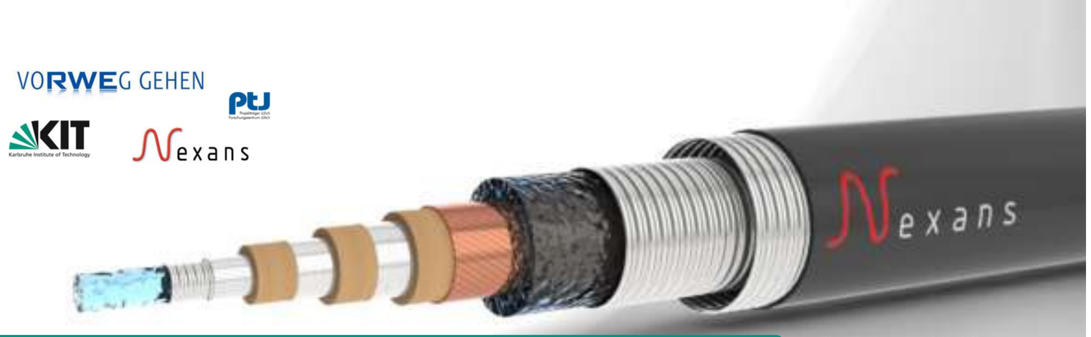
2019
Samsung announces shipment of high-performance foundry 28nm CMOS STT e-MRAM

Stuart Parkin
MPI Halle

‘Was kann man damit bauen?’

‘A deeply original behavior always results – at some point – on an economically viable application’

(H. Alloul & H. J. Schulz – Physique des électrons dans les solides)




POWER NETWORKS - SUPERCONDUCTIVITY

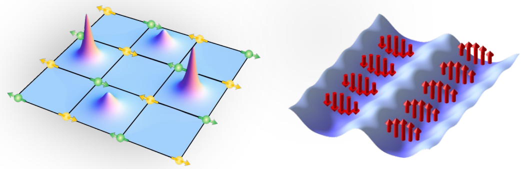
A world-first in France at Montparnasse train station: Nexans installs superconducting cables to strengthen and secure the power supply

JUN 9, 2022

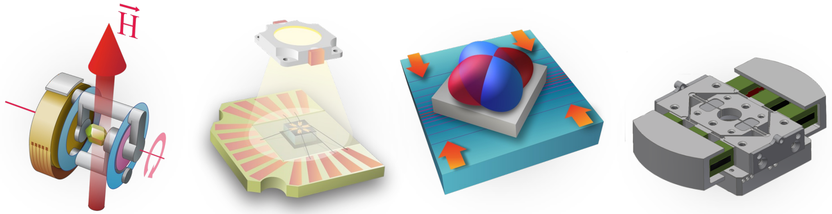
A Quantum Materials optimization loop

- **Design** materials
with tailored electronic properties
& functionalities

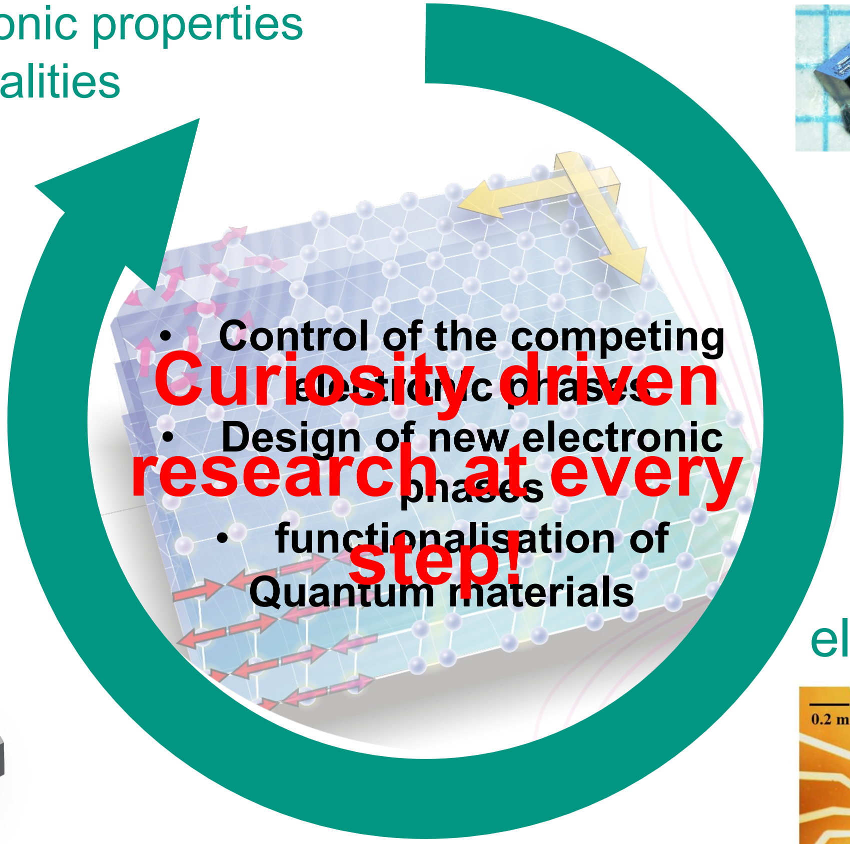
- **Model**
predict new electronic properties



- **Develop** new tuning knobs
to induce novel electronic states of matter



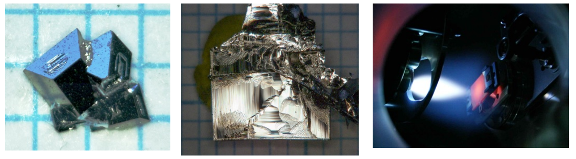
Strain tuning, symmetry breaking



- Control of the competing electronic phases
- Design of new electronic phases
- functionalisation of Quantum materials

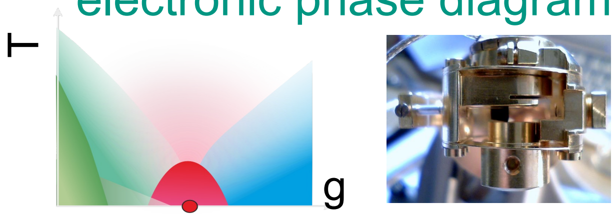
Curiosity driven research at every step!

- **Synthesis**
Growth of new quantum materials



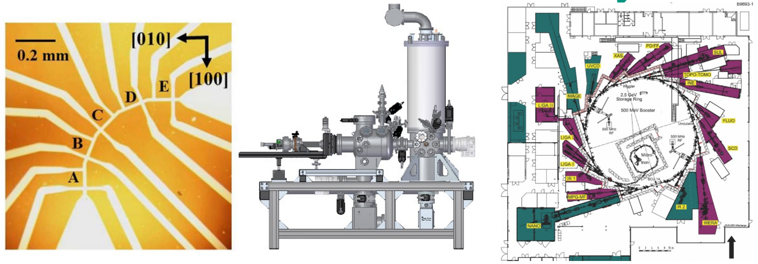
single crystals,
thin films,
interfaces,
monolayers

- **Mapping**
electronic phase diagram

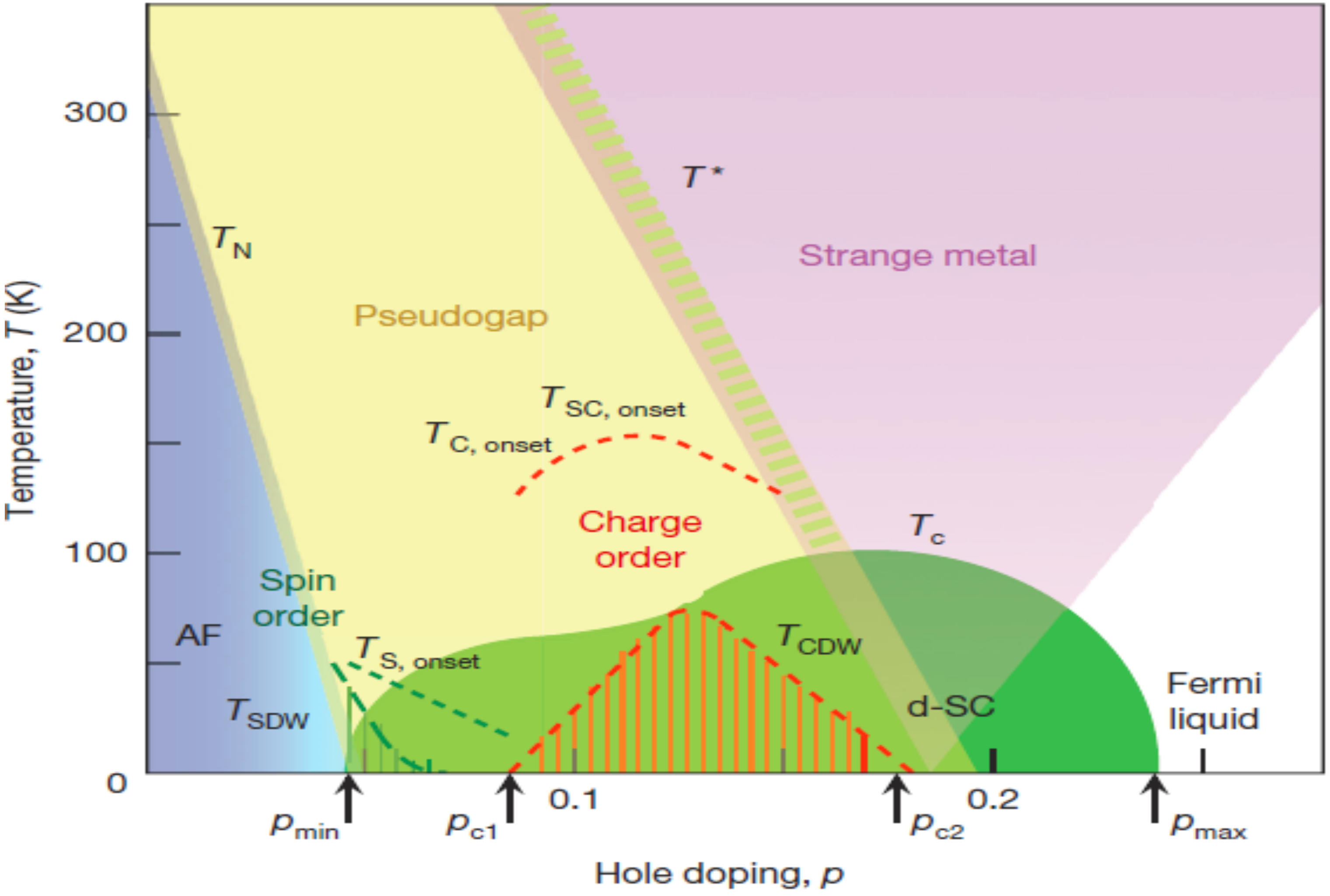


Coexisting, competing & intertwined orders

- **Understand**
electronic structure and dynamics

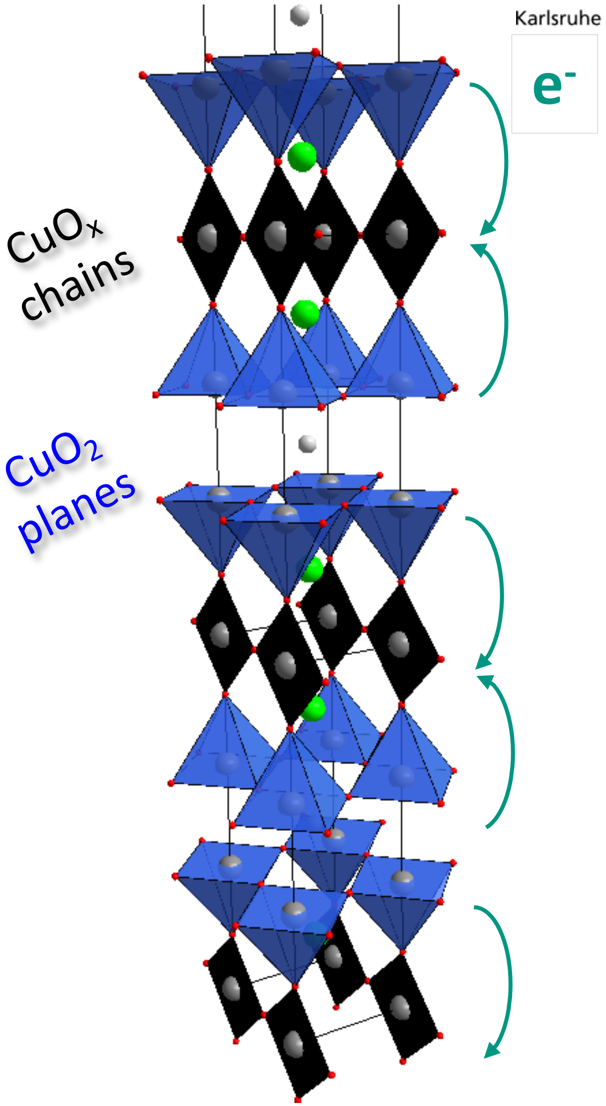


High-Tc Cuprates

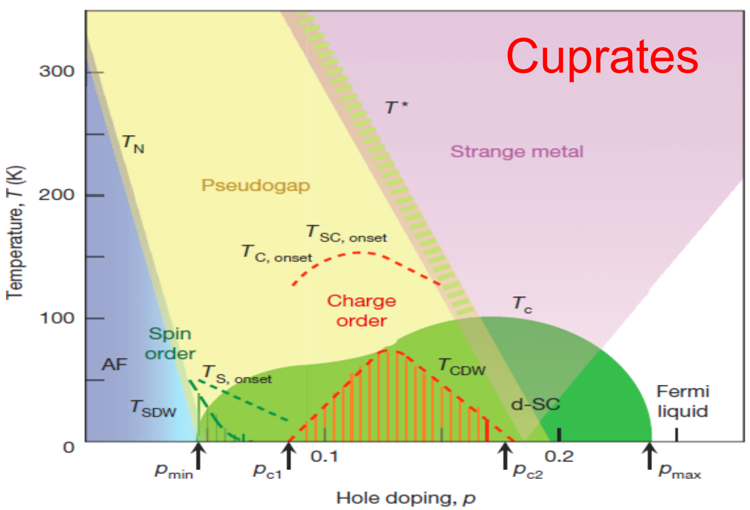


B. Keimer et al. Nature **518**, 179 (2015)

$YBa_2Cu_3O_{6+x}$



Elastic tuning of the electronic state of high-Tc cuprates



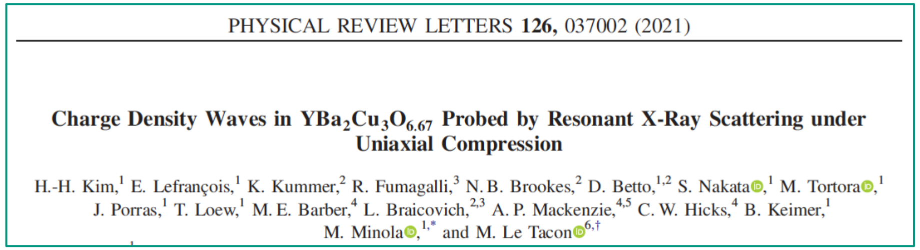
B. Keimer et al. Nature **518**, 179 (2015)

Kim *et al.*, *Science* **362**, 1040–1044 (2018) 30 November 2018

SUPERCONDUCTIVITY

Uniaxial pressure control of competing orders in a high-temperature superconductor

