Resolving Length Scale Dependent Transient Disorder Through an Ultrafast Transition

Emil S. Bozin

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IMPACT 2024

Cargèse, France, August 21

Resolving Length Scale Dependent Transient Disorder Through an Ultrafast Transition

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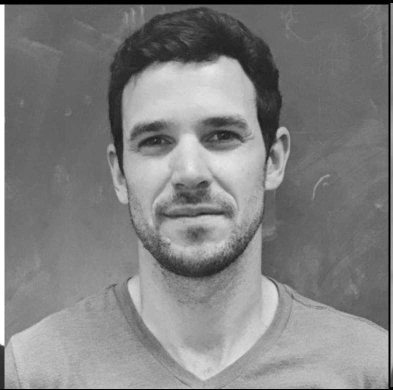

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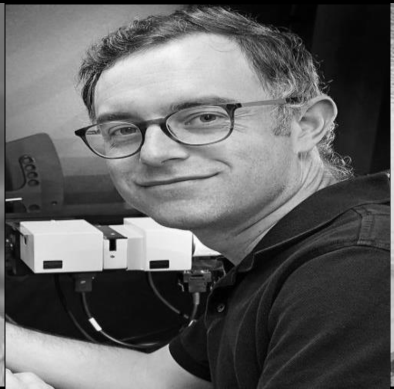

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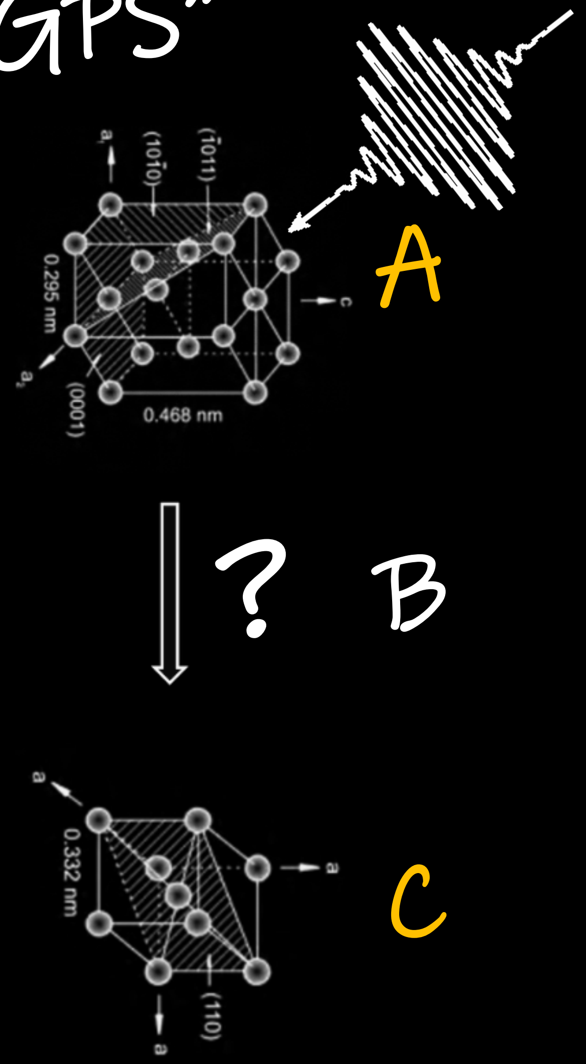
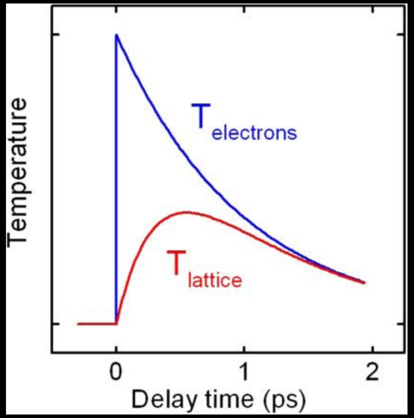
Length-scale sensitive atomic "GPS"



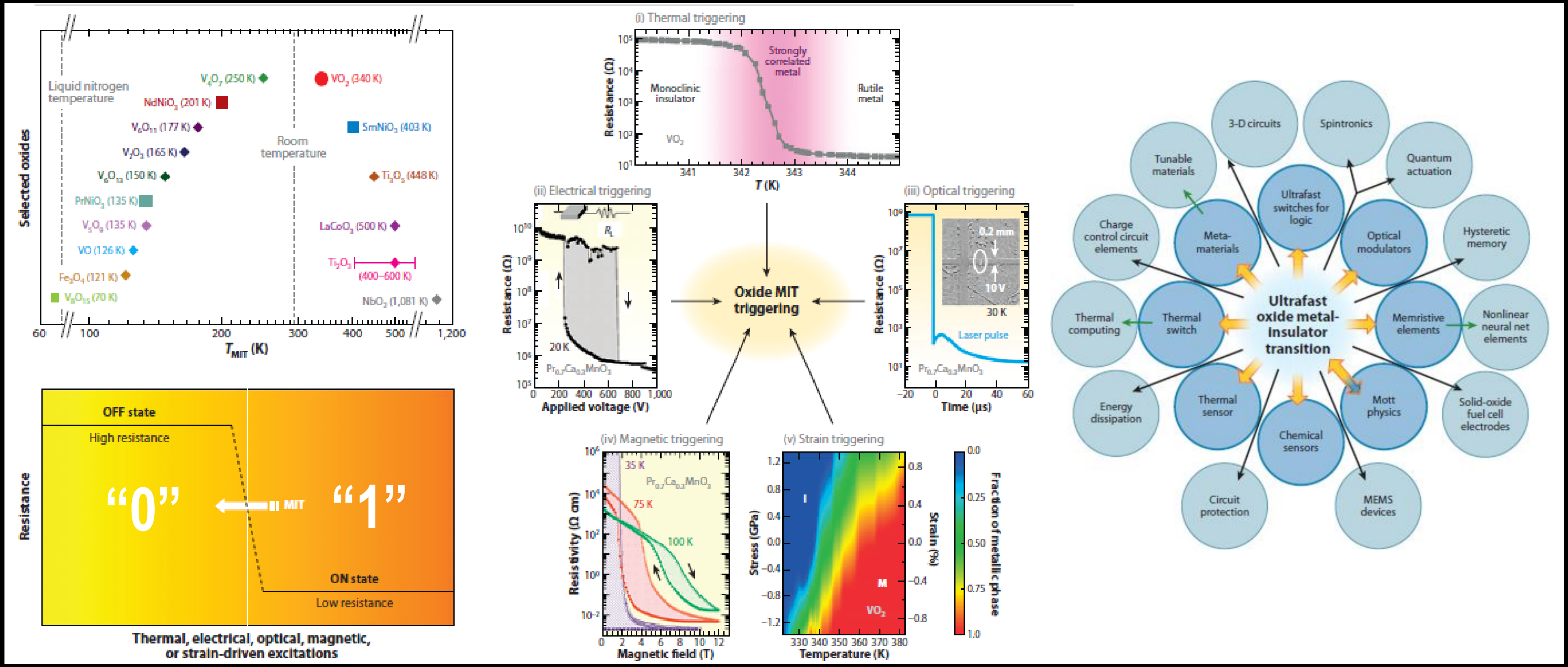
Materials with specialized & highly efficient properties

- Development increasingly relies on complex local structures that stray from the ideal of a perfect crystal
- Advancements in electronics technology drive a need for materials that switch between distinct states
  - electrical (e.g., memristors, ferroelectrics)
  - magnetic (e.g., ferromagnets, anti-ferromagnets)
  - structural (e.g., charge density wave states)

  - **A key example is the metal-insulator transition**
  - Why ultrafast? 1 picosecond is the timescale for
    - Electron – phonon **coupling**
    - Phonons (structural information) to travel ~ 6 nm
    - Femto- and pico- seconds are the **natural timescale** of **phase transitions**

