# Kinetics bottleneck during photoinduced ultrafast insulator-metal transition in 3D orbitally-driven Peierls insulator $CuIr_2S_4$

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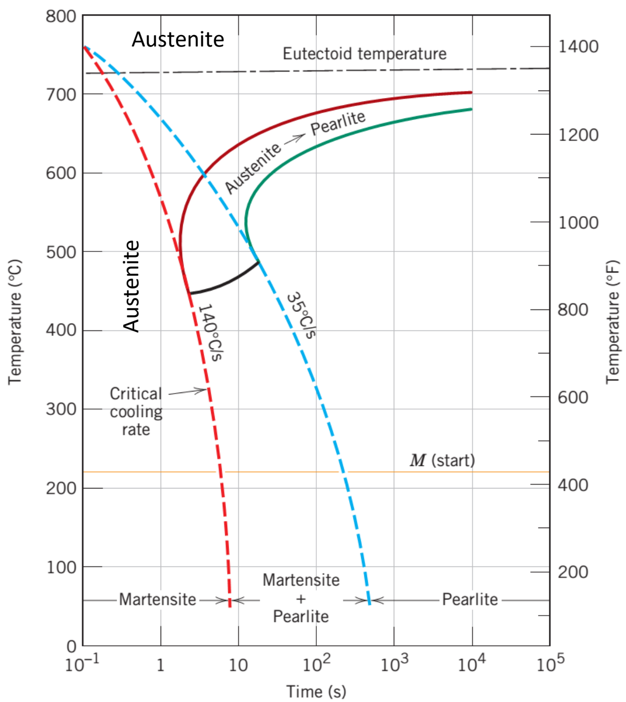
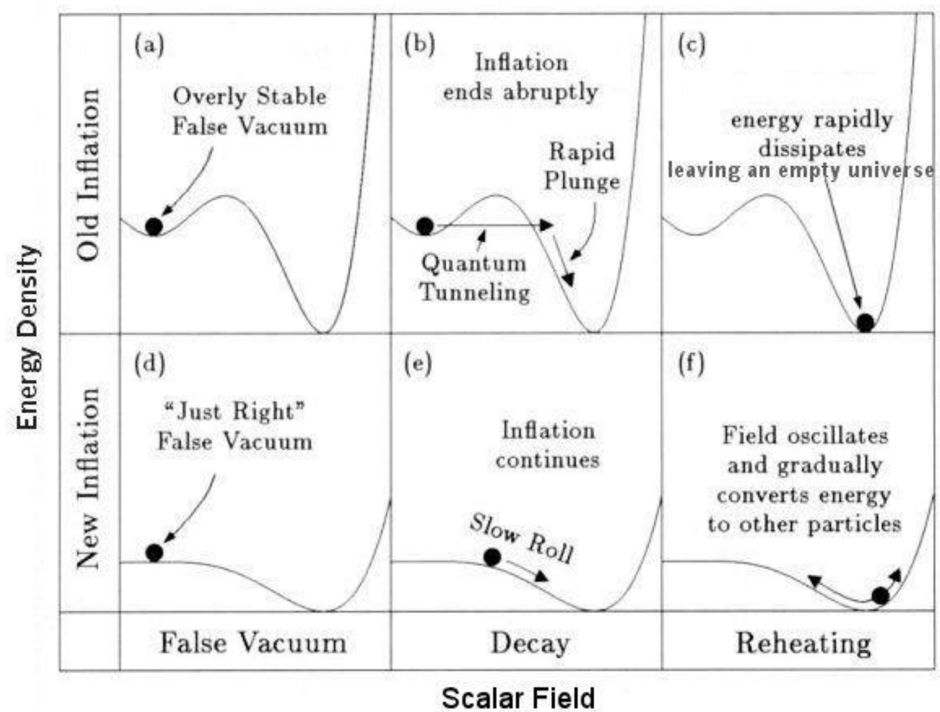
# Importance of phase transition kinetics