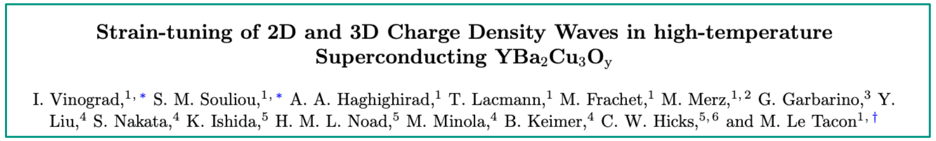
H.-H. Kim[1]*, S. M. Souliou[2]*†, M. E. Barber[3], E. Lefrançois[1,2], M. Minola[1], M. Tortora[1]‡, R. Heid[4], N. Nandi[3], R. A. Borzi[5], G. Garbarino[2], A. Bosak[2], J. Porras[1], T. Loew[1], M. König[3], P. M. Moll[3], A. P. Mackenzie[3,6], B. Keimer[1], C. W. Hicks[3], M. Le Tacon[4]§



PHYSICAL REVIEW LETTERS **126,** 037002 (2021)

Charge Density Waves in $YBa_2Cu_3O_{6.67}$ Probed by Resonant X-Ray Scattering under Uniaxial Compression

H.-H. Kim,[1] E. Lefrançois,[1] K. Kummer,[2] R. Fumagalli,[3] N. B. Brookes,[2] D. Betto,[1,2] S. Nakata,[1] M. Tortora,[1] J. Porras,[1] T. Loew,[1] M. E. Barber,[4] L. Braicovich,[2,3] A. P. Mackenzie,[4,5] C. W. Hicks,[4] B. Keimer,[1] M. Minola,[1,*] and M. Le Tacon[6,†]



Strain-tuning of 2D and 3D Charge Density Waves in high-temperature Superconducting $YBa_2Cu_3O_y$

I. Vinograd,[1,*] S. M. Souliou,[1,*] A. A. Haghighirad,[1] T. Lacmann,[1] M. Frachet,[1] M. Merz,[1,2] G. Garbarino,[3] Y. Liu,[4] S. Nakata,[4] K. Ishida,[5] H. M. L. Noad,[5] M. Minola,[4] B. Keimer,[4] C. W. Hicks,[5,6] and M. Le Tacon[1,†]

- Pressure/stress is a good tool to investigate the interplay between SC and CDW orders

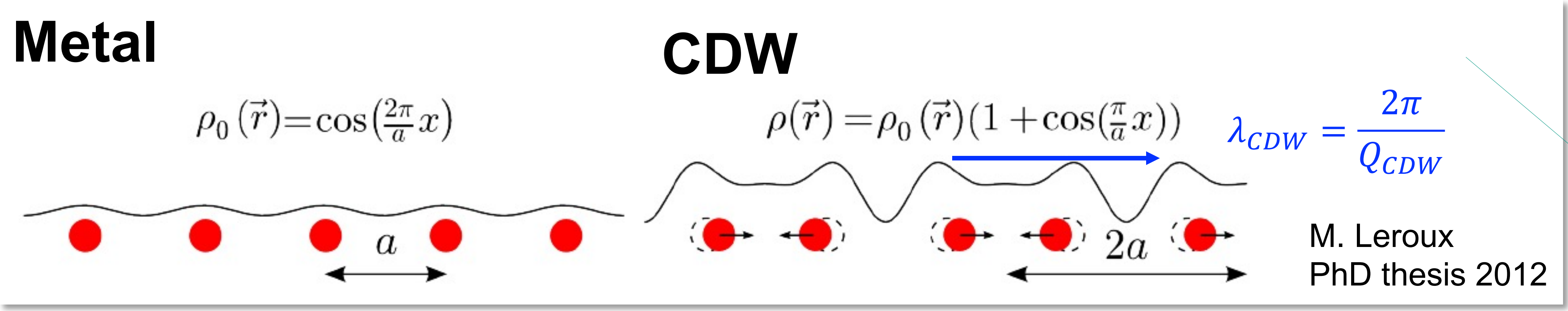
S. M. Souliou, I. Vinograd, R. Heid
A. Haghighirad, M. Merz, T. Lacmann

C.W. Hicks, M. E. Barber,
H. Noad, K. Ishida, A.P. Mackenzie

H.-H. Kim, E. Lefrançois, H. Gretarsson,
M. Minola, S. Nakata, B. Keimer

A. Bosak, G. Garbarino, M. Krisch
N. Brookes, K. Kummer

Charge Density Wave?

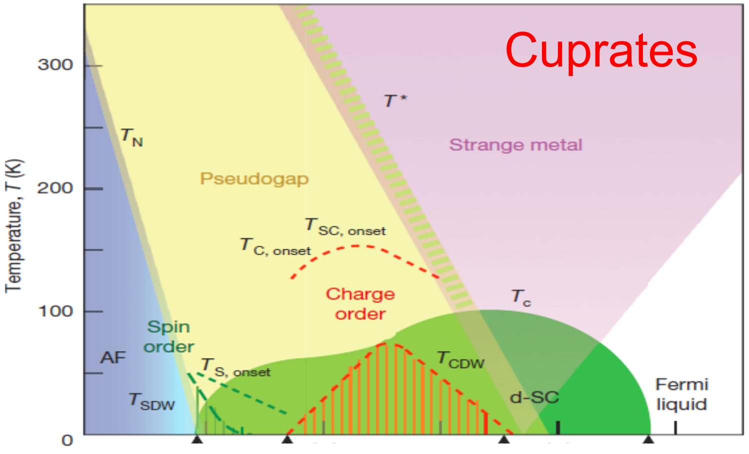


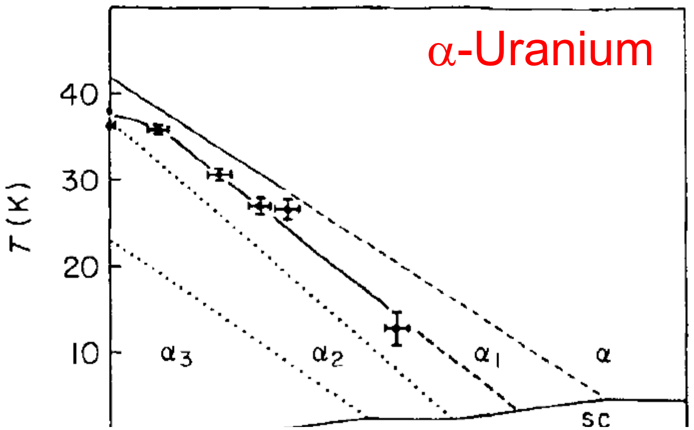
M. Leroux
PhD thesis 2012

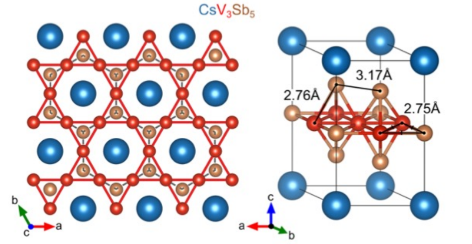
Instability of a metallic system towards the formation of a periodic modulation of the charge density

Original prediction: R. Peierls in the 50s on 1D chains

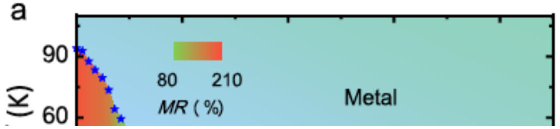
Charge density waves and superconductivity….





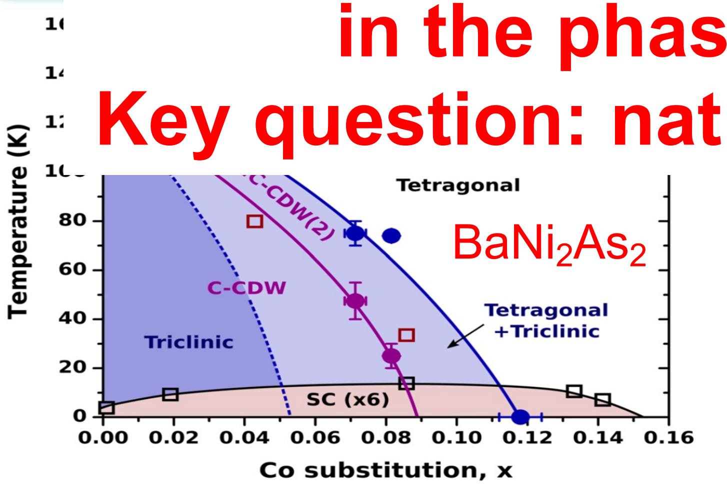


Ortiz *et al.* Phys. Rev. Lett. **125**, 247002 (2020)

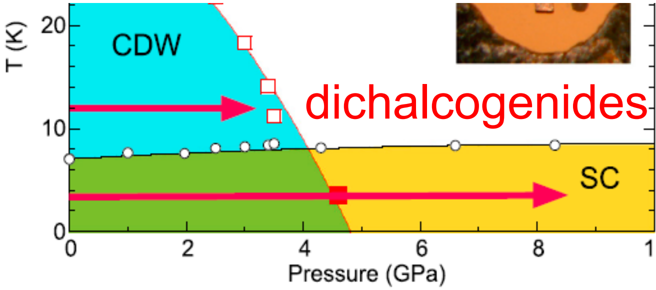


CDWs appear close to superconductivity in the phase diagrams of many quantum materials.

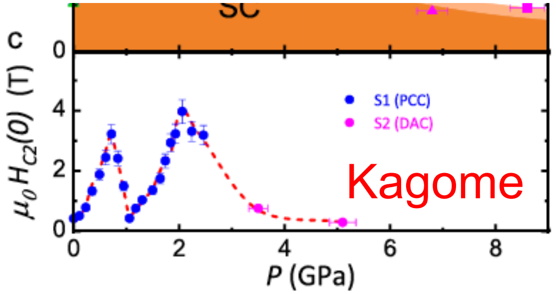
Key question: nature of the interplay between these two orders?



Lee *et al.* Phys. Rev. Lett. 122, 147601 (2019)



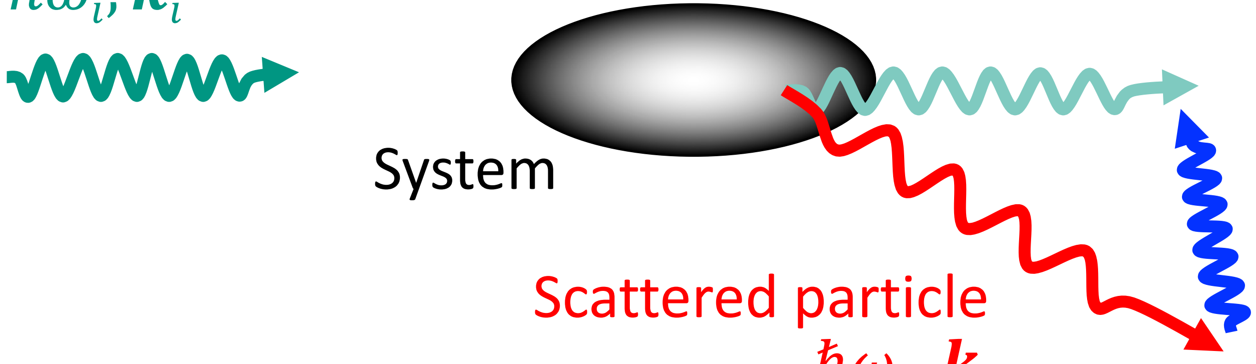
Feng et al. PNAS **109** 7224 (2012)



Yu *et al.* Nat. Comm. **12**, 3645 (2021)

Scattering as a probe

Neutrons
Photons
Electrons



Incident particle

$\hbar\omega_i, \boldsymbol{k}_i$

Initial Final

$|\varphi_i\rangle \Rightarrow |\varphi_f\rangle$

System

$\hbar\omega, \vec{Q}$

Scattered particle

$\hbar\omega_s, \boldsymbol{k}_s$

Conservation Laws

$\hbar\omega = \hbar\omega_i - \hbar\omega_s$ Energy transferred to the system

$\boxed{\hbar\omega = 0 \Rightarrow \text{Static correlations (Structure)}}$

$\hbar\omega \neq 0 \Rightarrow$ dynamics - Excitations

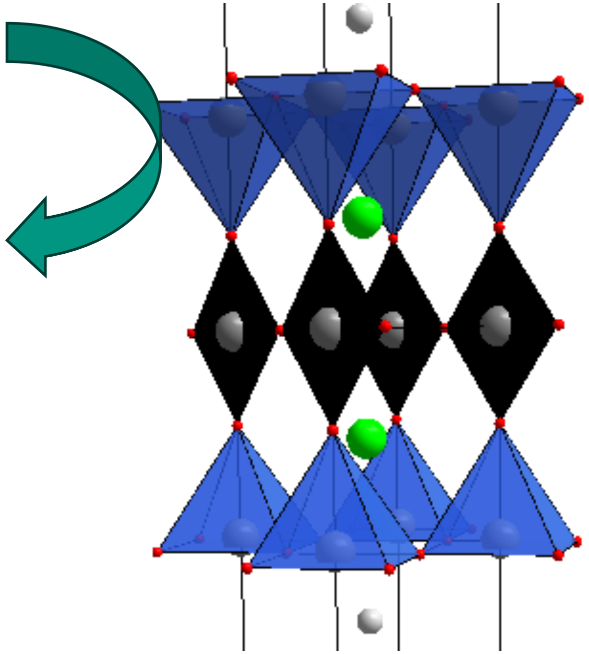
$\boldsymbol{Q} = \boldsymbol{k}_i - \boldsymbol{k}_s$ Momentum transferred to the system

$\boxed{\boldsymbol{Q} = 0 \text{ (mod. } G_{hkl}) \Rightarrow \text{homogeneous correlations}}$

$\boldsymbol{Q} \neq 0 \Rightarrow$ inhomogeneous correlations, dispersion

Tuning parameters for superconductivity in the cuprates

Chemical doping



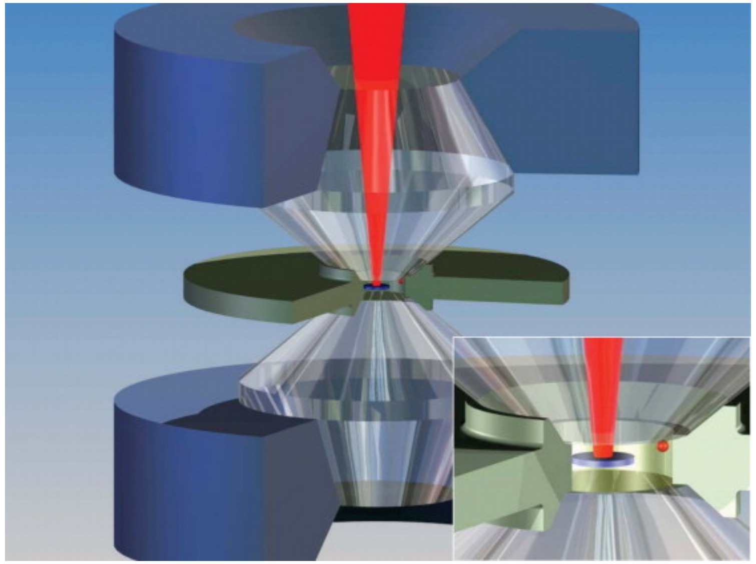
Novel synthesis for each doping - disorder