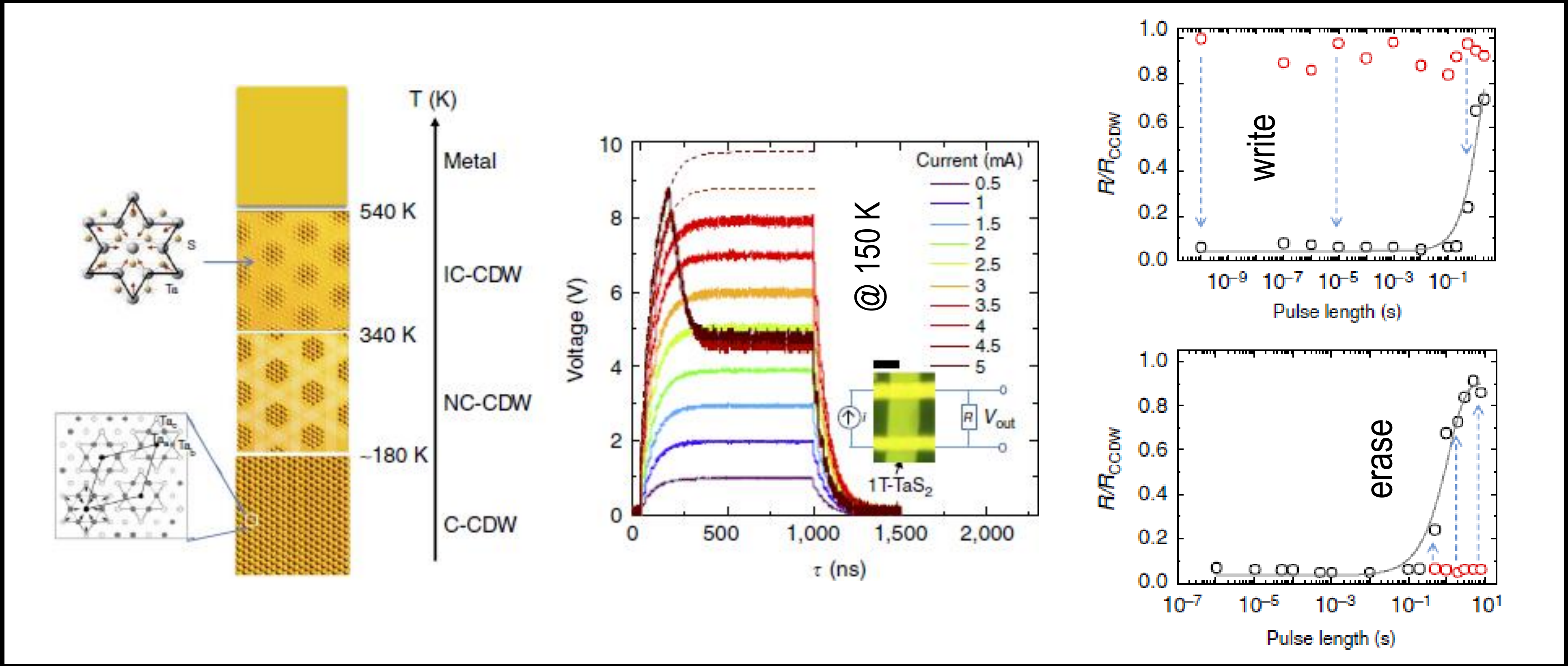


Oxide electronics utilizing ultrafast MIT



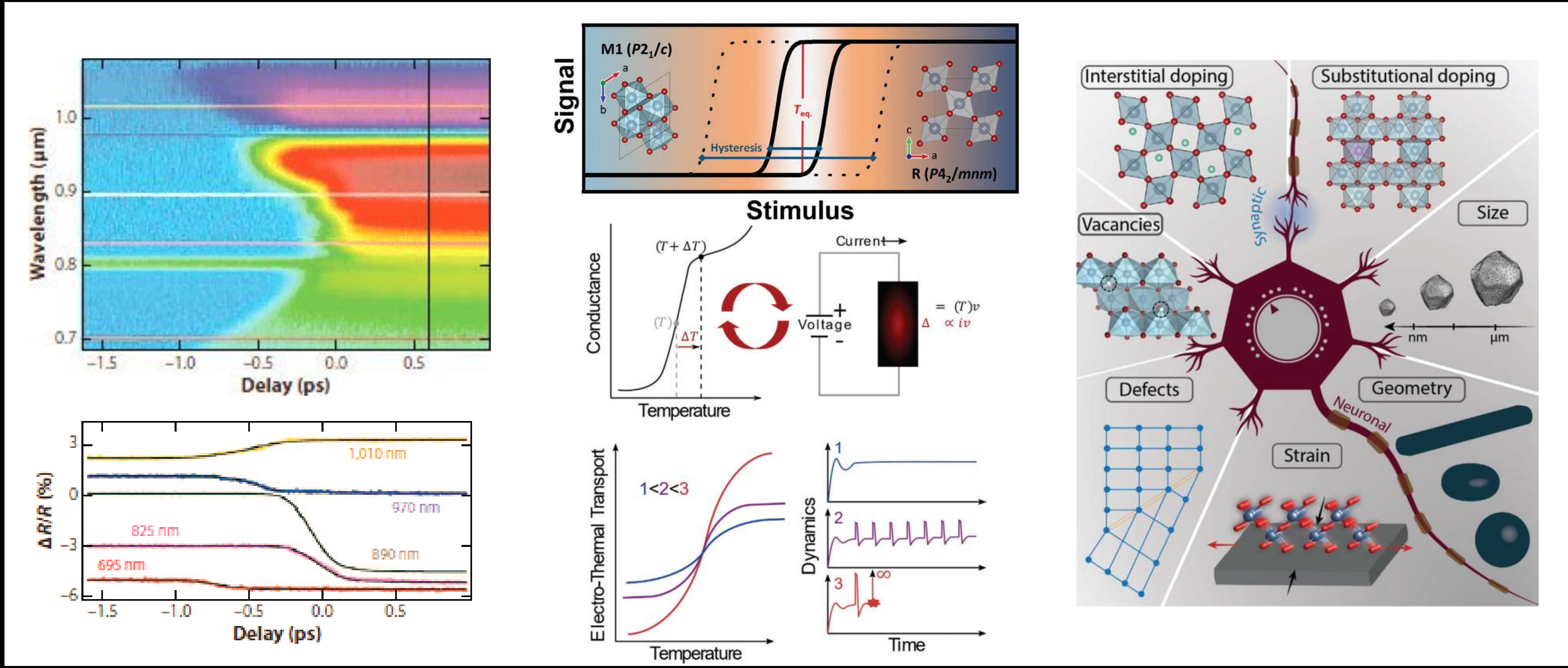
Oxides Z Yang et al Annu. Rev. 2011

Fast resistance switching involving hidden CDW states



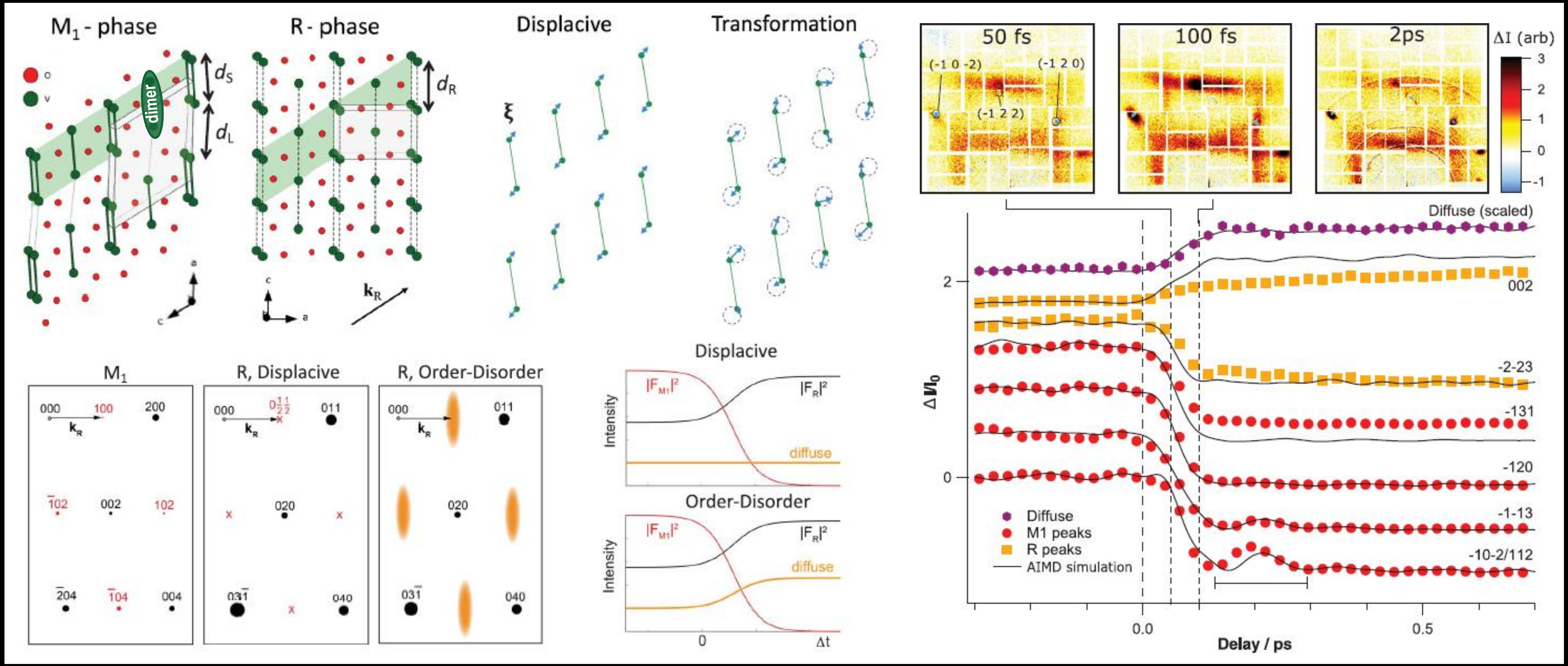
1T-TaS_2 I Vaskivskyi et al Nat. Com. 2016