## Martensite formation in steel



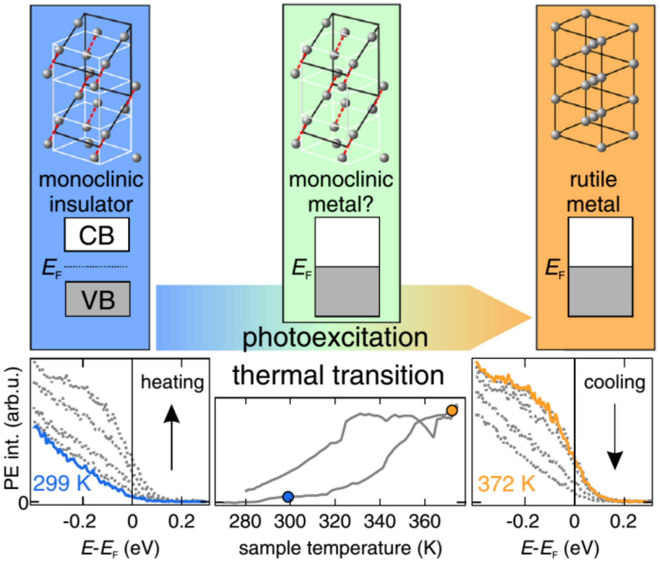

Callister, William D. *Materials science and engineering an introduction*. John Wiley, 2007

## Inflation of the early universe

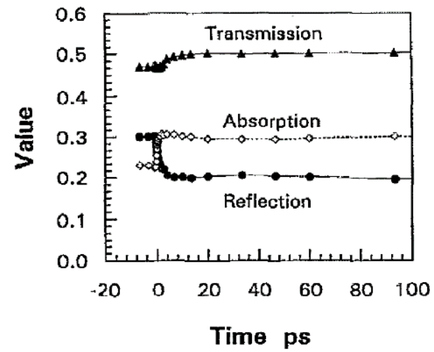



Review of the Universe, Inflation Theory in website: universe-review.ca

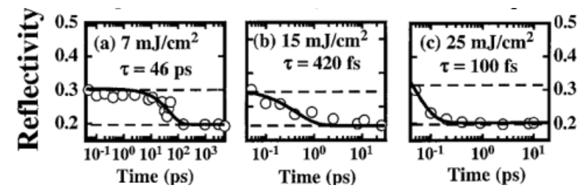
# Ultrafast insulator-metal transition in $VO_2$



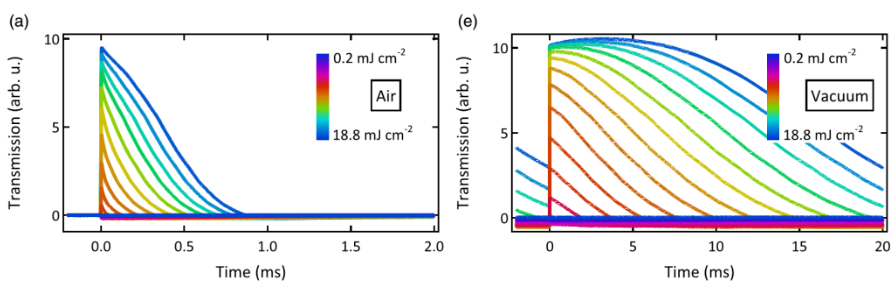

Wegkamp et al., PRL **113**,216401 (2014)