Magnetic field

LNCMI Grenoble

Very large fields needed to suppress SC
~25 T < H < ~150 T

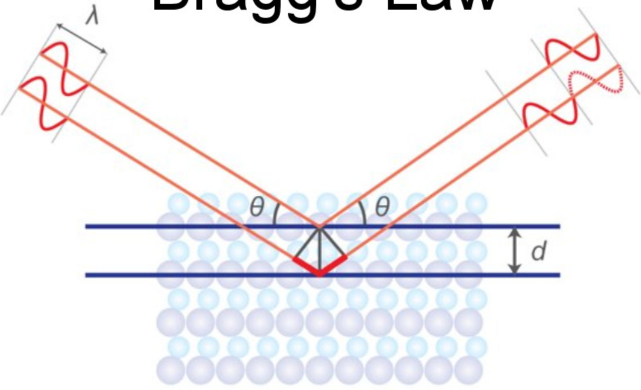
Pressure



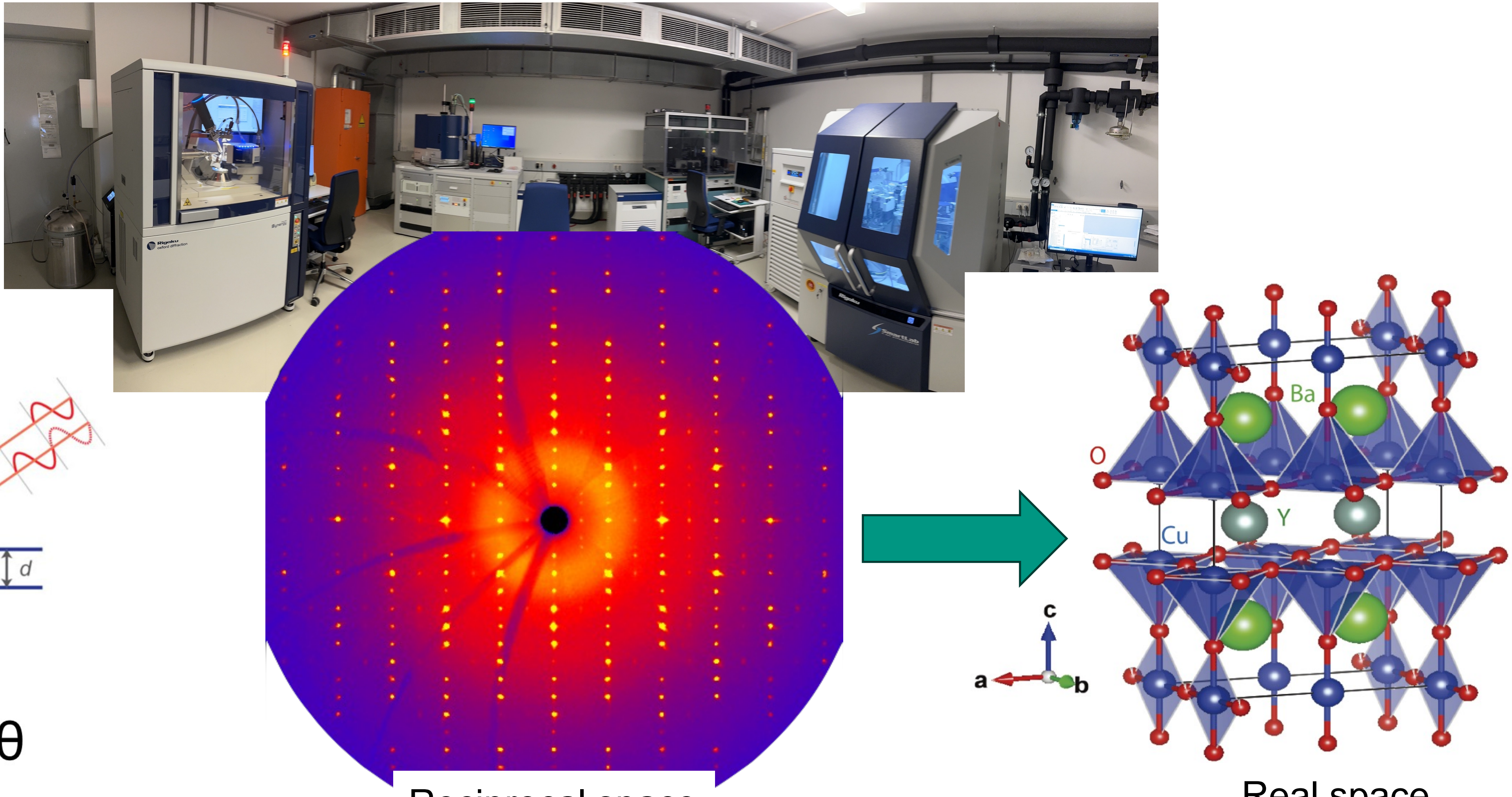
Small quantities of materials to study

Charge Density Wave in the Cuprates

Bragg's Law



$$n\lambda = 2d\cdot\sin\theta$$

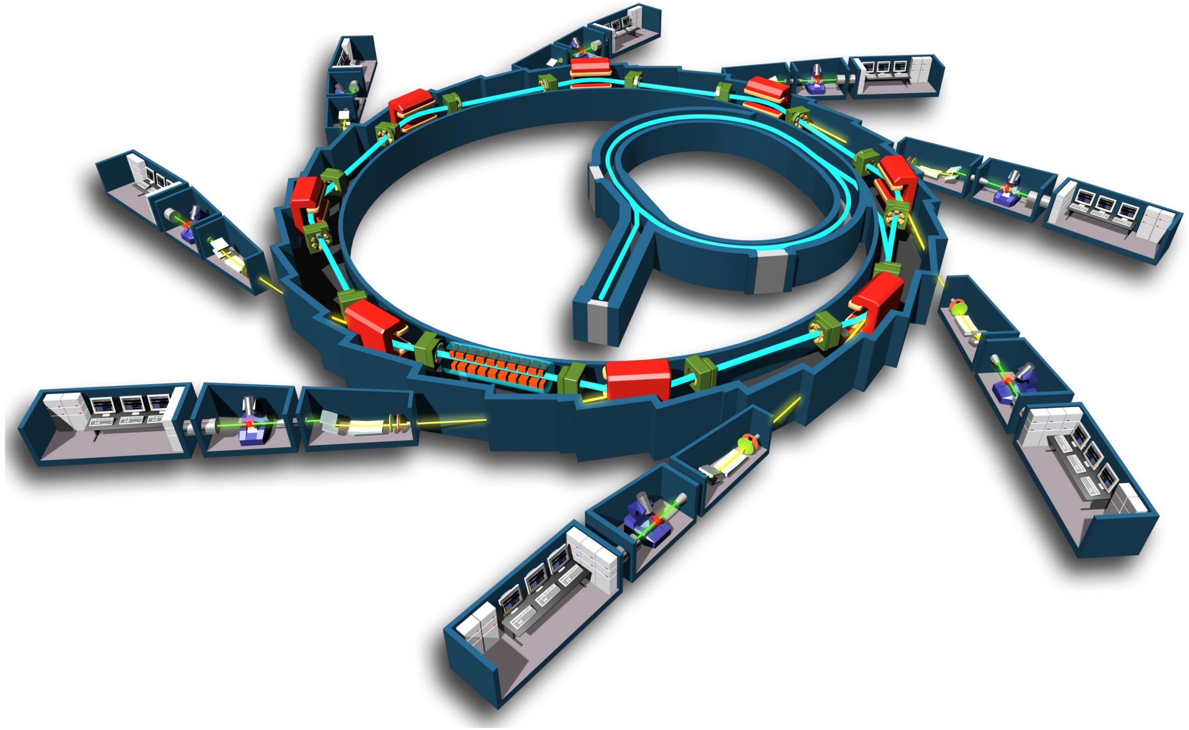


Reciprocal space

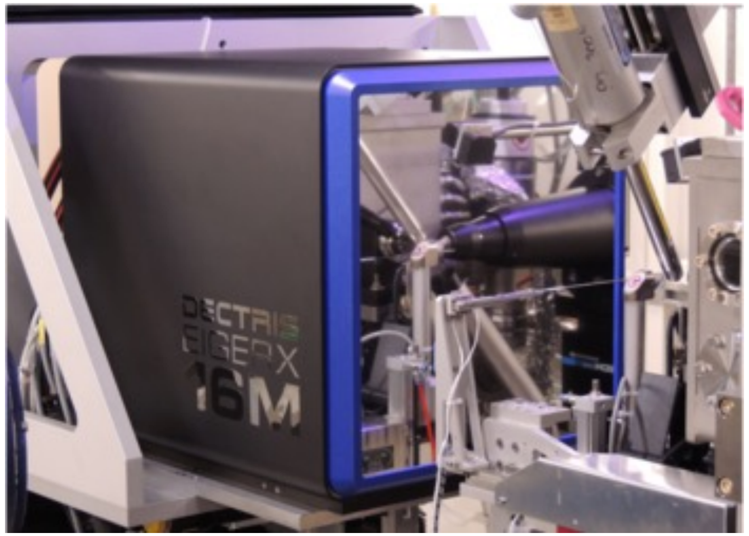
Real space

Charge Density Wave in the Cuprates

Brighter x-ray sources (synchrotron radiation facilities)

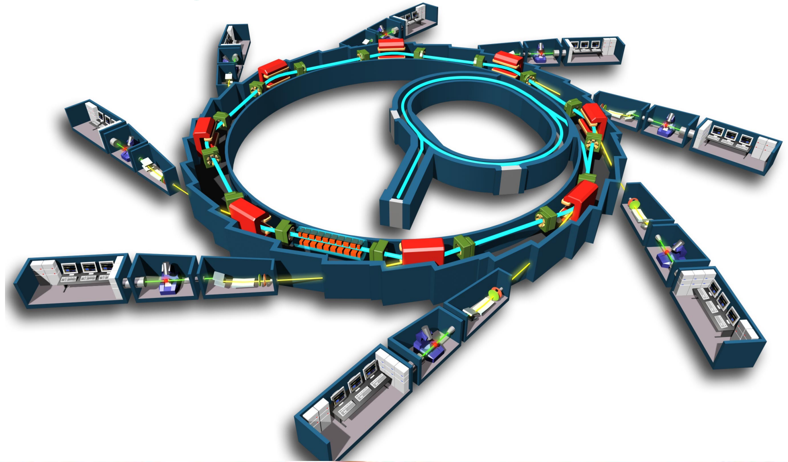


Latest generation detectors

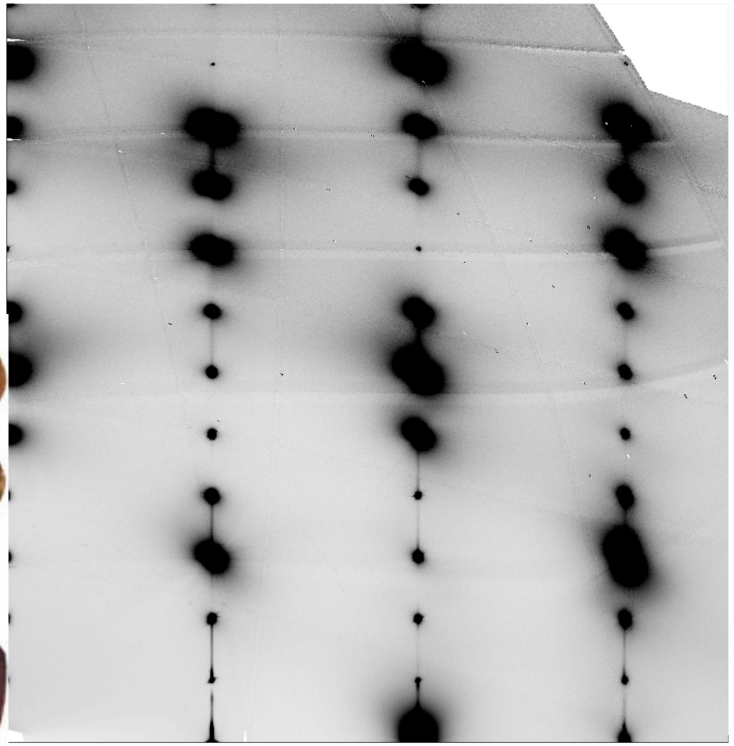


- Huge dynamical range
- No background
- No cross-talk

Charge Density Wave in the Cuprates

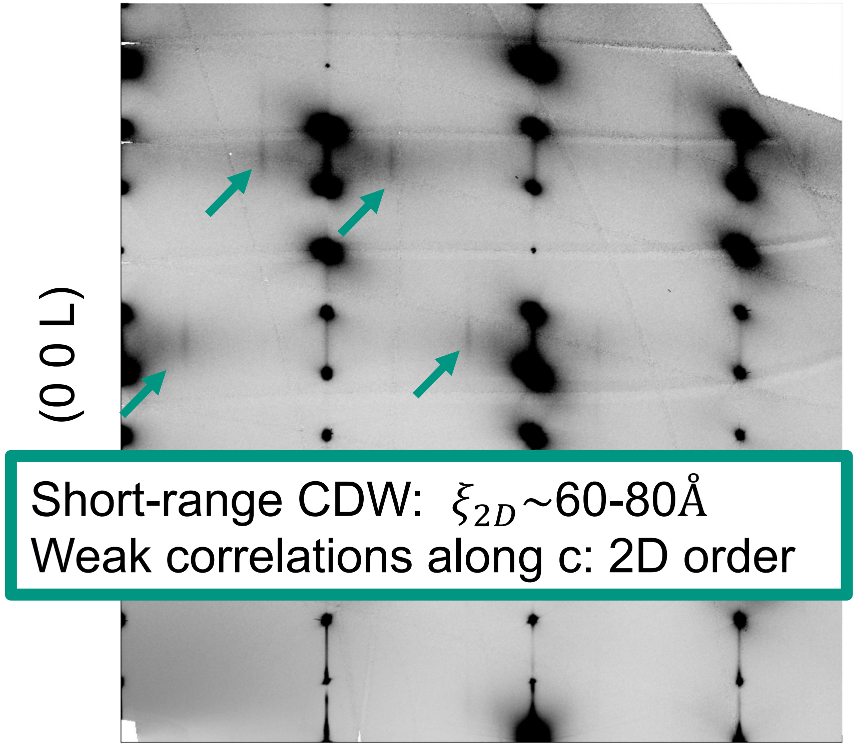


(0 K L) plane at Room Temperature



(0 K 0)