Harnessing the MIT of VO_2 in Neuromorphic Computing



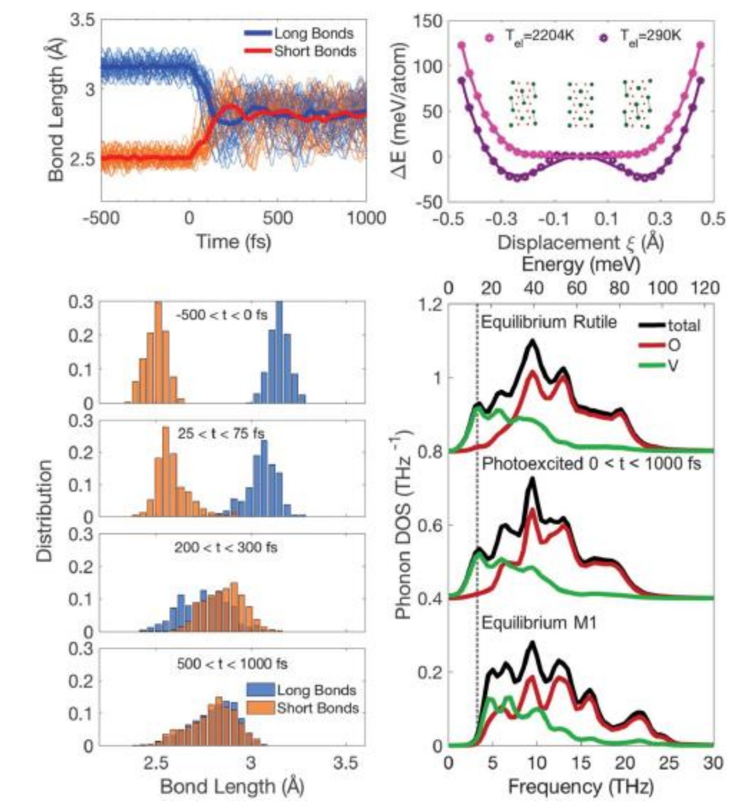
Switching in VO_2 P Schofield et al Adv. Mat. 2022

Ultrafast disordering of V-V dimers in photoexcited VO_2



Atomic disordering in photoexcited VO_2 is central to the uf-MIT mechanism S Wall et al Science 2018

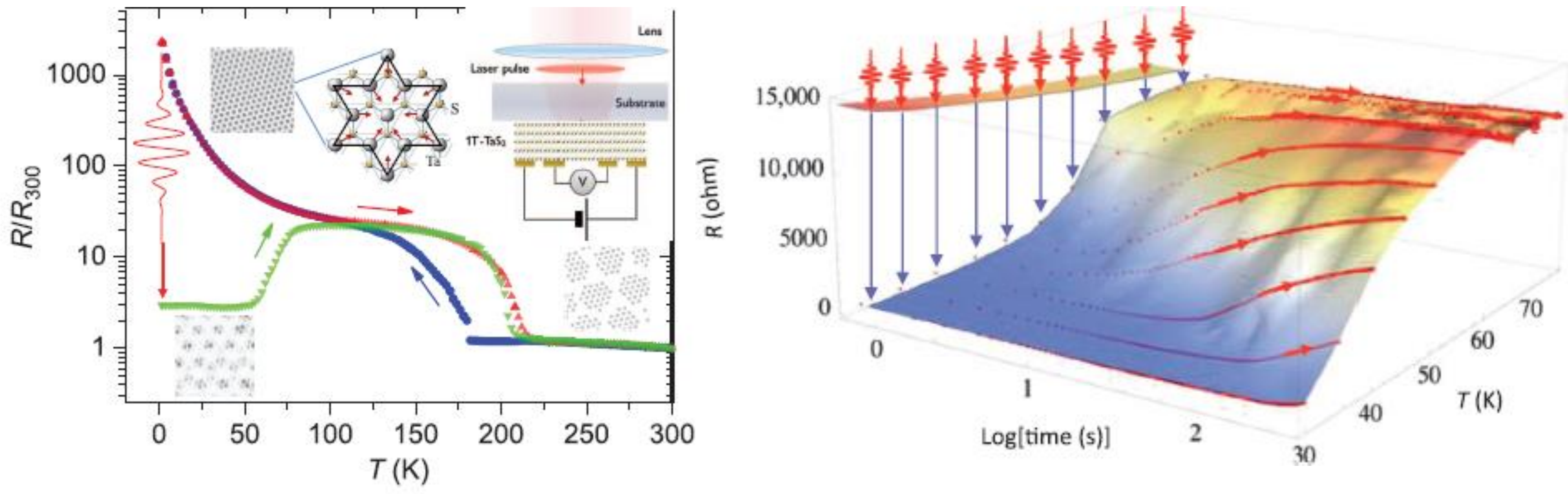
Ultrafast disordering of V-V dimers in photoexcited VO_2



- Simulated VO_2 response under photoexcitation based on first-principles DFT calculations!
- Diffuse scattering generally difficult to interpret beyond the O/DO scenario
- Limited Q-space coverage, typically over a single Brillouin zone

***Atomic disordering** in photoexcited VO_2 **is central** to the uf-MIT mechanism* S Wall et al Science 2018

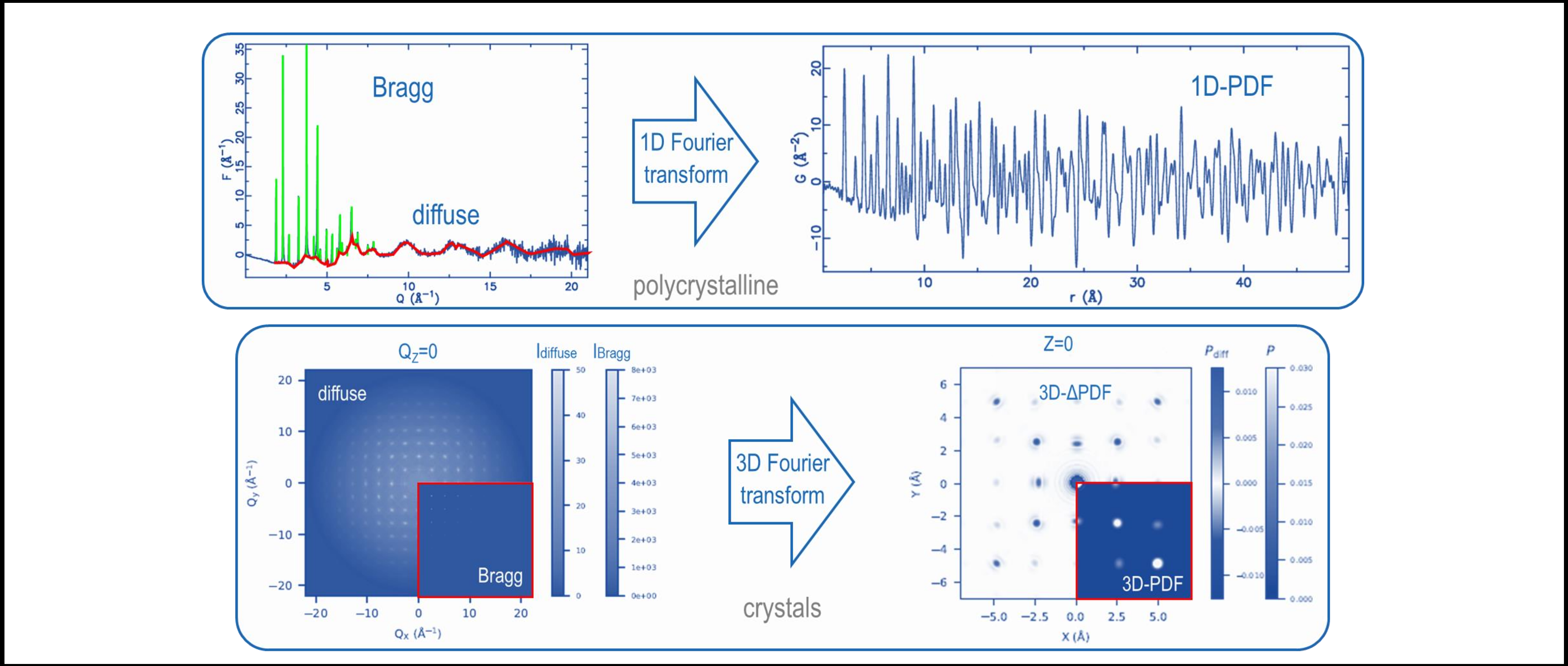
T-controlled relaxation of the hidden state in 1T-TaS_2



- What is the symmetry of the hidden state?
- What impacts the metastability? Why is ~50 K a special T?