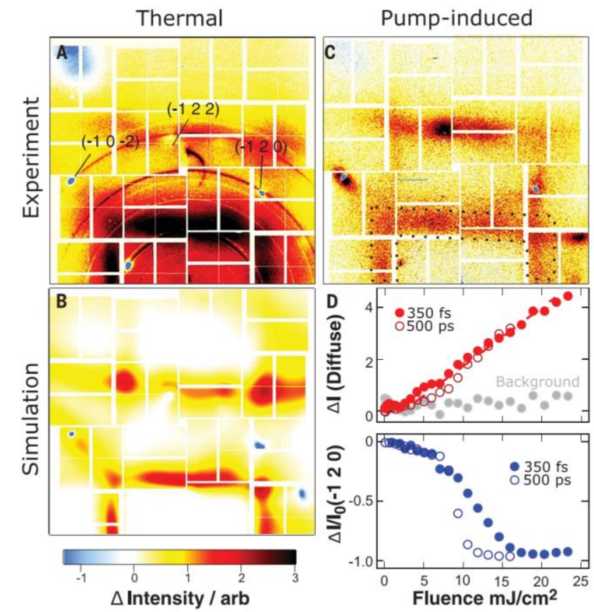

M.F. Becker et al., Appl. Phys. Lett. **65**, 1507 (1994).