(0 K L) plane at 90 K

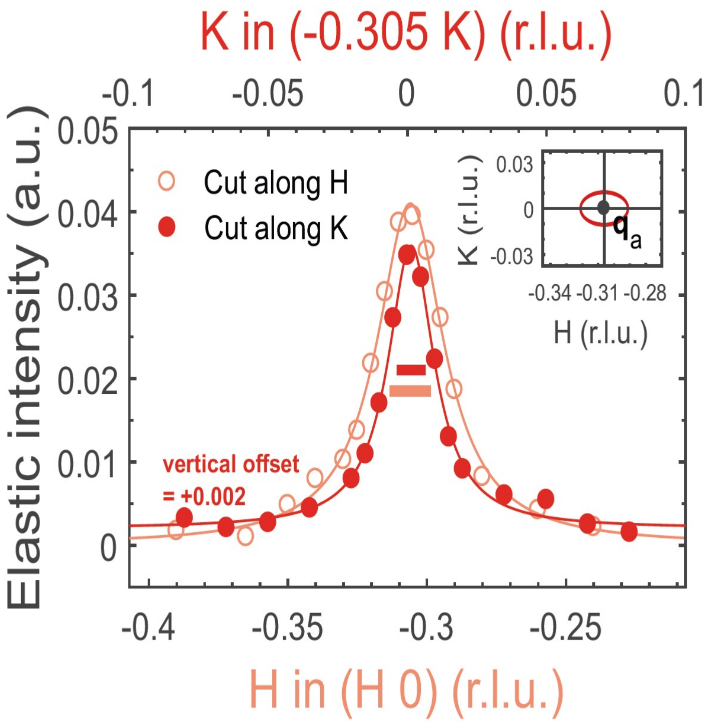


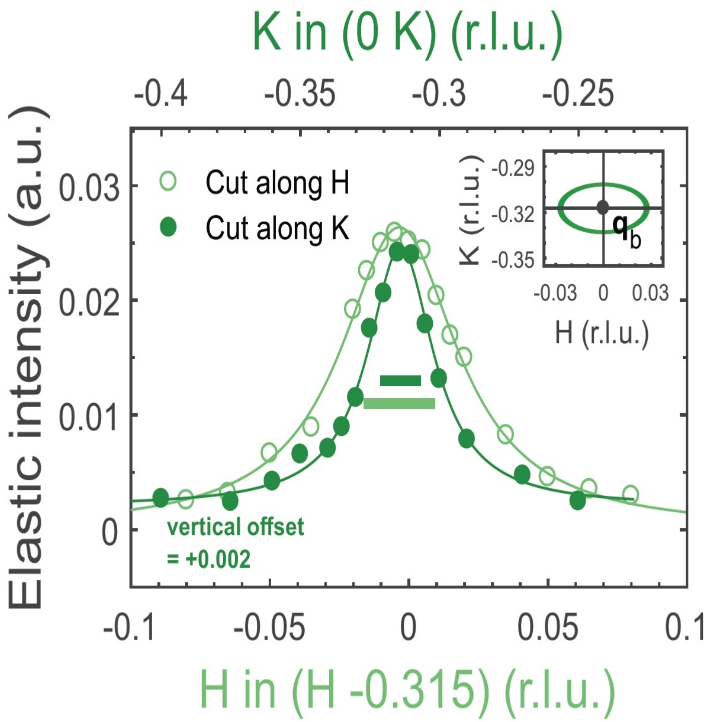
Short-range CDW: ξ_{2D}~60-80Å
Weak correlations along c: 2D order

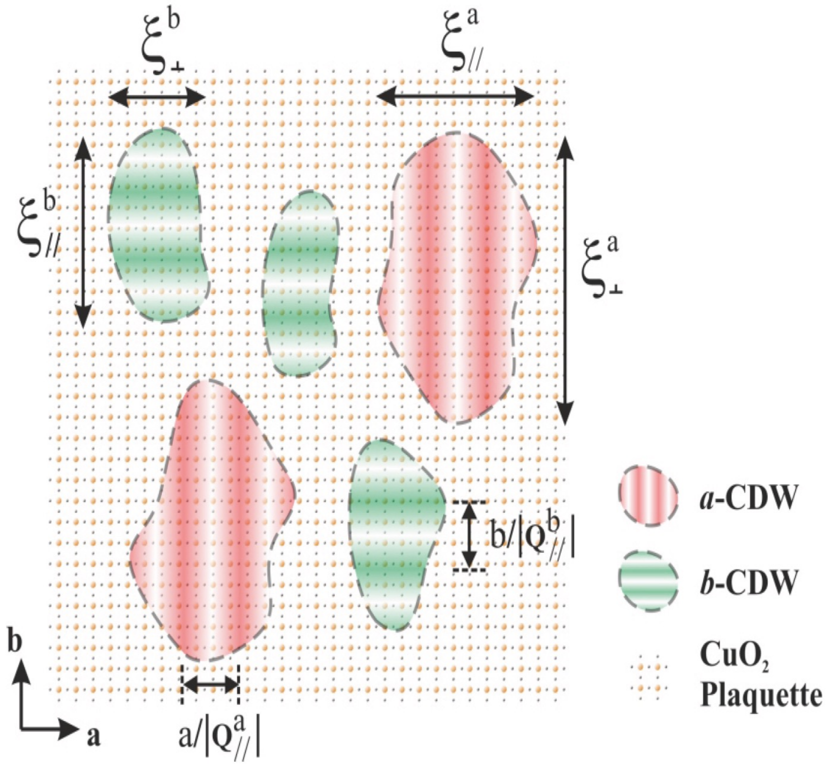
(0 K 0)

Ghiringhelli, MLT et al. Science **337**, 821 (2012)
MLT *et al.* Nat. Phys. **10**, 52 (2014)

CDW ‚morphology‘ (RIXS - ID32/ESRF)



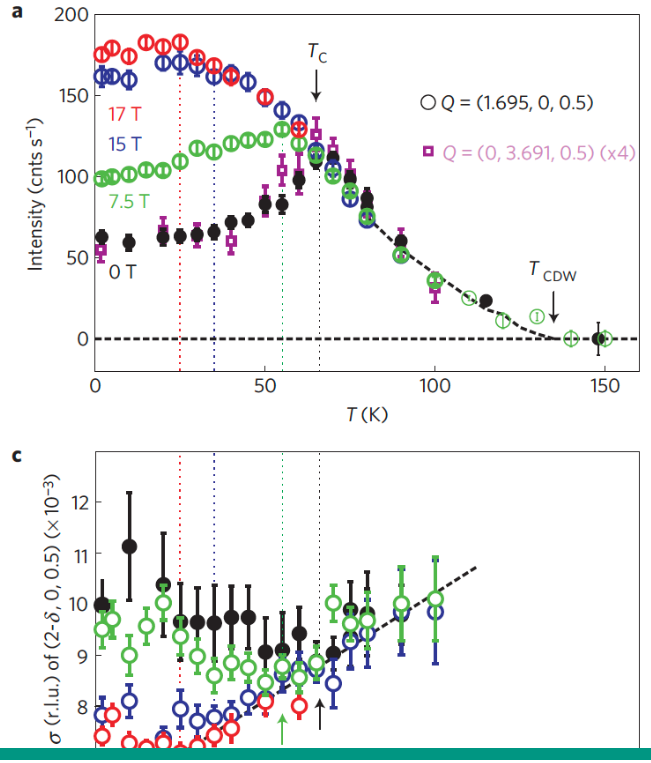




- Anisotropic, unidirectional CDW domains (cf. Comin et al. Science **347**, 1335(2015))

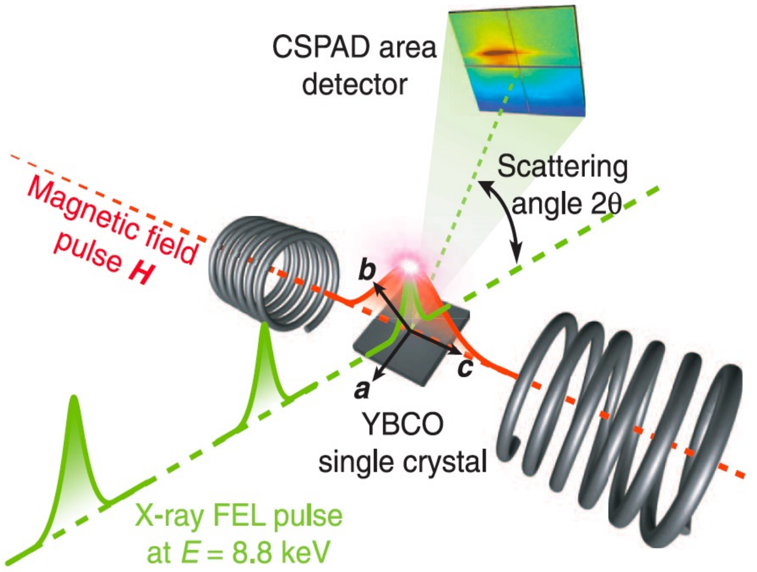
H.-H. Kim et al. Phys. Rev. Lett. **126** 037002 (2021)

CDW in the Cuprates: effect of magnetic field

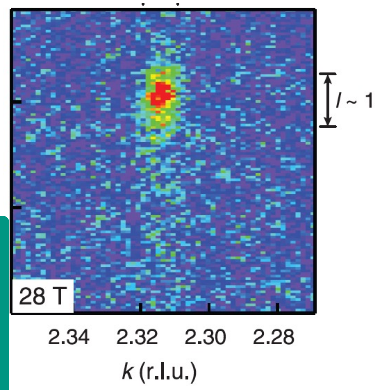


Short-range CDW: ξ_{2D}~60-80Å
Weak correlations along c: 2D order

Increase of CDW with H-field:
Evident competition with SC

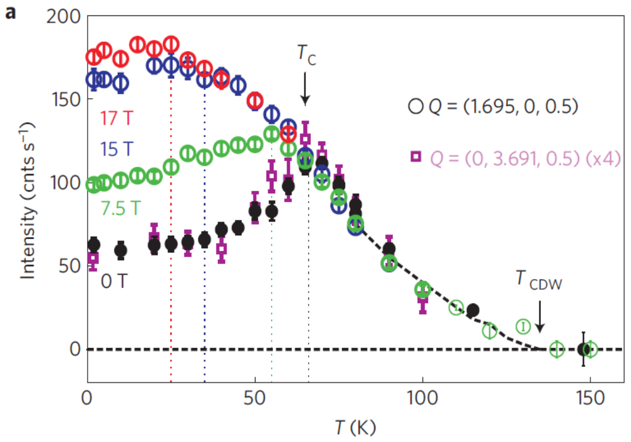


Using very large pulsed fields:
long-range CDW: ξ_{3D}~200 Å at 26T
ξ_l~ 40 Å at 26T: 3D Order

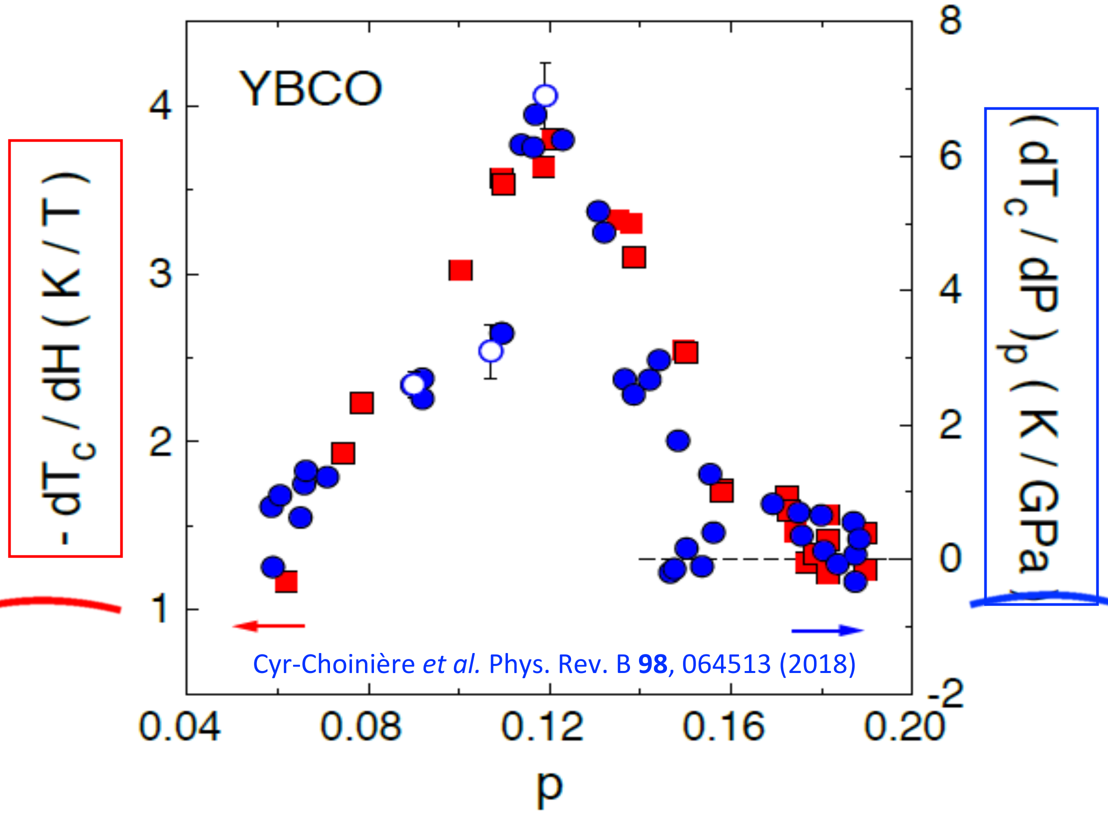


- Nature of the interplay between CDWs and Superconductivity?
- Insights on the microscopic mechanism behind the CDW?
- Relationship between the 2D CDW and the field-induced 3D CDW?

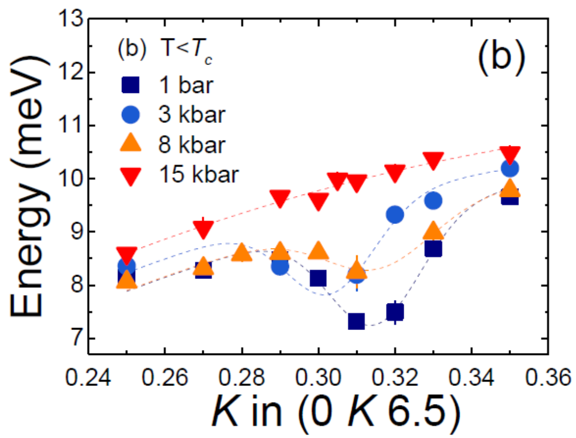
Pressure vs Magnetic Field



Chang et al., Nat. Phys. **8**, 871 (2012)



Cyr-Choinière *et al.* Phys. Rev. B **98**, 064513 (2018)



S. M. Souliou *et al.*, *PRB* **97**, 020503(R) (2018)

Magnetic Field

$$\frac{dT_c}{dH} < 0$$

Enhances CDW

Yet what if we could suppress superconductivity with pressure?