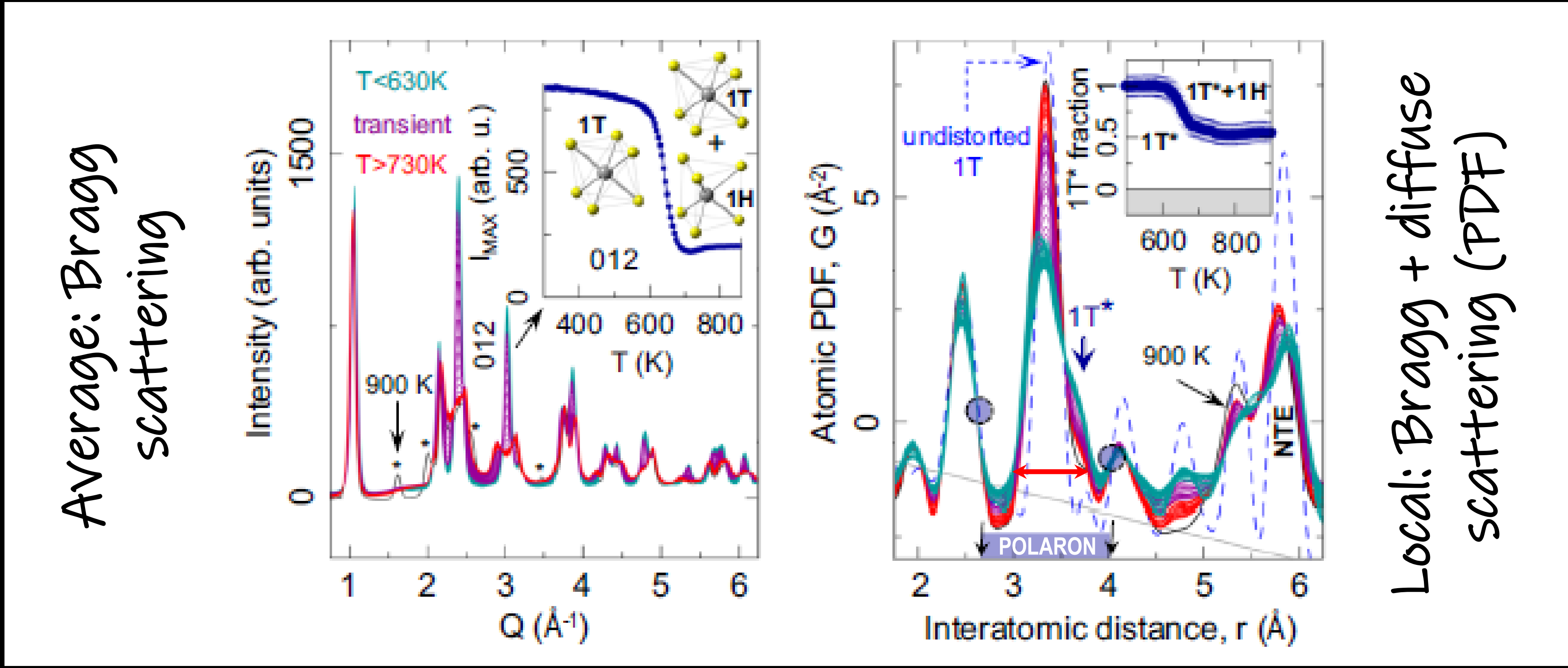
*Controlling **the metal-to-insulator relaxation** of the **metastable** hidden quantum state* I Vaskivskyi et al Sci. Adv. 2015

Advanced Fourier maps: pair distribution function approach



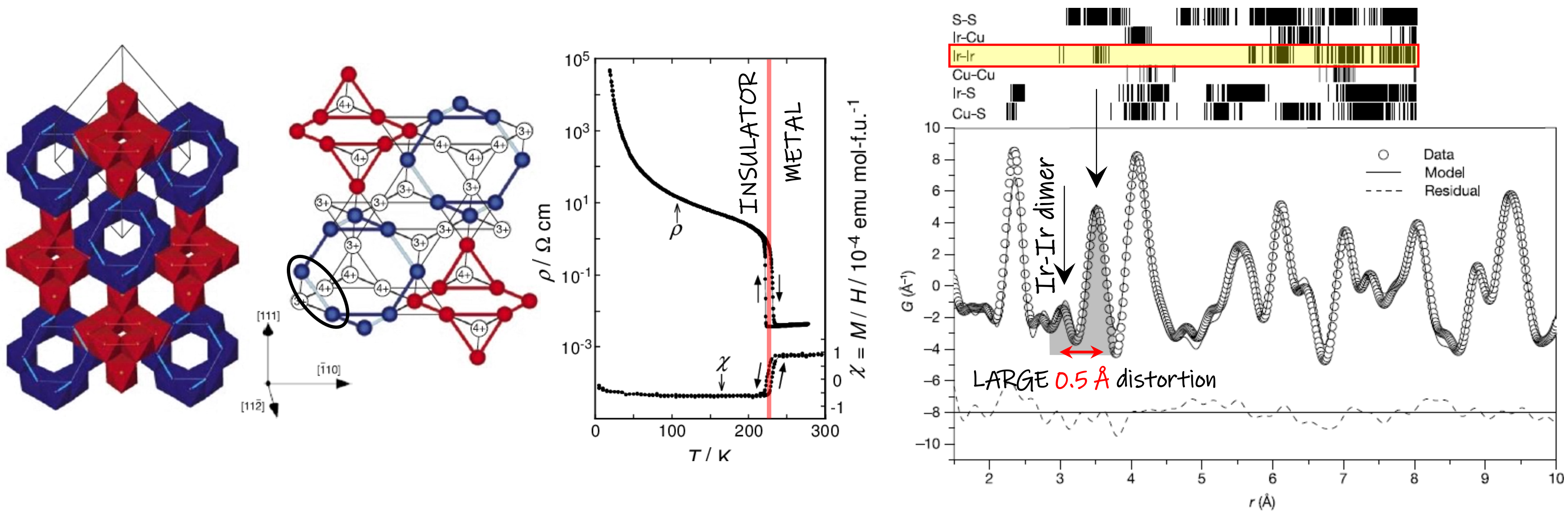
In studies ***at equilibrium****, the pair distribution function* ***(PDF) plays an integral role*** *in characterizing* ***locally broken structural symmetry*** *and* ***structural disorder***

Polarons in the metallic state of 1T-TaS_2 in equilibrium



Charge ordering driven by ***polaron crystallization into a Wigner crystal-like state*** *E Bozin et al Nat. Comm. 2023*

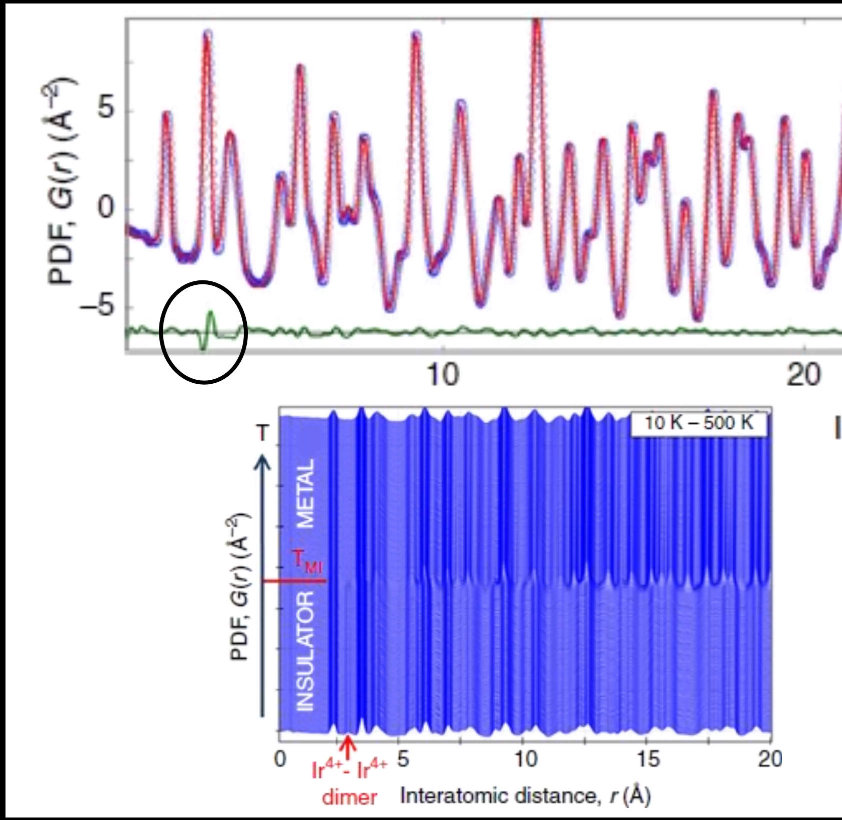
Temperature driven MIT in $CuIr_2S_4$ (equilibrium)