A. Cavalleri et al., PRL **87**, 237401 (2001)

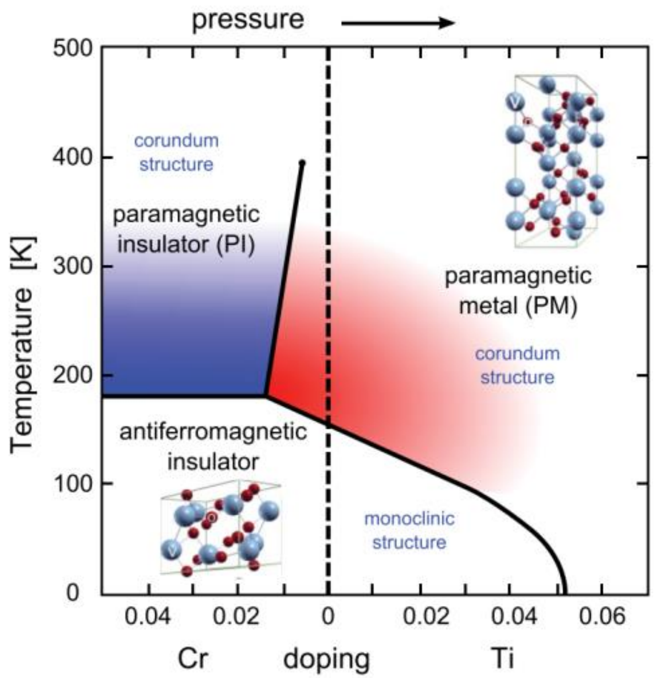



L. Vidas et al., PRX **10**, 031047 (2020)

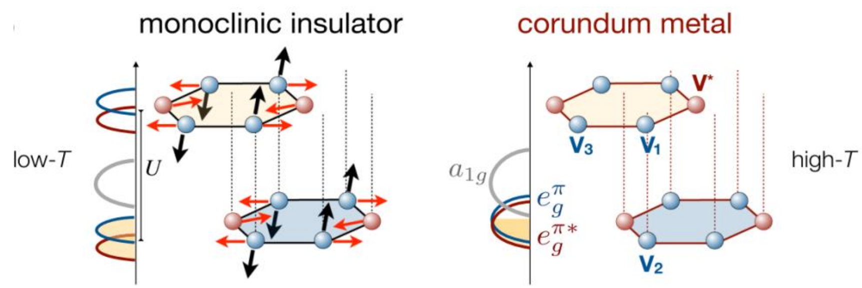



S. Wall et al., Science **362**, 572–576 (2018)

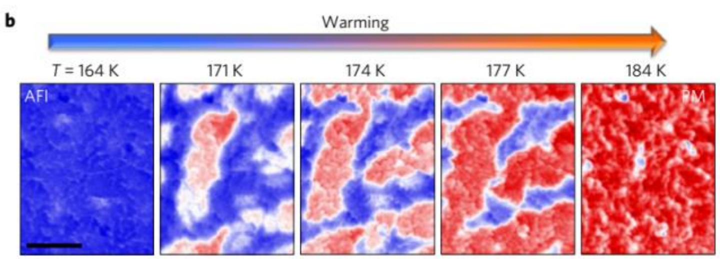
# Not so ultrafast in $V_2O_3$



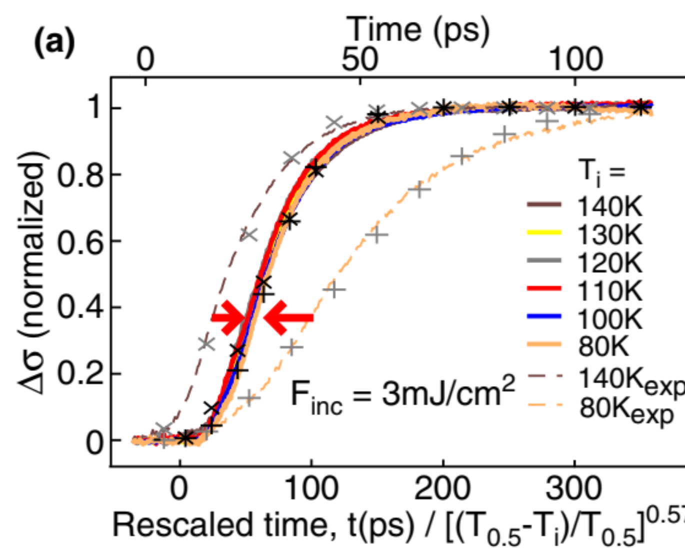

Hansmann et al., Phys. Stat. Sol. B **250**, 1251 (2013)




Ronchi et al., PRB 100, 075111 (2019)

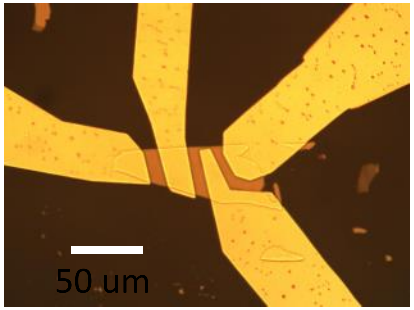



McLeod, A. S., et al., *Nature Physics* **13**, : 80 (2017).



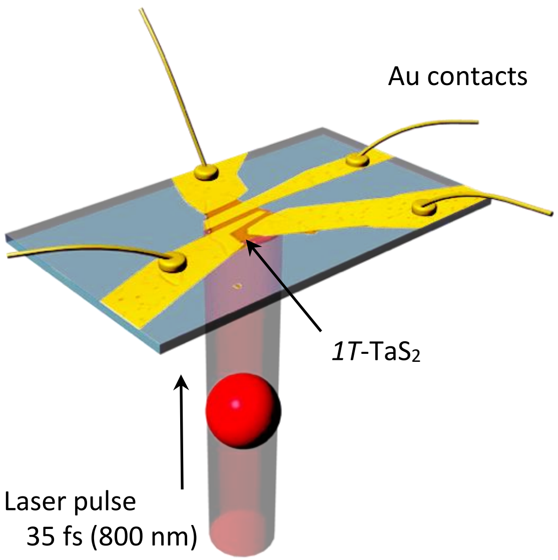

E. Abreu et al., PRB 92, 085130 (2015)

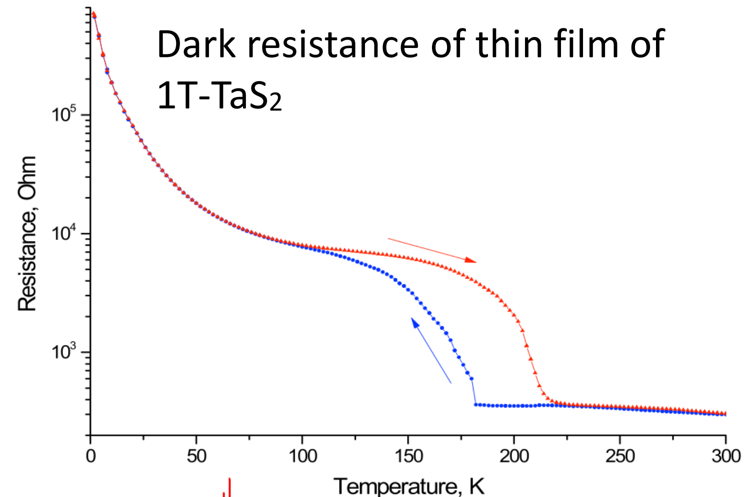
# Switching to a metastable hidden state in 1*T*-$TaS_2$