Hydrostatic pressure

$$\frac{dT_c}{dP} > 0$$

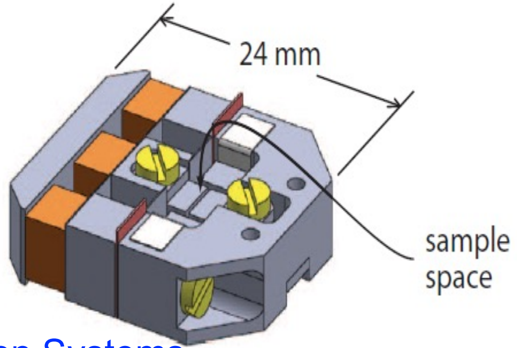
Suppresses CDW

Uniaxial stress device

Piezoelectric-based apparatus for uniaxial stress application
continuous, well-controlled uniaxial compression

MAX-PLANCK-INSTITUT
FÜR CHEMISCHE PHYSIK FESTER STOFFE

C.W. Hicks et al., Rev. Sci. Instr. 85, 065003 (2014)
C. W. Hicks et al., Science 344, 283 (2014)
A. Steppke et al., Science 355, 1 (2017)

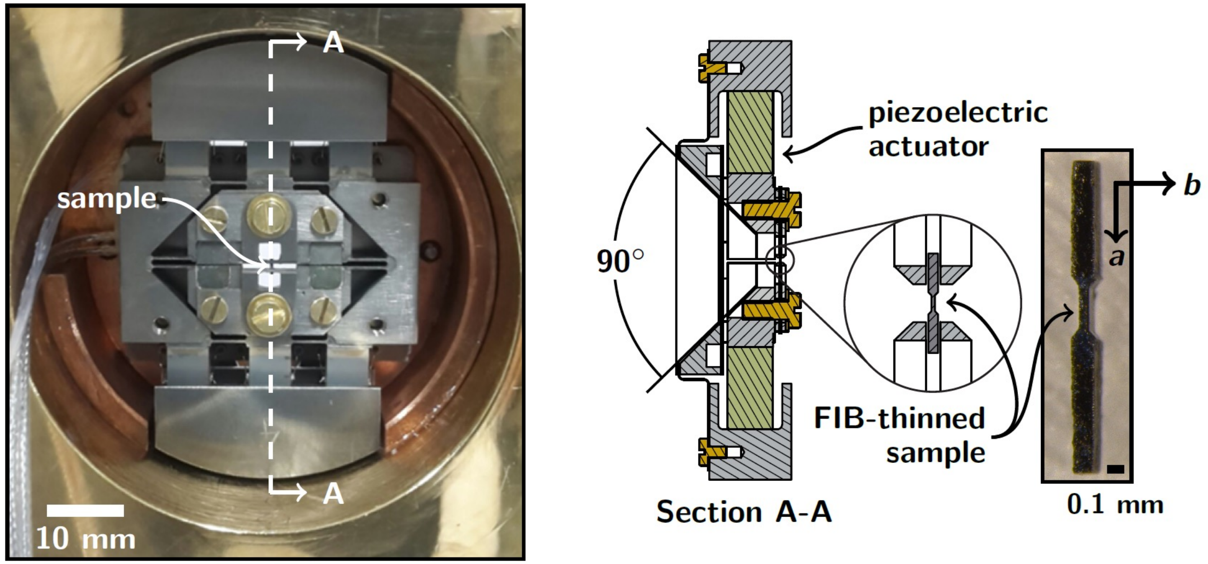


More information: Uniaxial Stress Technique and Investigations of Correlated Electron Systems, Springer Thesis, M.E. Barber (2018)

modified version:
✓transmission geometry
✓adapted for HP cryostat

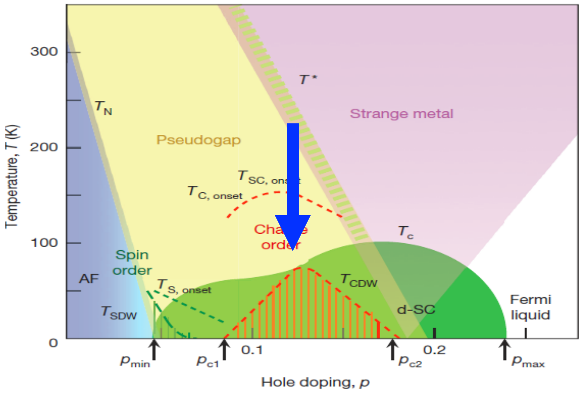
+

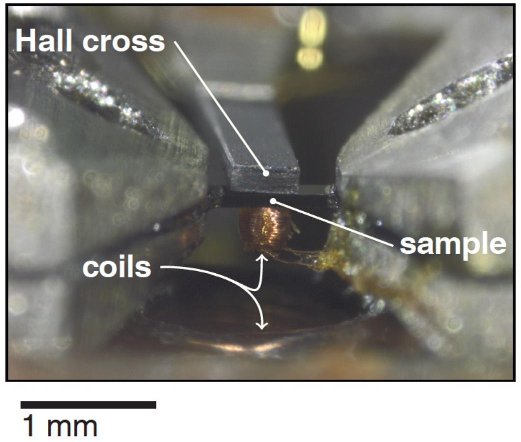
a-axis UD $YBa_2Cu_3O_{6.67}$ needles
plasma-FIB thinned in the center

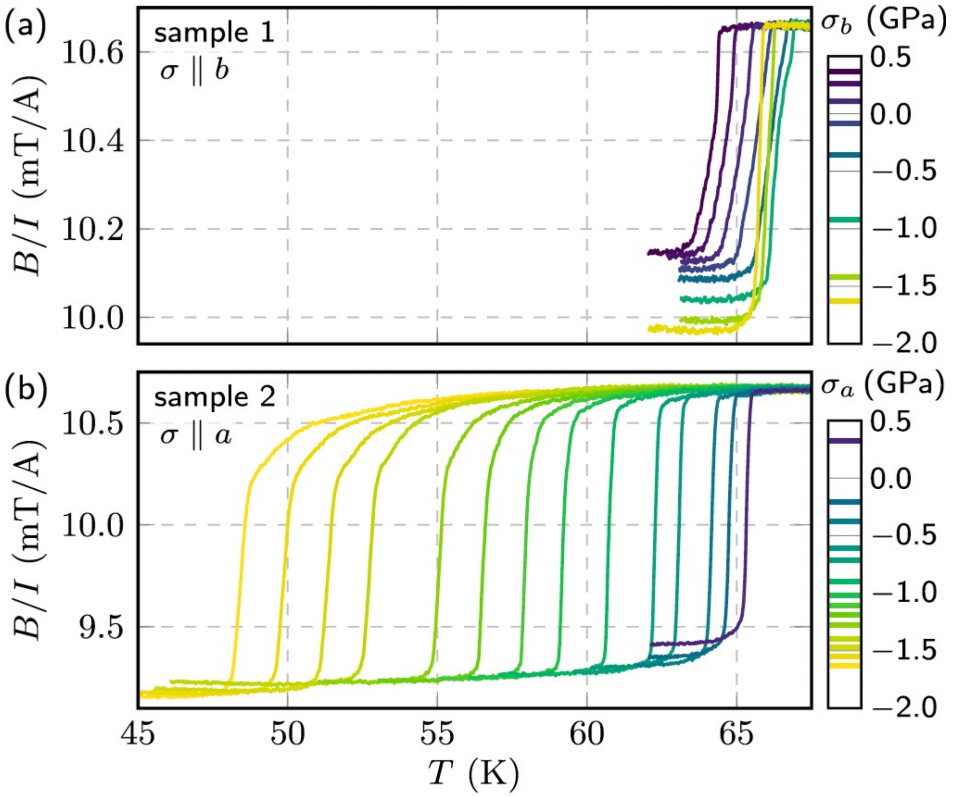


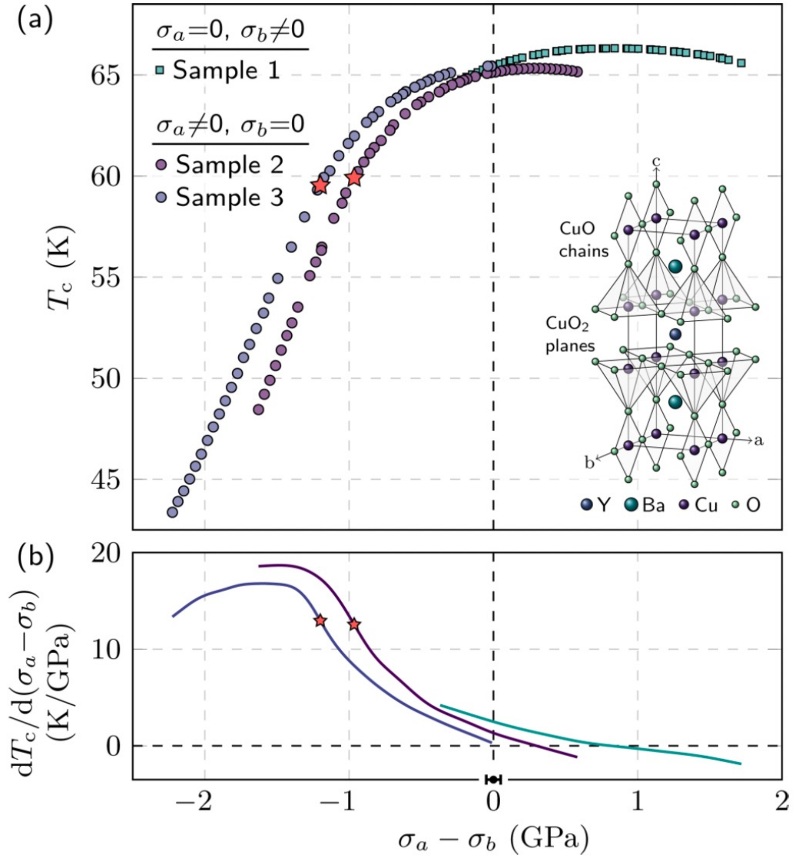
T_c data under uniaxial stress

1.5 GPa ~
1% compression





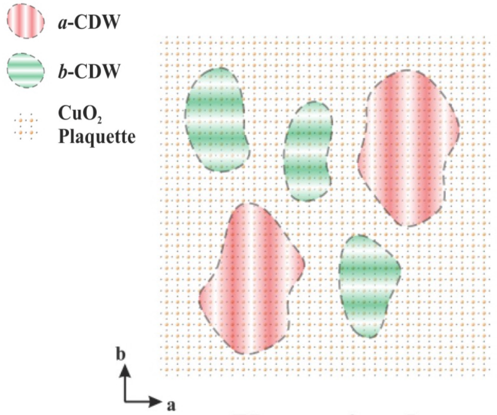




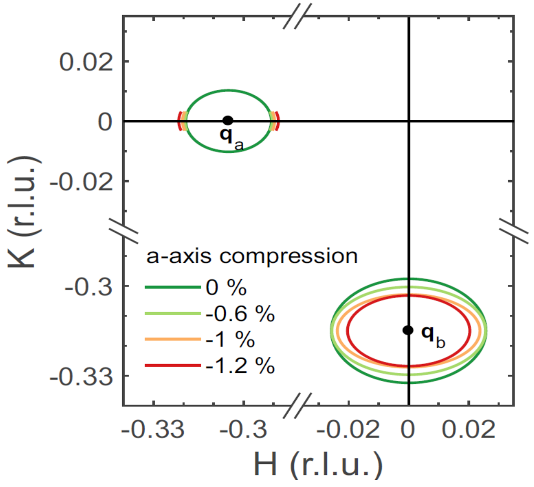
Barber, M. E. *et al. Phys. Rev. B* **106**, 184516 (2022).

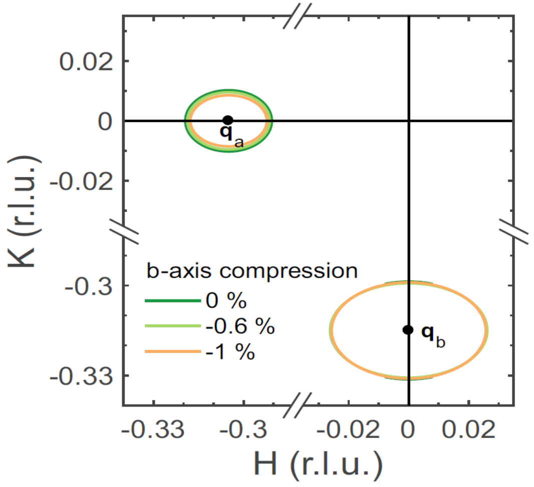
- Homogeneous and efficient suppression of superconductivity with uniaxial pressure //a

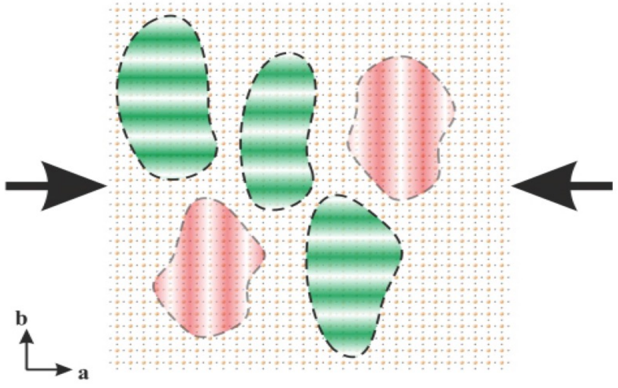
Uniaxial pressure dependence of the CDW



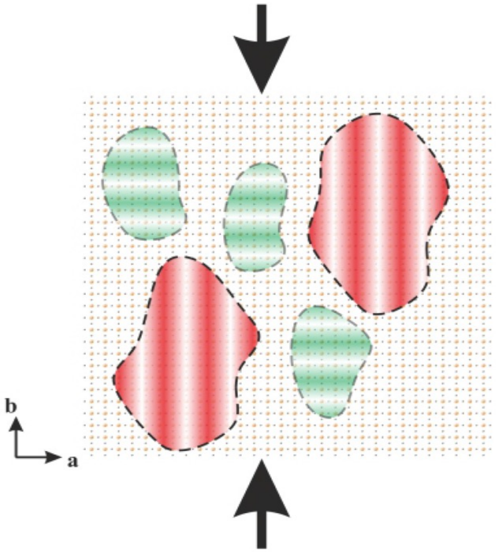
Unstrained







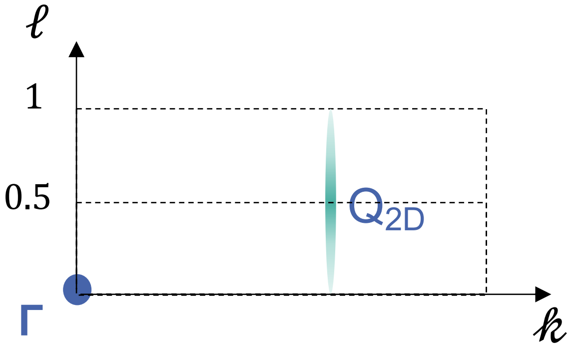
***a*-axis compression**

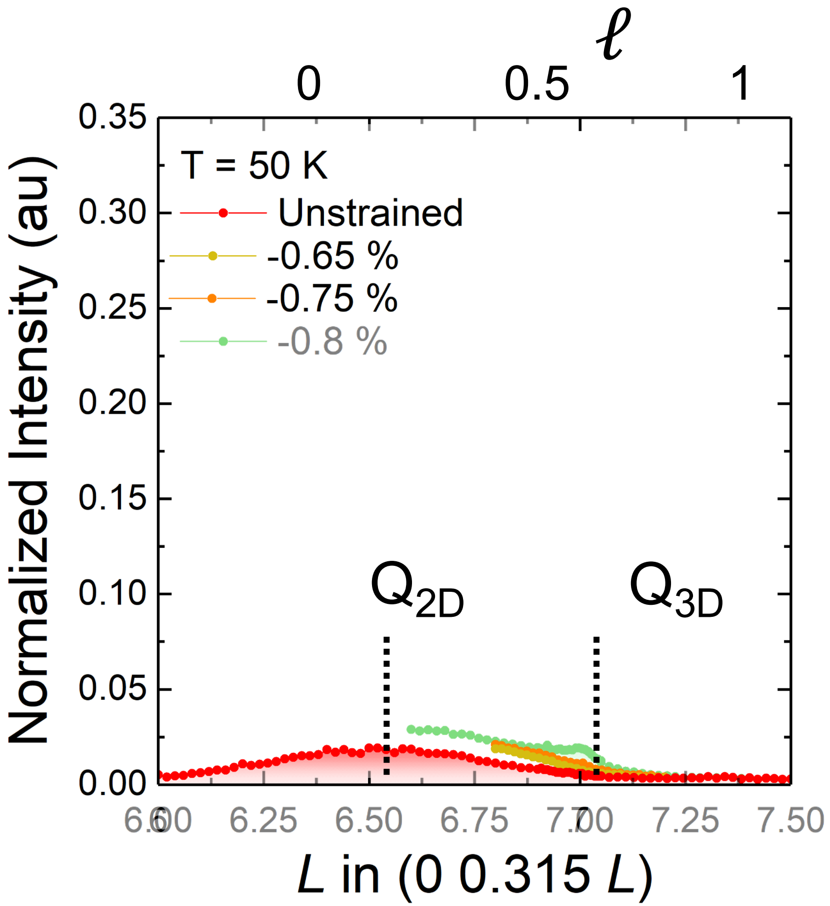


***b*-axis compression**

H.-H. Kim et al. Phys. Rev. Lett. **126** 037002 (2021)