MIT in $CuIr_2S_4$ proposed as an orbitally driven Peierls transition

Dimerized lattice in $CuIr_2S_4$ P Radaelli et al Nature 2002

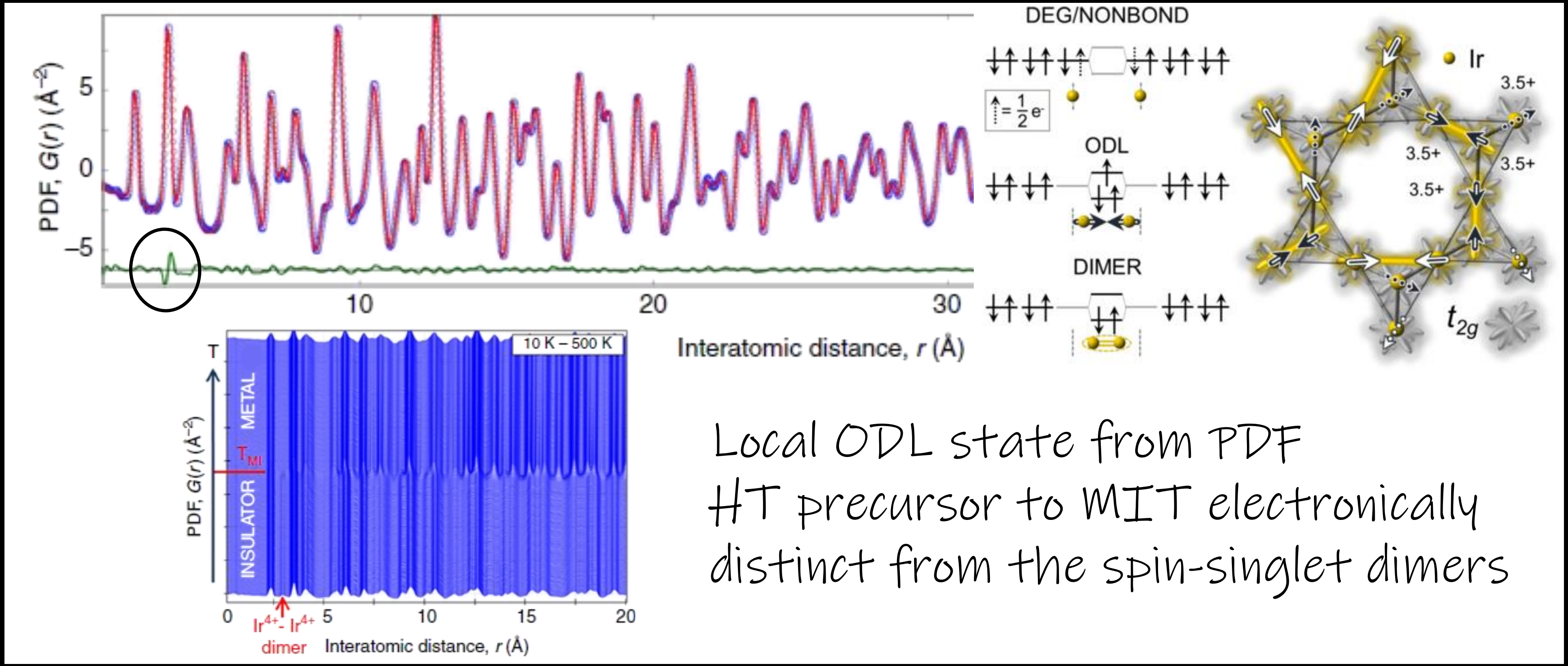
Local orbital degeneracy lifting as a precursor to MIT



Local ODL state from PDF
HT precursor to MIT electronically distinct from the spin-singlet dimers

Distinct local state of broken symmetry in metallic regime of $CuIr_2S4$ E Bozin et al Nat. Comm. 2019

Local orbital degeneracy lifting as a precursor to MIT



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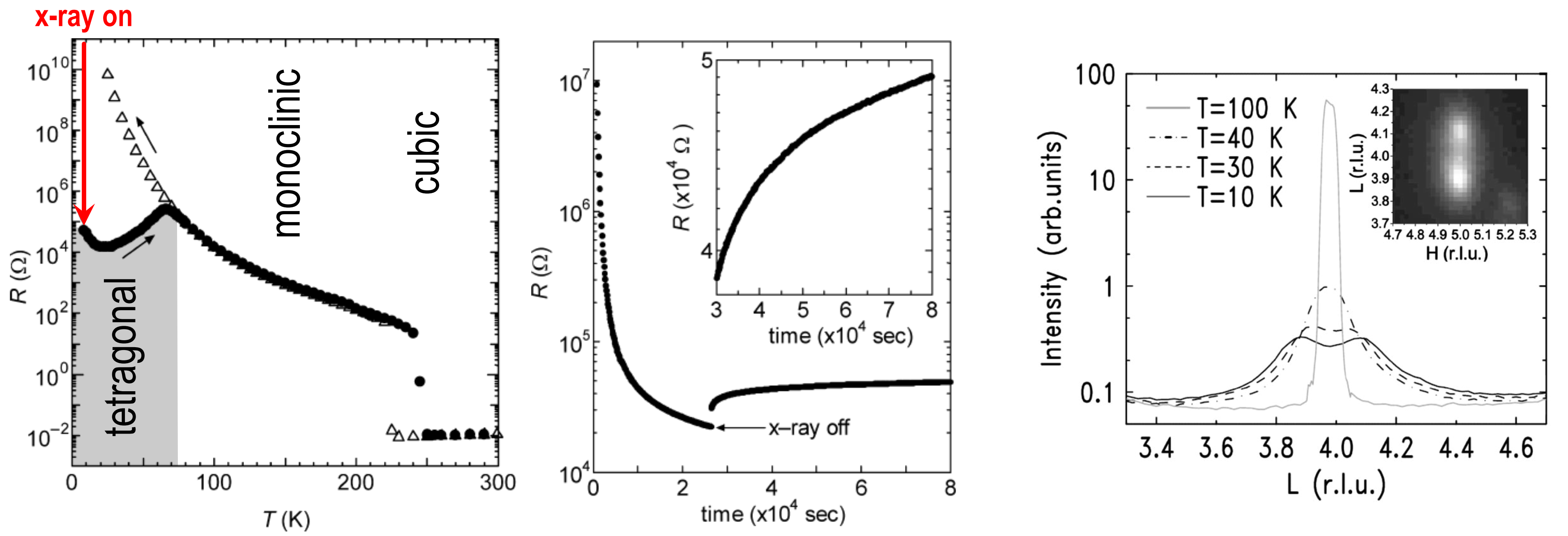
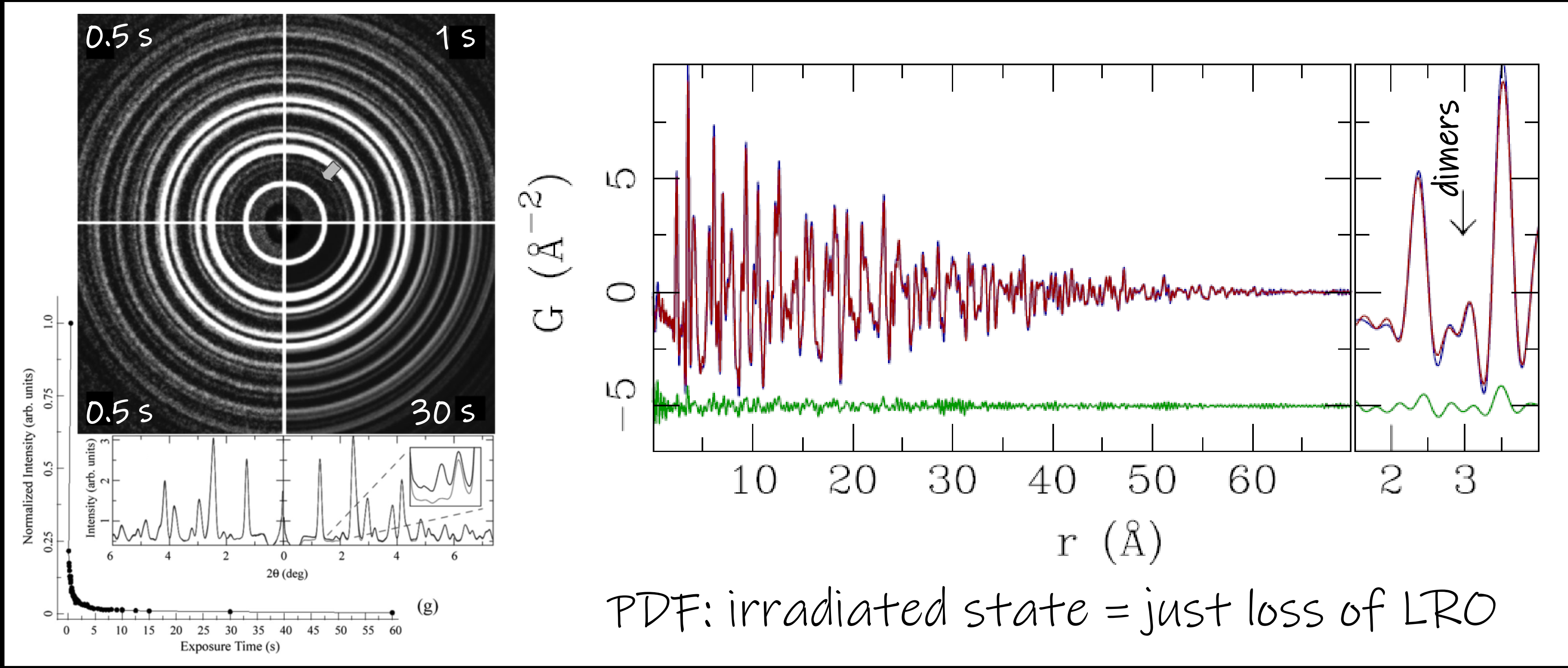
Dimer LRO removed through irradiation (e, X-ray, UV)



Dimer removed upon LT irradiation or just loss of long-range order?