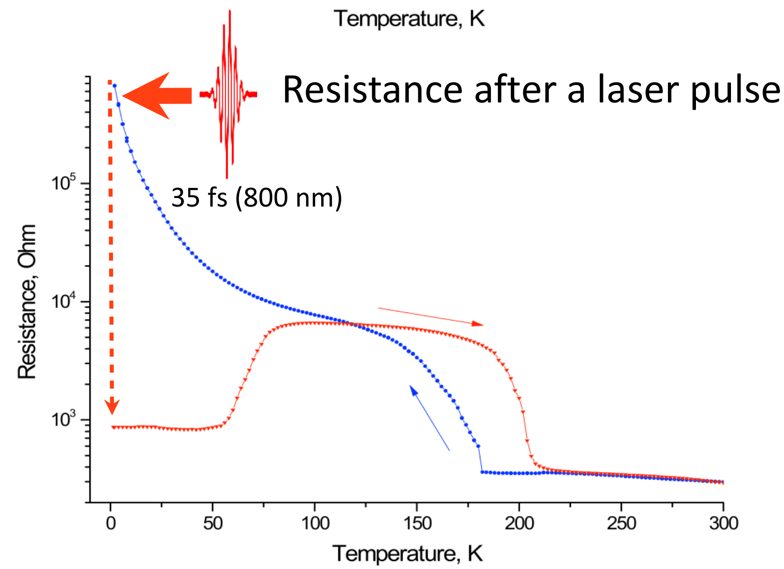




1*T*-$TaS_2$ single crystal, ~100 nm thick.
Au contacts by laser lithography (LPKF LDI).