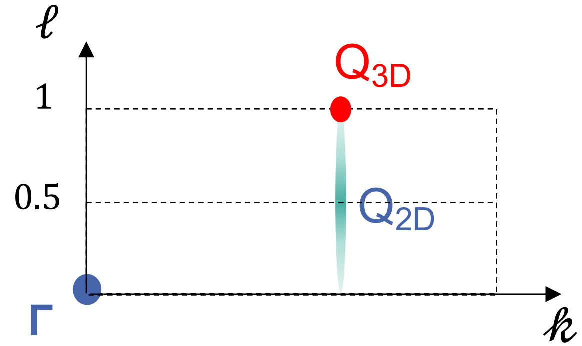
Uniaxial stress and 3D-order



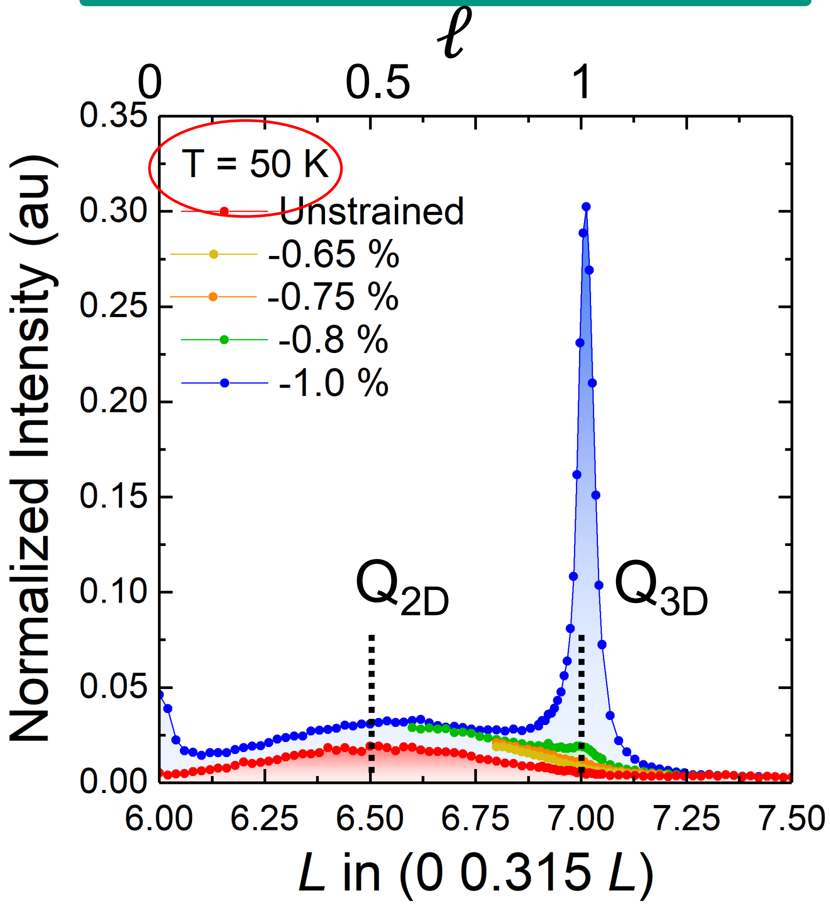


H.-H. Kim, S. M. Souliou et al. Science **362**, 1040 (2018)

Uniaxial stress and 3D-order

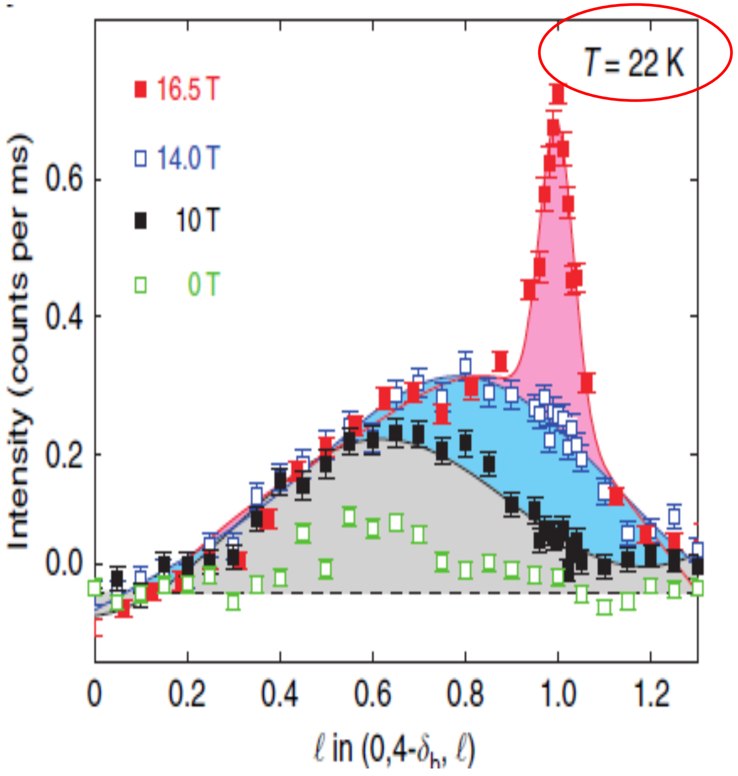


1% strain
long-range: $\xi_{3D} \sim 310$ Å
3D: $\xi_l \sim 94$ Å



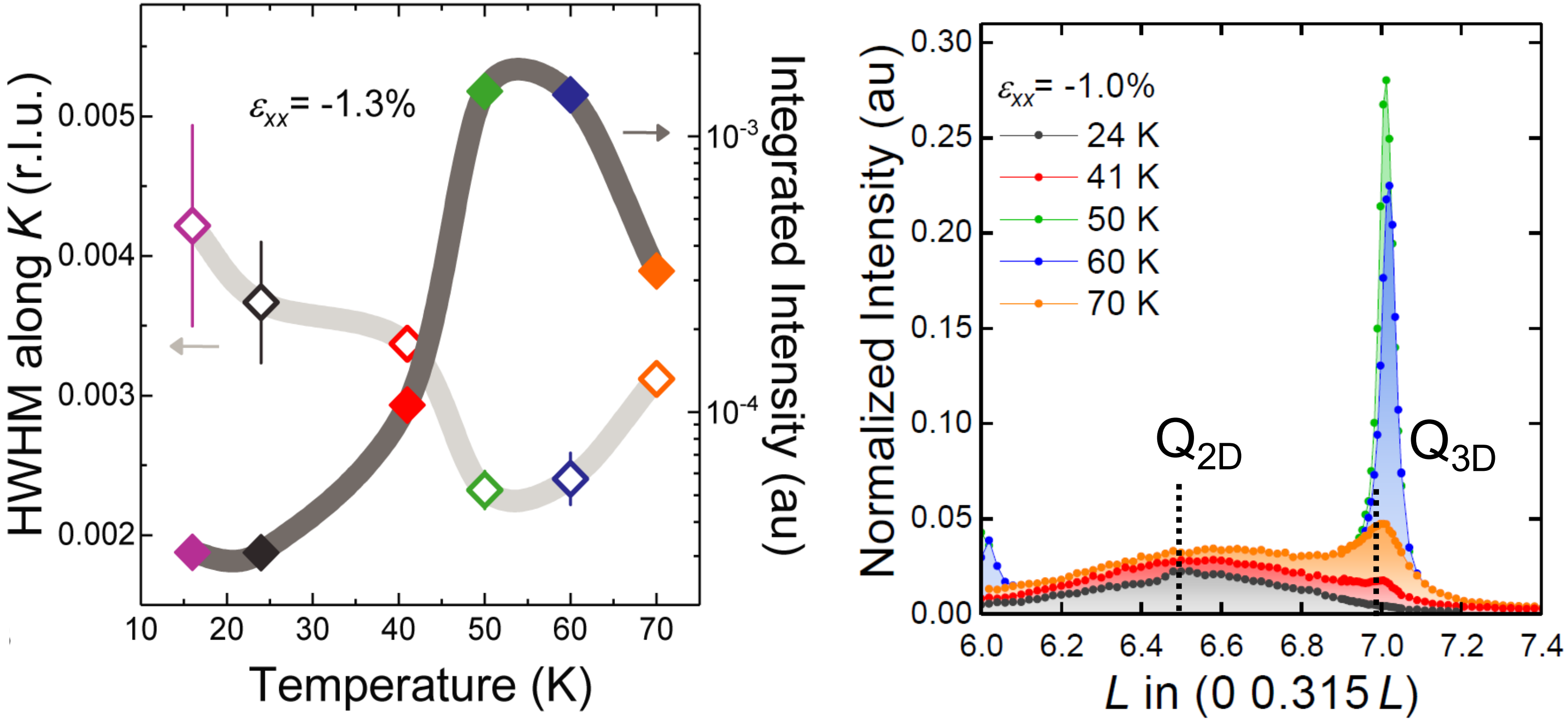
H.-H. Kim, S. M. Souliou et al. Science **362**, 1040 (2018)

H = 26T
long-range: $\xi_{3D} \sim 200$ Å
3D: $\xi_l \sim 40$ Å at 26T

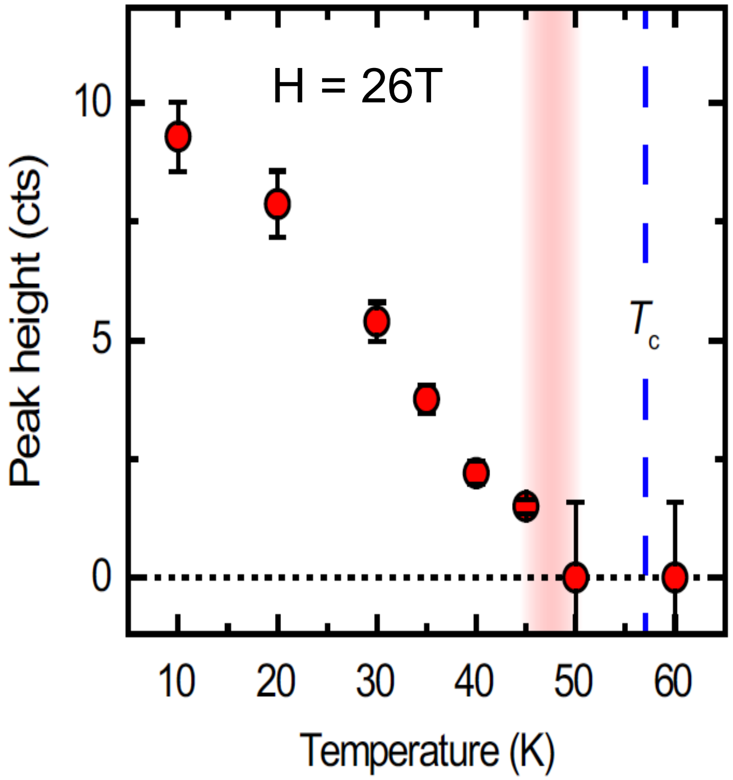


Chang et al. Nat. Com. **7**, 11494 (2016)

Temperature dependence of the 3D-CDW



H.-H. Kim, S. M. Souliou et al. Science **362**, 1040 (2018)

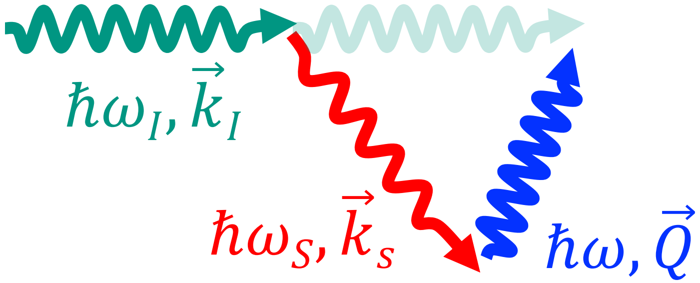


Gerber et al. Science **350**, 949 (2015)

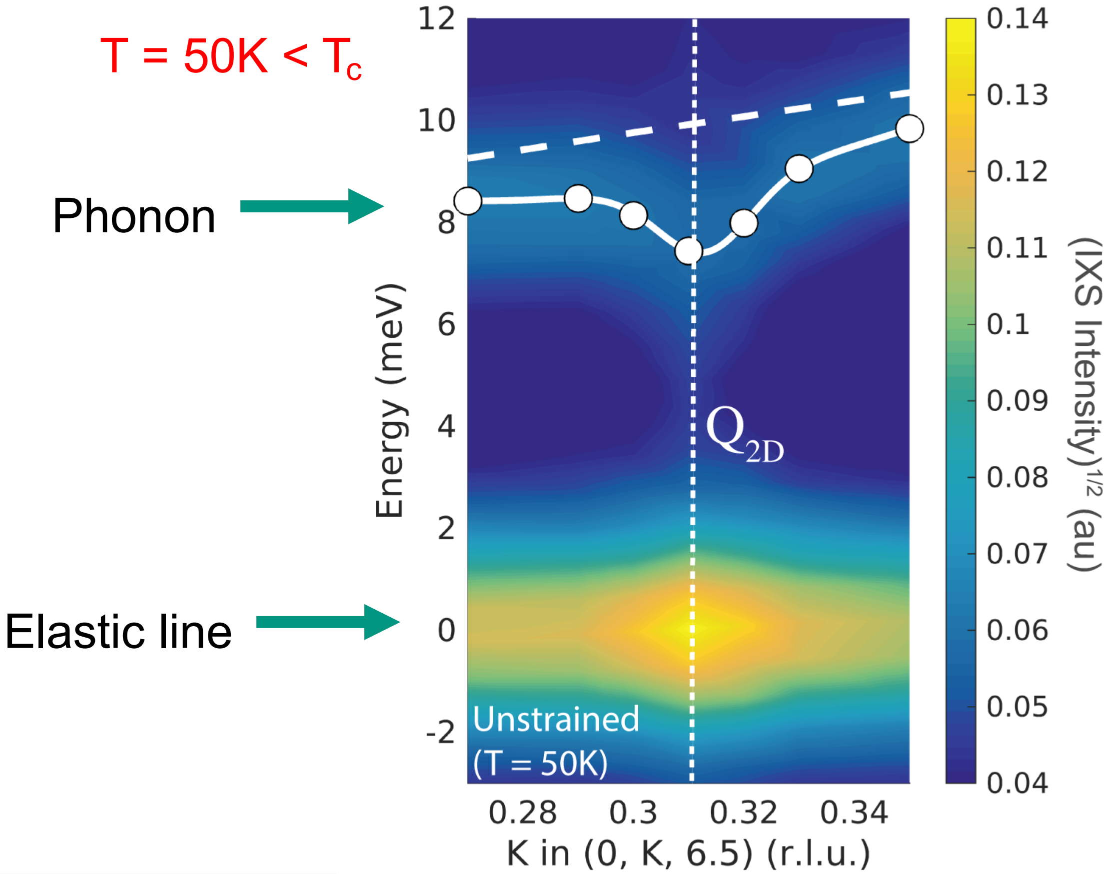
- Complete suppression at low T: very strong competition with superconductivity
- 3D order present **even above the uncompressed T_c**