T Furubayashi et al Sol. Sta. Comm. 2003 & V. Kiryukhin et al PRL 2006

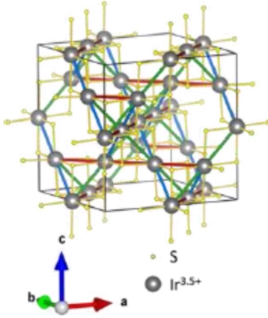
Dimer disorder through irradiation (e, X-ray, UV)



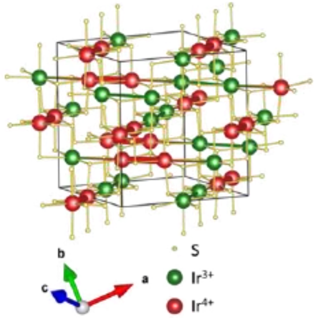
Dimers persist intact in the x-ray irradiated state E Bozin et al PRL 2011

Ultrafast reflectivity studies – new transient state

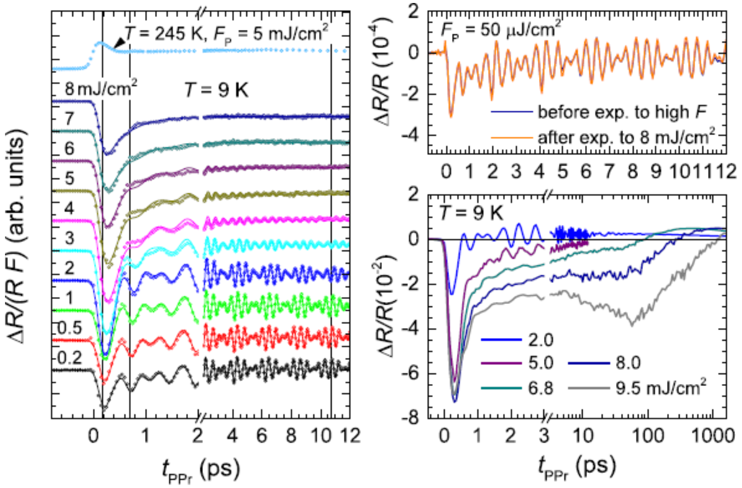
HT cubic



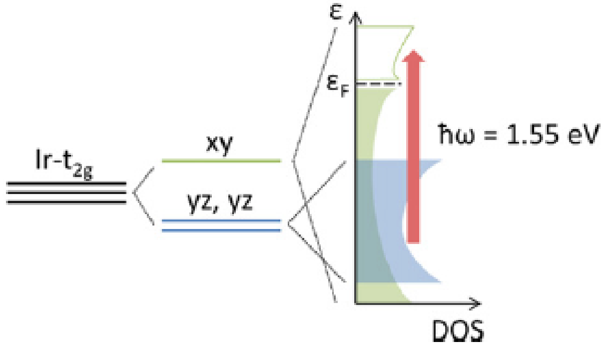
LT triclinic



transient reflectivity pump-fluence dependence



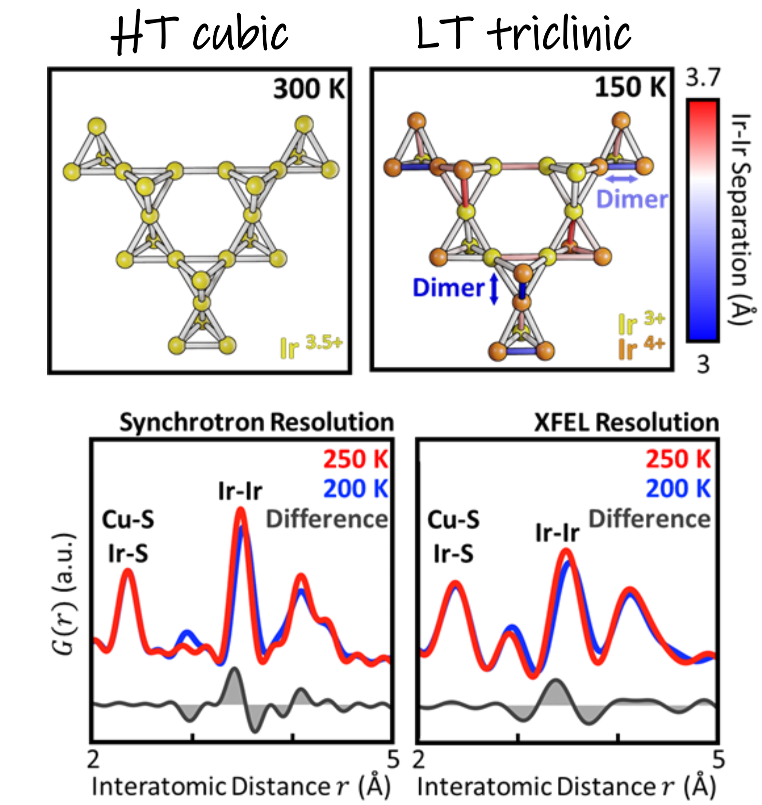
dominant optical transition



- Reflectivity decreasing & recovering over sub-ps and tens of ps timescales, respectively
- **Unidentified** transient state **weakly conducting**, suggestive of **strong dimerization being removed**

*Pumped phase: **a new transient structure** and **not a return to the HT state*** *M Naseska et al New J Phys 2020*

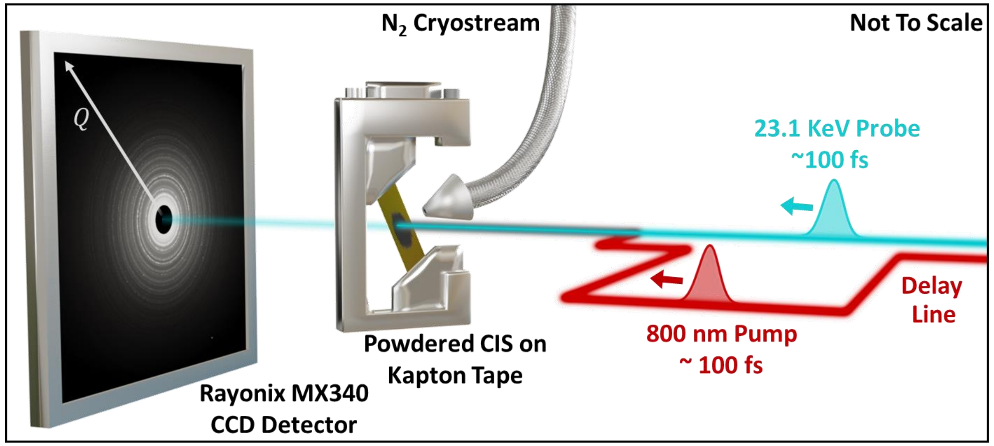
$CuIr_2S_4$ – PDF from APS reference measurements



- The removal of strong dimerization in CIS would generate a **large PDF response signal**
- Should be **clearly resolvable** in an XFEL measurement, Ir is a strong X-ray scatterer
- This pumped IM transition is ideal for **appraising the uf-PDF technique**
- Simultaneously examining how CIS transitions between insulating and conducting states

J Griffiths et al Nat. Matter. 2024

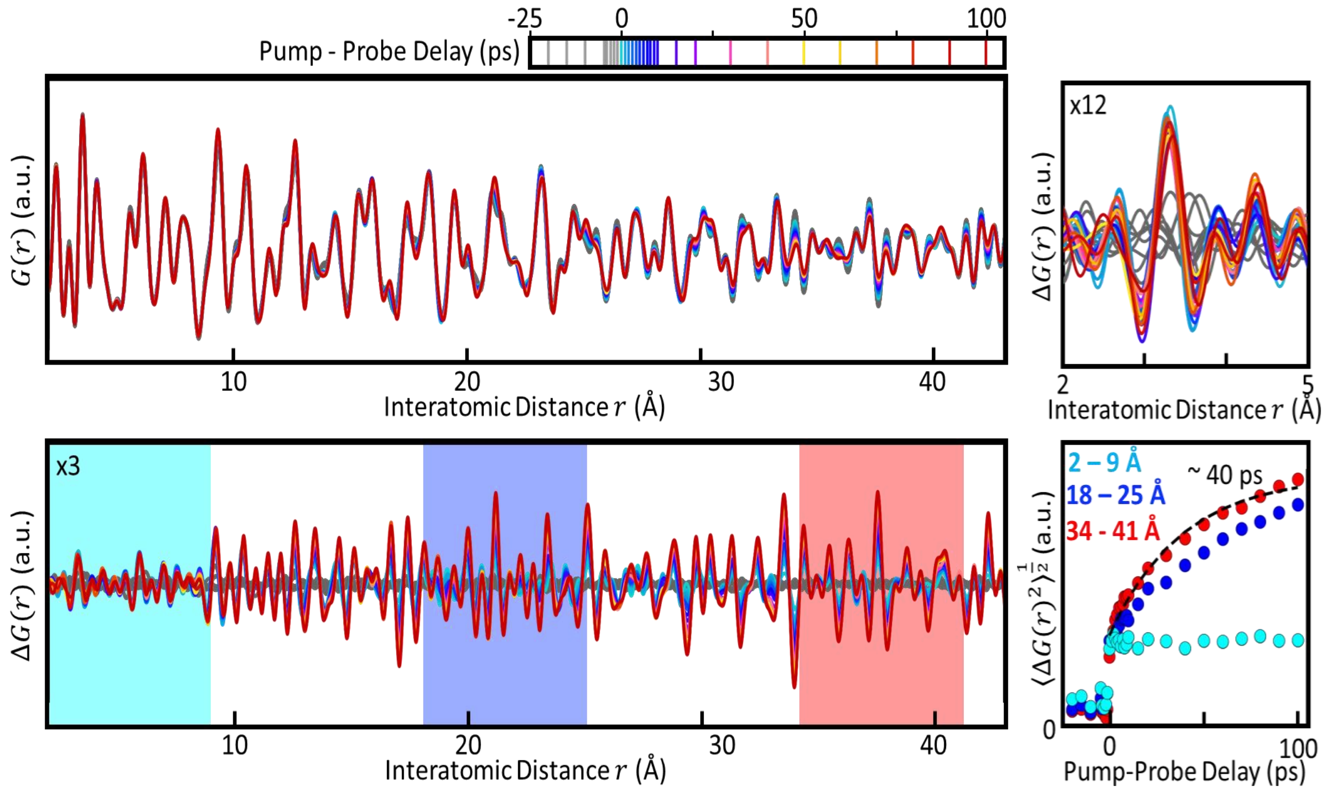
uf-PDF experiment MFX beamline of LCLS XFEL, SLAC



- CIS ground to ~**0.7 μm** particles
- Probe Energy: **23.1 KeV**
- Pump Energy: **800 nm**
  41 μJ over **400 μm** Gaussian spot
- Temperature: **150 K**
- Sample-Detector Distance: **7 cm**
- Pump-Probe Range: **-20 to 100 ps**
- Pump-Probe Resolution: **1 ps**
- **Stroboscopic** Measurement

J Griffiths et al Nat. Matter. 2024

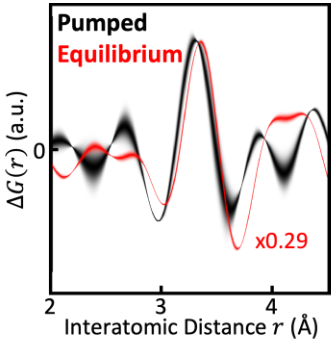
uf-PDF observations at 150 K



At pump:
Structure changes over **all** length scales
"Strong" dimers are destroyed
Can't resolve "weak" dimers from no dimers
Dimers destroyed over 20 – 30 % of the sample

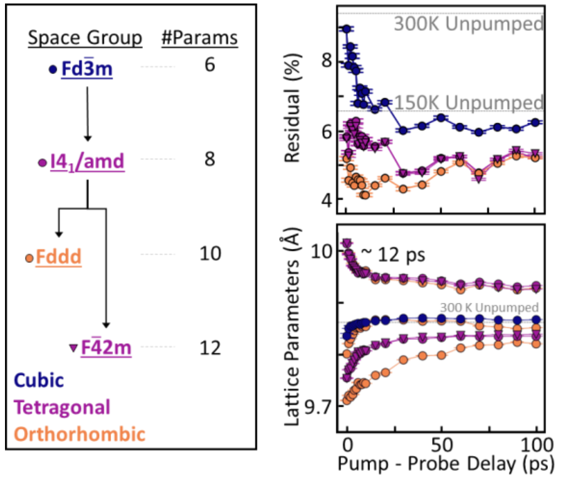
After pump:
Sub-unit cell structure ~constant
Longer length scale structure evolves over ~ 40 ps

Evolution of longer-range order



J Griffiths et al Nat. Matter. 2024

Small box modeling – a way to local symmetry



"Small box": provides qualification & quantification tool

Compare PDF to representative crystal model

Framing device for PDF information → **interpretability**

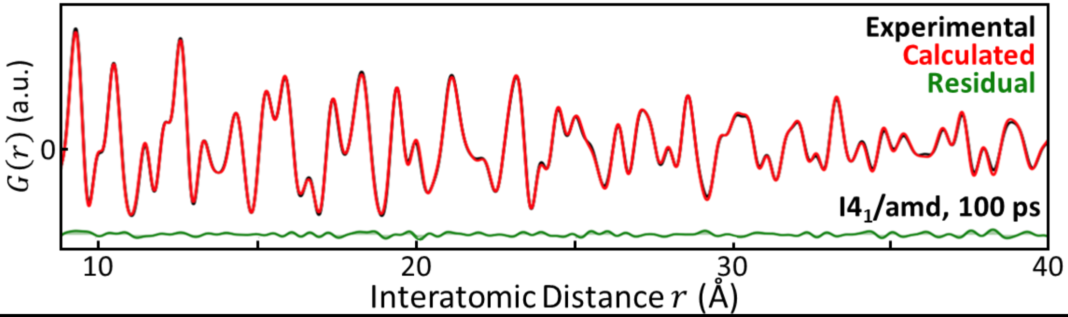
Unit cell with symmetry constraints:

Atom **positions** with unit cell

Atomic Displacement Parameters (ADPs)

Thermal motion: **temporal** variance

Disorder: **spatial** variance



Residual: $\sqrt{\int [G_{obs}(r) - G_{calc}(r)]^2\, dr \Big/ \int G_{obs}^2(r) dr}$

Non-local **symmetry increases** with delay-time!

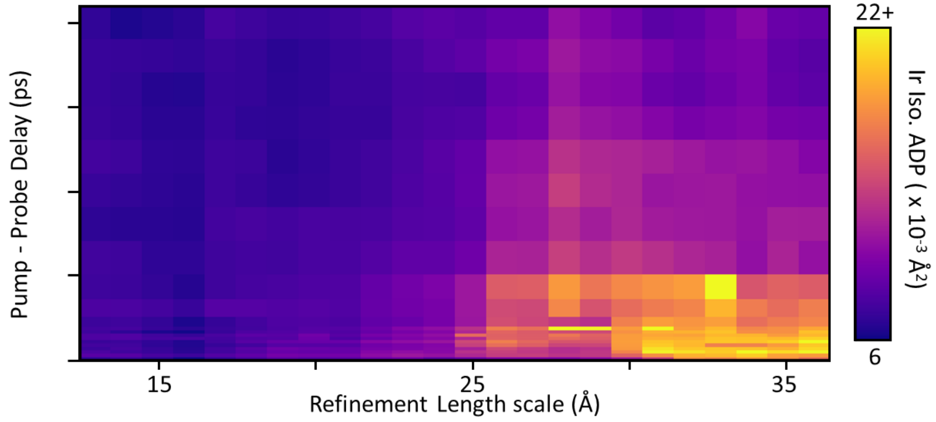
J Griffiths et al Nat. Matter. 2024

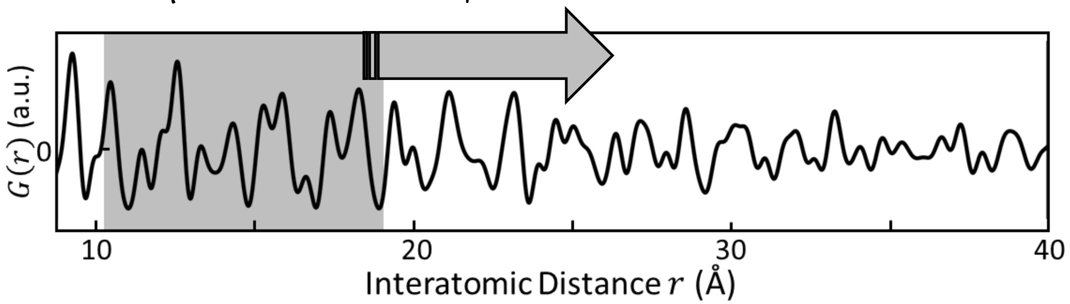
Mapping the disorder via (r, t) ADP modeling

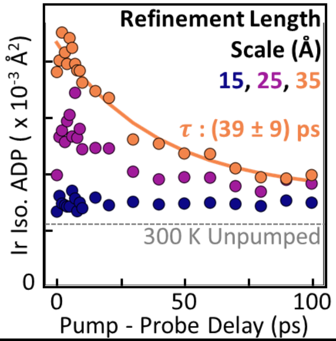
Refine I41/amd over a sliding window
- 8.8 Å window width
- 1 Å sliding step

No dependance of structure parameters

- Strong Ir ADP dependance
- Disorder > 2 unit-cell distance
- Decays over ~ 40 ps