CDW signature in Phonon spectra

Inelastic x-ray Scattering



T = 50K < T_c



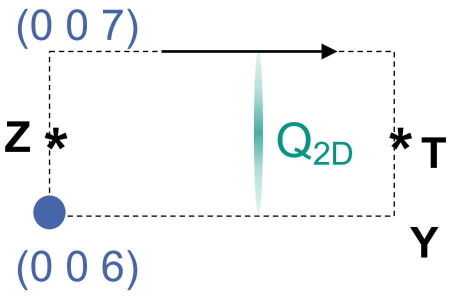
- GIANT superconductivity-induced Kohn anomaly at Q_{2D}

➢ 2D-CDW is not a soft-mode driven CDW

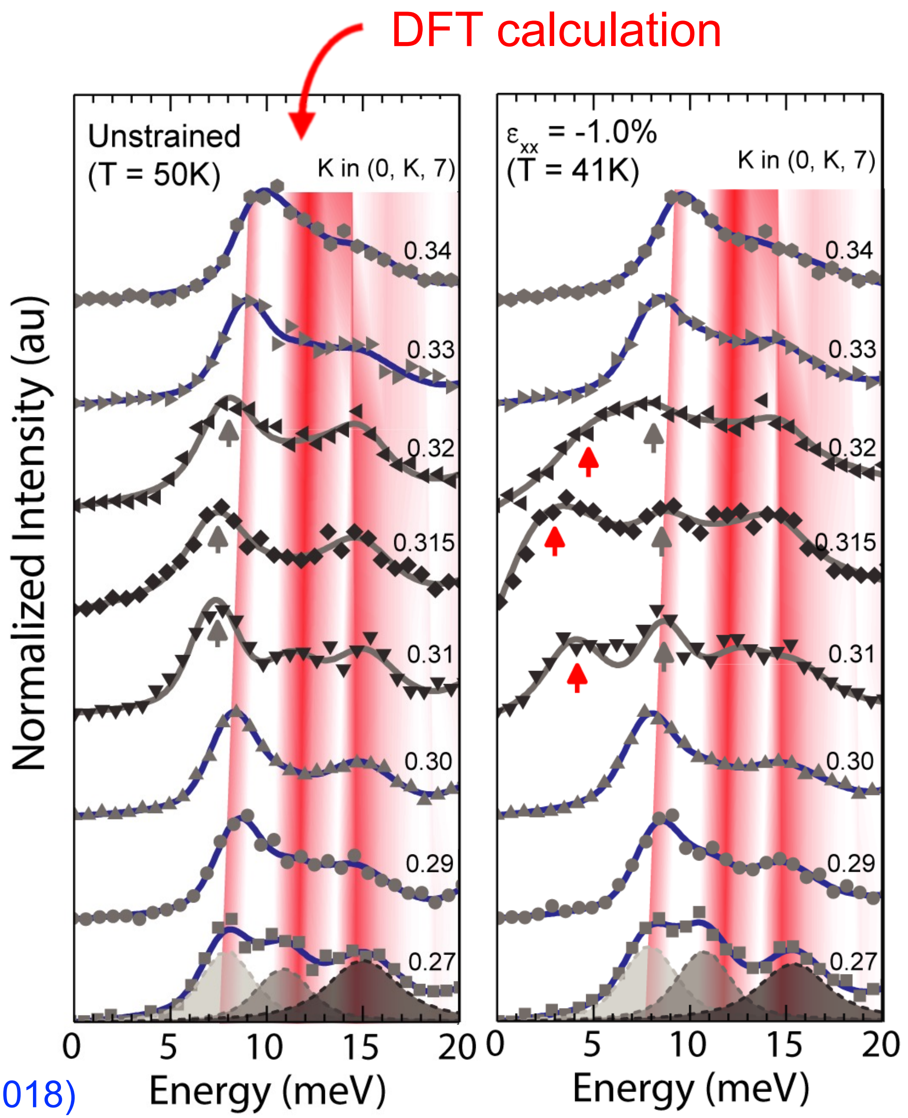
MLT *et al.* Nat. Phys. **10**, 52 (2014)

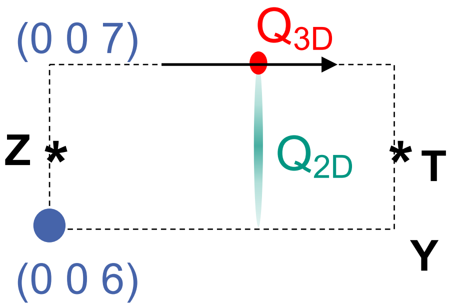
H.-H. Kim, S. M. Souliou et al. Science **362**, 1040 (2018)

Inelastic x-ray scattering: Phonon anomalies



SC-induced softening of the acoustic mode: extends along L


DFT calculation



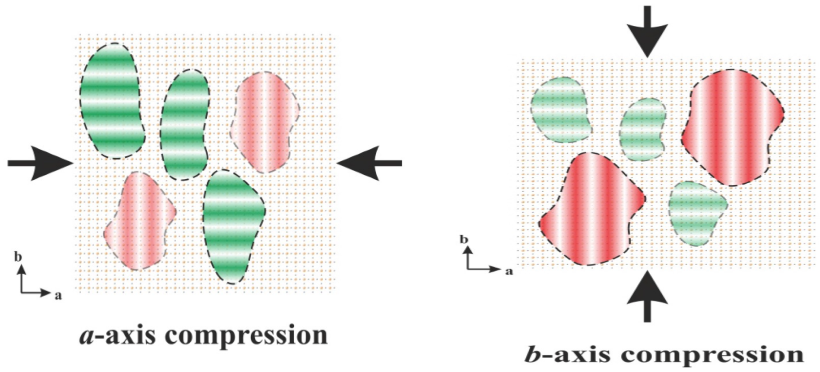
- Complete Softening of an optical phonon associated with the formation of the 3CDW

H.-H. Kim, S. M. Souliou et al. Science **362**, 1040 (2018)

A few things we learned

- Response of CDW to uniaxial stress is symmetric
    - b-CDW domains grow under a-stress
    - a-CDW domains grow under b-stress

➢ **The CDW is unidirectional and biaxial**



- The formation of long-range CDW order is associated with a lattice dynamics anomaly enhanced by stress as SC is suppressed

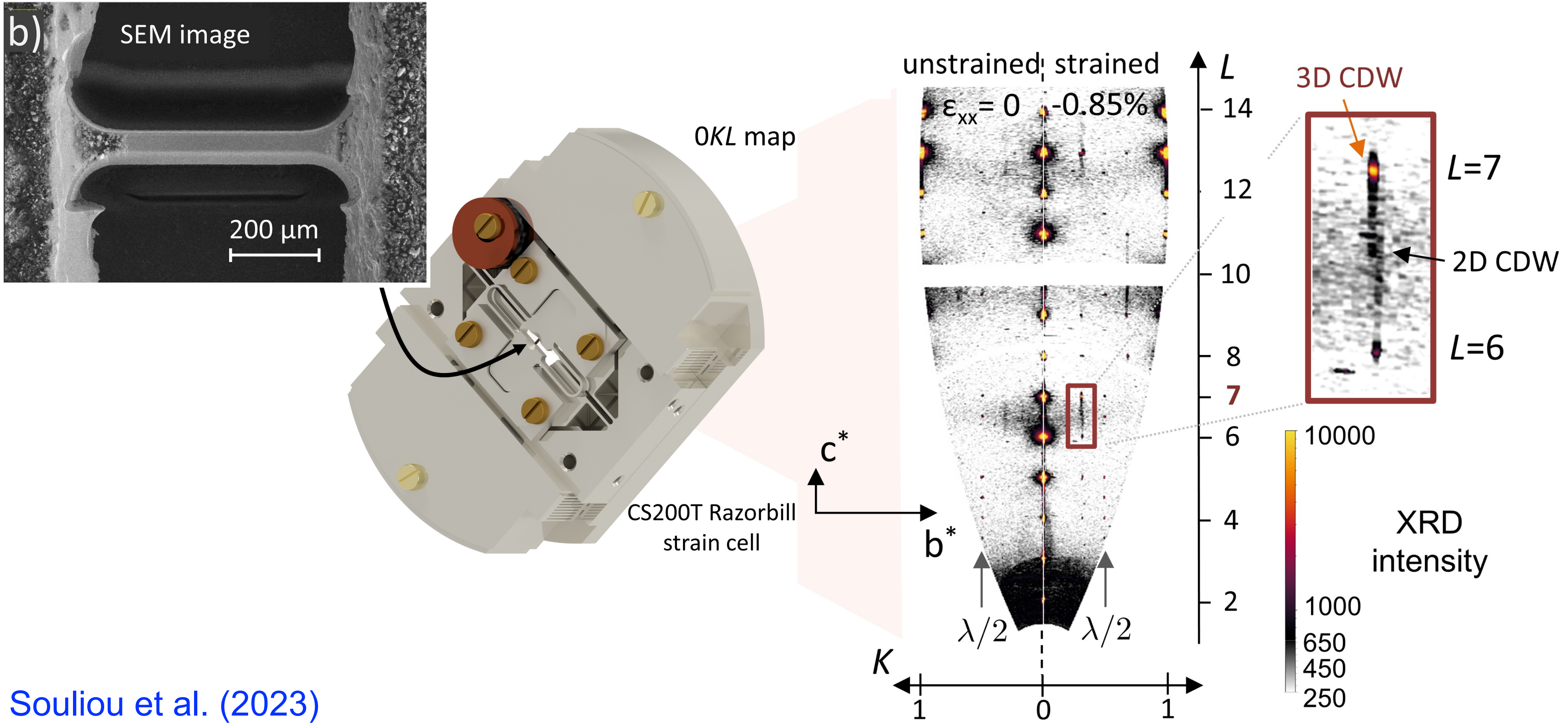
➢ **The 3D CDW is soft-phonon-driven: lattice plays an active role**

The CDW is seen in ***all cuprates*** *and seem to be the main competitor to high-Tc superconductivity and the thermodynamically stable state when SC is suppressed.*

➢ ***Suppressing CDW ordering tendencies should yield better superconductors!***

What do we do exactly to the crystal structure when we apply strain?

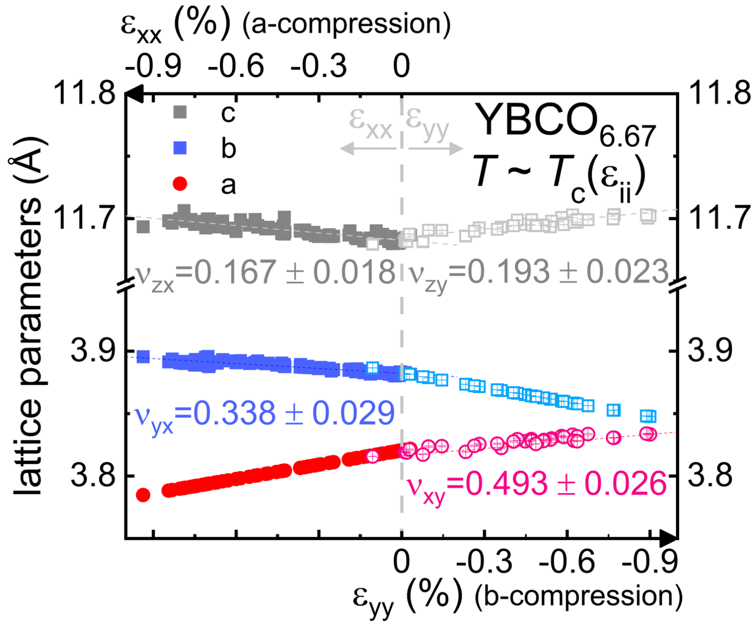
2D vs 3D CDW – an xrd study

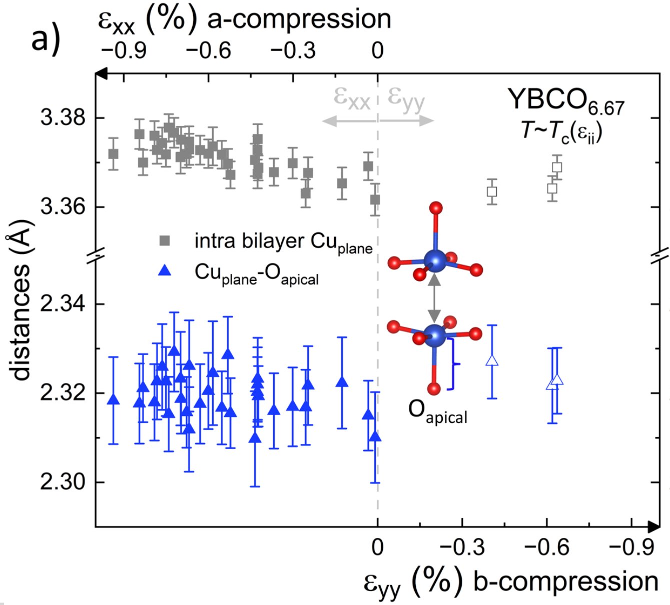


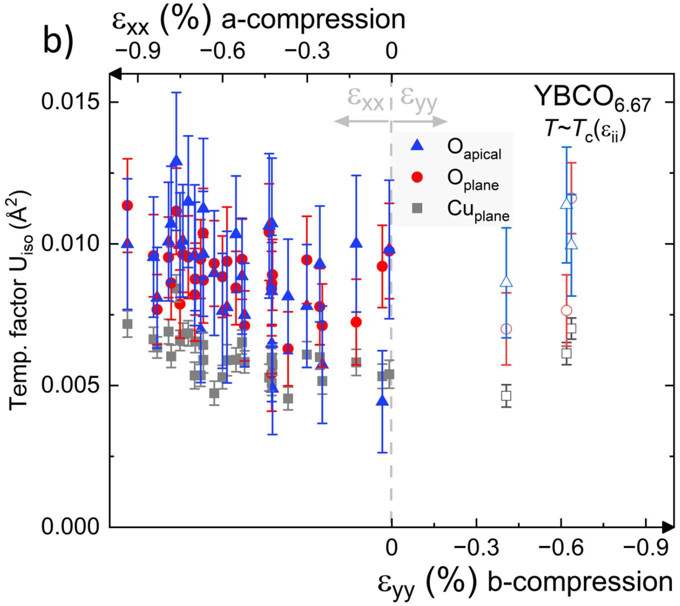
Vinograd, Souliou et al. (2023)