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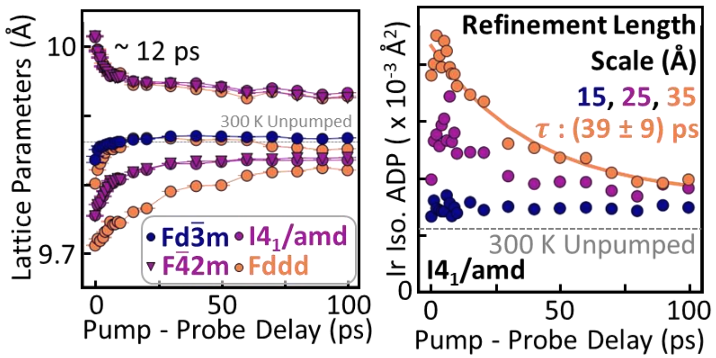
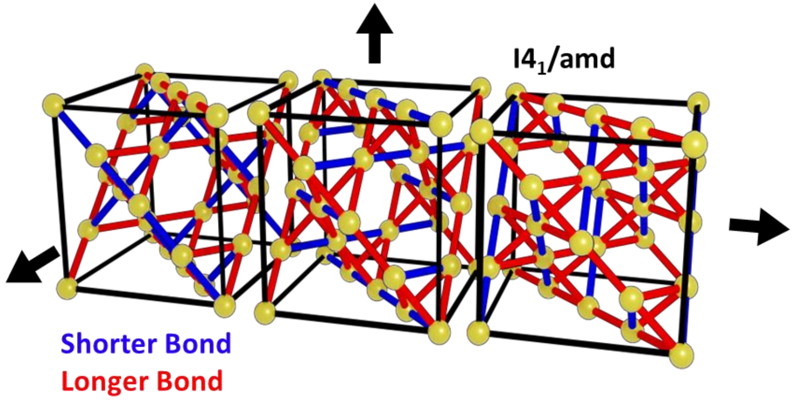
Identification of multiple time- & length-scales

Evolution contains **two** timescales:

Lattice parameters: **12 ps**

Disorder: **40 ps**





Same local interatomic distances

Different spatial arrangement of bond-lengths

Different local structural configurations → same local PDF

Changing proportion of configurations → change in bulk structure

Any proportion of configurations can be ordered or disordered

Ordering timescale is **independent**

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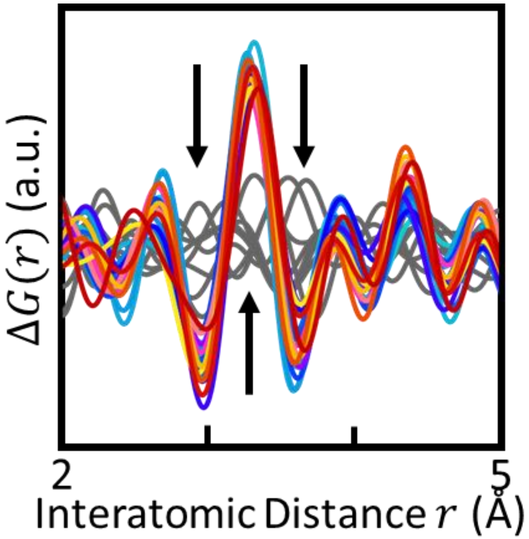
Summary

- Optical pumping **removes** strong dimerization in $CuIr_2S_4$ (sub-ps regime)
  - System does **not** return to high temperature cubic phase
- Removal of dimers is initially spatially **disordered**
  - Order reestablished over ~40 ps
- **ADP mapping** leverages PDF strengths
  - Tracks disorder in space and time
- uf-PDF is **feasible** at current XFEL facilities
  - Need favorable sample
  - Need reference synchrotron measurements
- Can apply to other transiently disordered systems
  - e.g. VO_2, 1T-TaS_2



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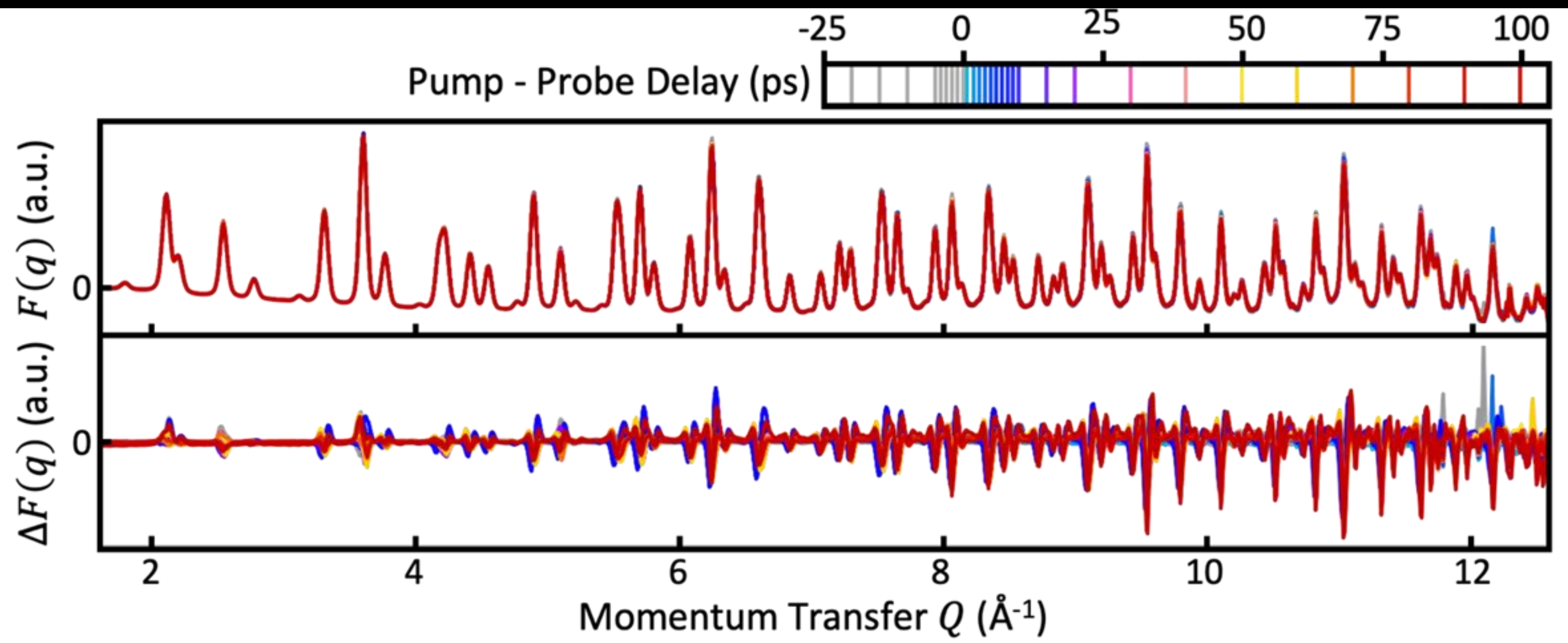
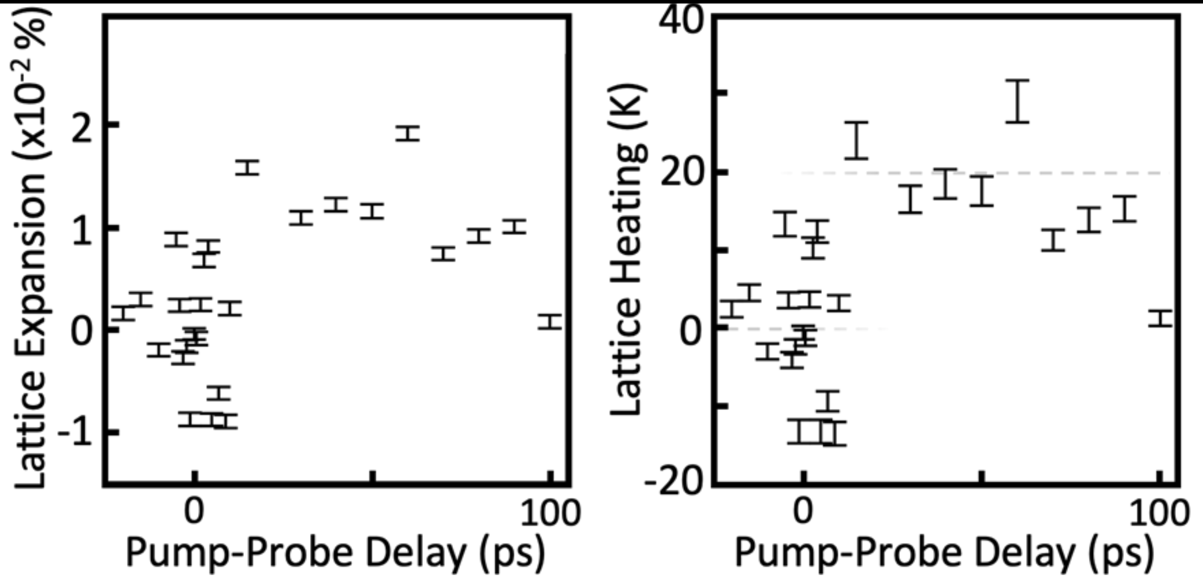
Extras

300 K Pumping



Only a weak heating response, seen clearly by the drop in high Q peak intensities.
Any peak shift due to lattice shifting is much smaller than the peak width.

300 K Pumping



Thermal lattice expansion of the cubic metallic phase at 300 K under 27μJ of pump laser energy, extracted using the shift of Bragg diffraction peaks.
Using APS measurements of the same powder at equilibrium at 250 K and 300 K, a linear thermal expansion coefficient. This converts the lattice expansion into approximately **20 K of laser heating**. Note that the heating onset is delayed by approximately 10 ps in accordance with the two-temperature model of lattice heating.

Sliding Window Fits