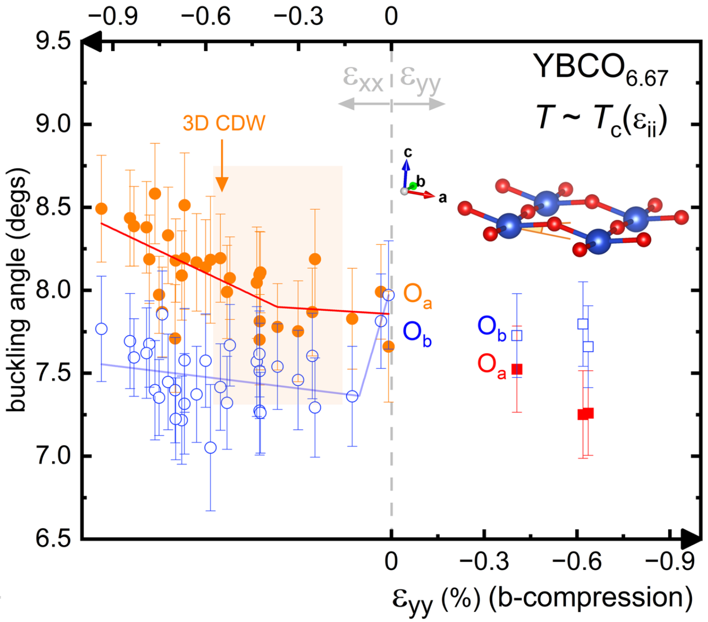
Detailed structural refinement

- ➢Refined Poisson ratio
- ➢Bond lengths
- ➢Buckling etc…

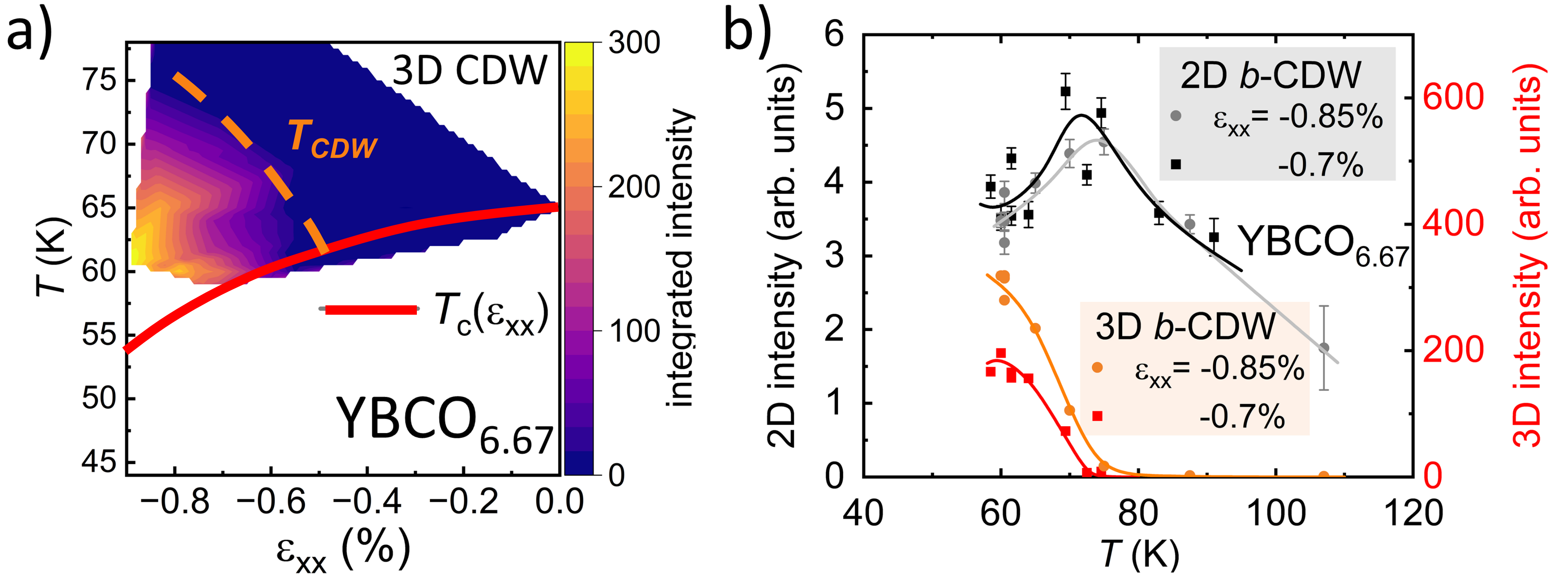








XRD study of the 3D CDW



- Quantitative determination of the strain and of its effects on the crystal structure
- Strain-temperature phase diagram of the 3D CDW
- Evidence for competition between 2D and 3D : the long-range 3D-CDW grows from the 2D correlations

Vinograd, Souliou et al. (2023)

More generally…

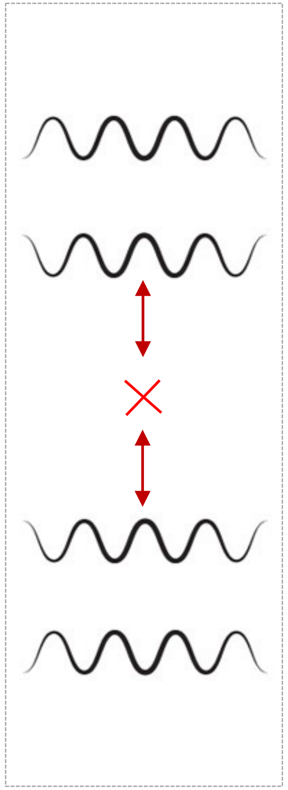
- the crystal lattice can be used as a ‘clean’ way to tune the electronic phase of quantum materials (statically but also dynamically)
- It can be combined with structural and spectroscopic studies to gain fresh insights on the nature of the interplay between competing electronic phases
- It can ultimately guide the design of functional quantum materials with tailored electronic properties

Dimensional crossover in CDW

Short-range 2D CDW

defect pins

CDW maxima

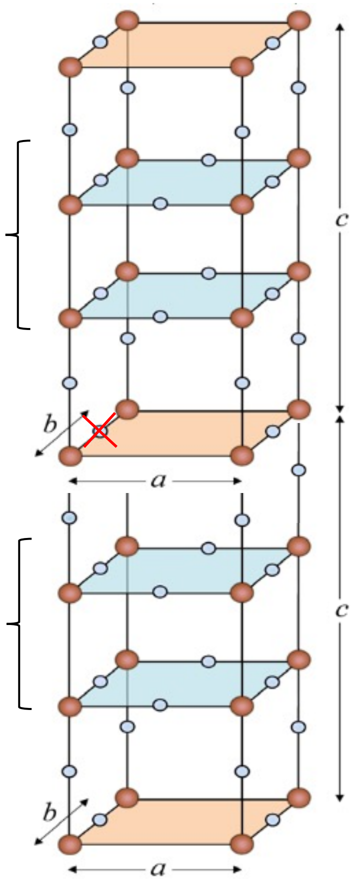


L=0.5

CuO_2

bilayer

chain layer



Caplan *et al.*, PRL **119**, 107002 (2017)

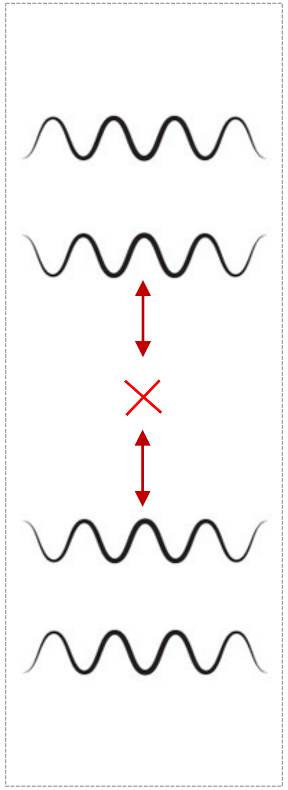
Dimensional crossover in CDW

Short-range 2D CDW

Long-range 3D CDW

defect pins

CDW maxima

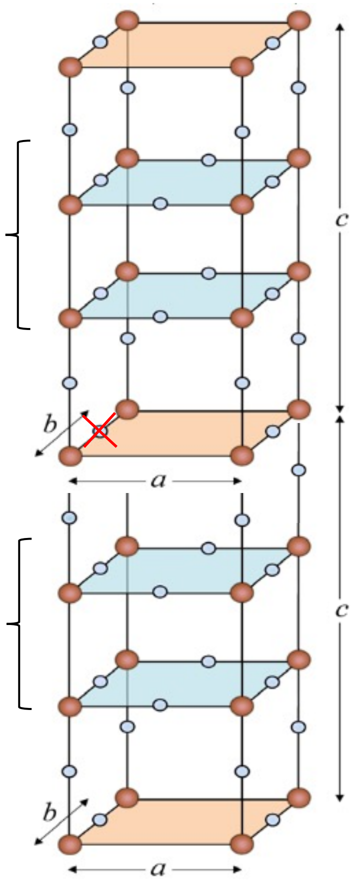


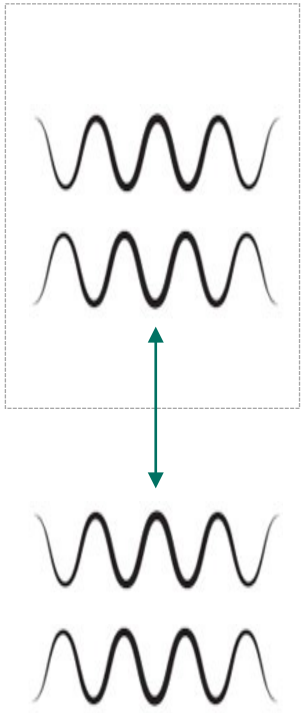
L=0.5

CuO_2

bilayer

chain layer





minimal

Coulomb repulsion

L=1

Caplan *et al.*, PRL **119**, 107002 (2017)

Inelastic Photon Scattering

Raman Scattering: Inelastic scattering of ‘visible’ light

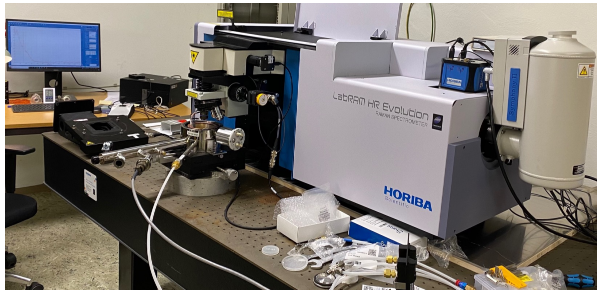
$\hbar\omega_I \sim 1.5 - 4$ eV

$\lambda_I \sim$ 3000 – 7000 Å >> a   ($Q \sim 0$ probe)

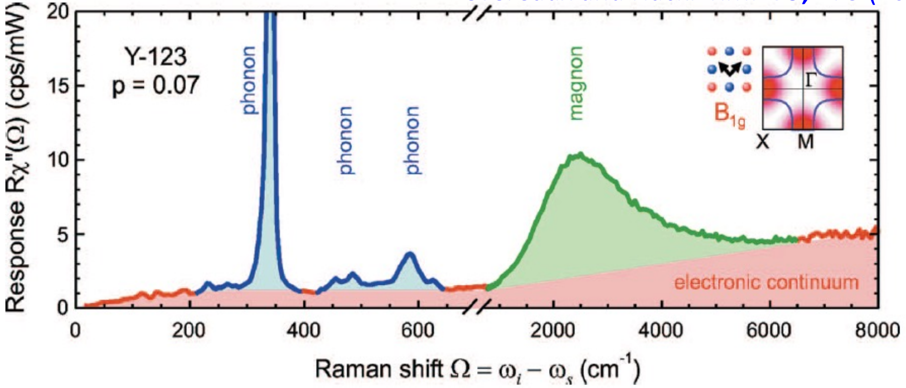
Energy resolution ~ 0.1 meV

Selection rules:

- phonon symmetries
- k-space selectivity (electronic)



Devereaux and Hackl RMP **79,** 175 (2007)



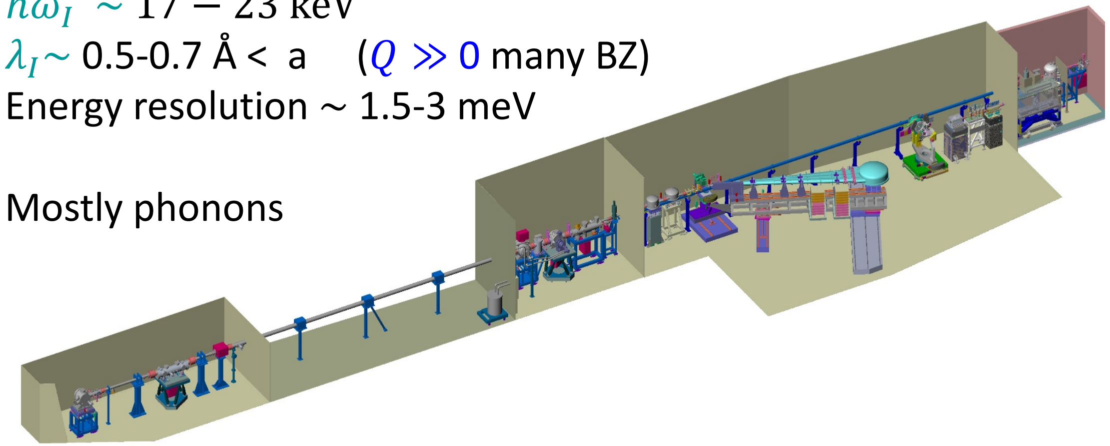
IXS: high resolution inelastic scattering x-ray scattering

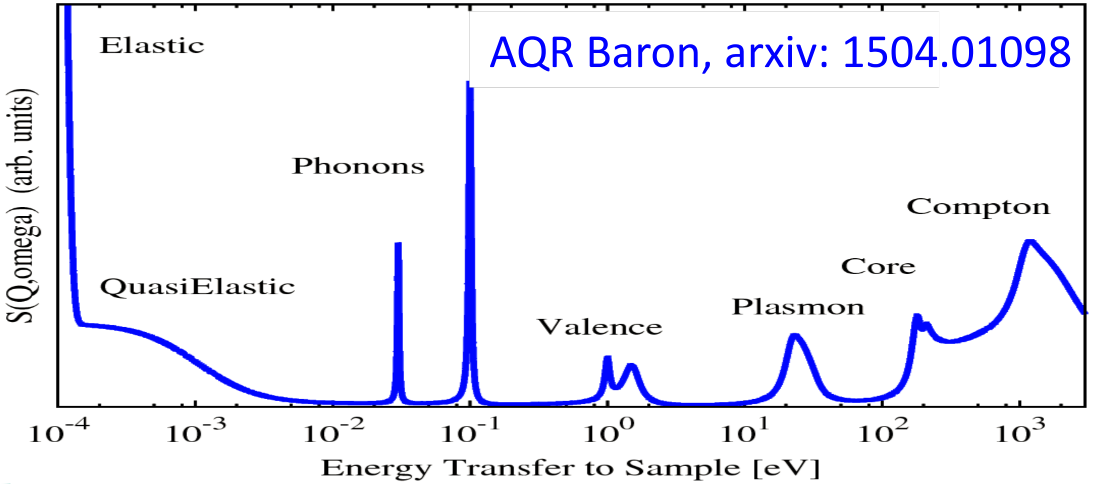
$\hbar\omega_I \sim 17 - 23$ keV

$\lambda_I \sim$ 0.5-0.7 Å < a   ($Q \gg 0$ many BZ)

Energy resolution ~ 1.5-3 meV

Mostly phonons





AQR Baron, arxiv: 1504.01098