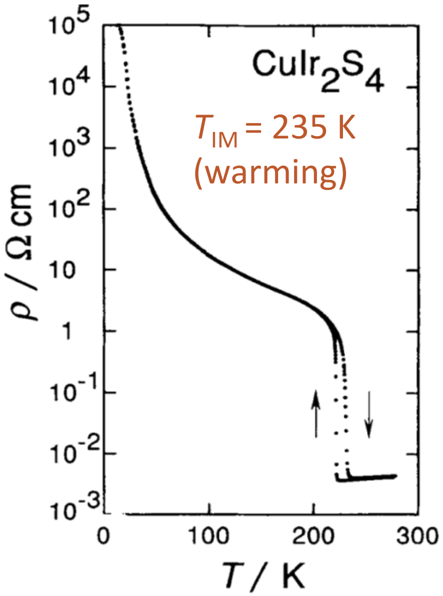


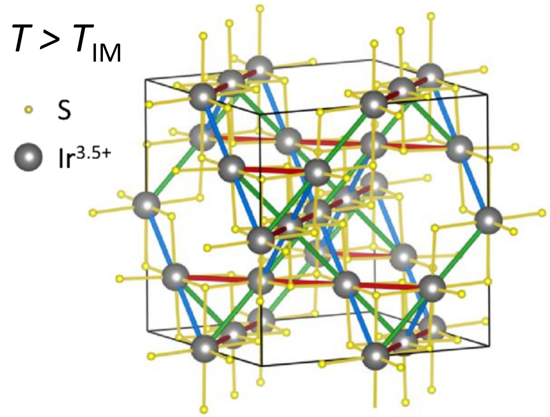



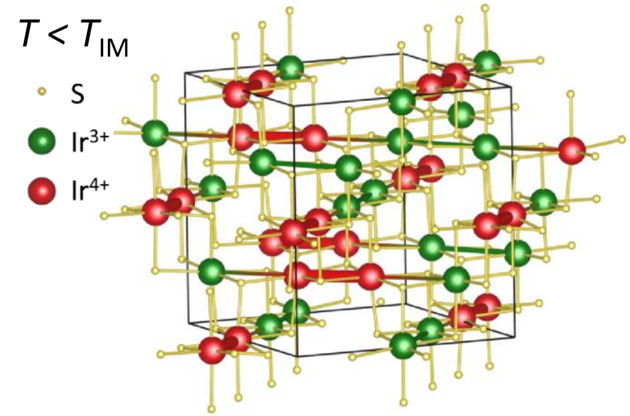

L. Stojchevska, et. al., *Science* **344**, 177-180 (2014)
I. Vaskivskyi et al., *Science Advances* **1**, e1500168 (2015)

# Metal-insulator transition in $CuIr_2S_4$



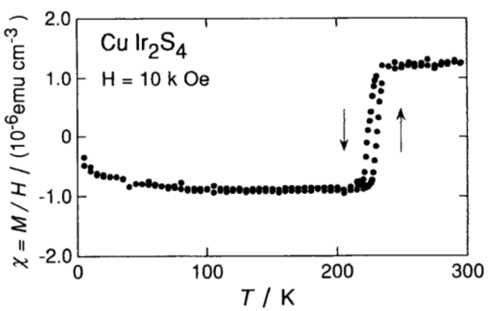




cubic spinel structure

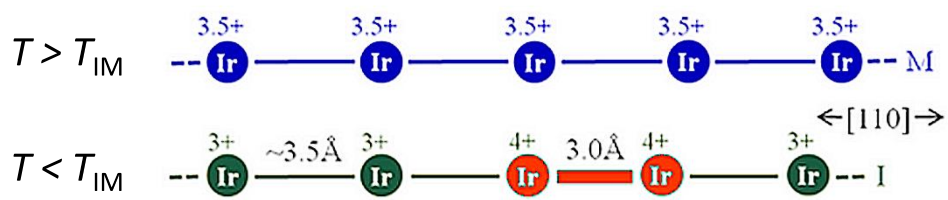



monoclinic

gap: $\Delta_I \sim 0.15$ eV



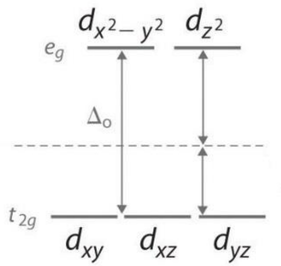

avg. valence: $Ir^{3.5+}$: [Xe]$4f^{14}5d^{5.5}$

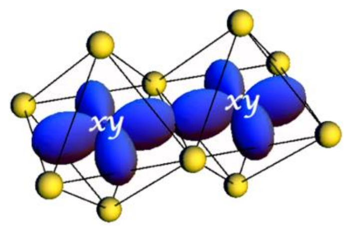


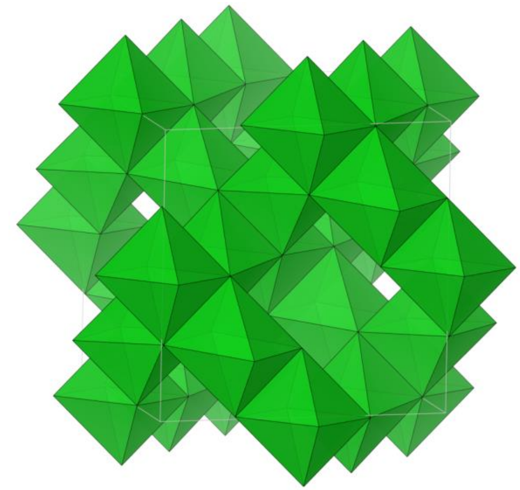

T. Hagino et al., Phil. Mag. B, **71**, 881-894 (1995).

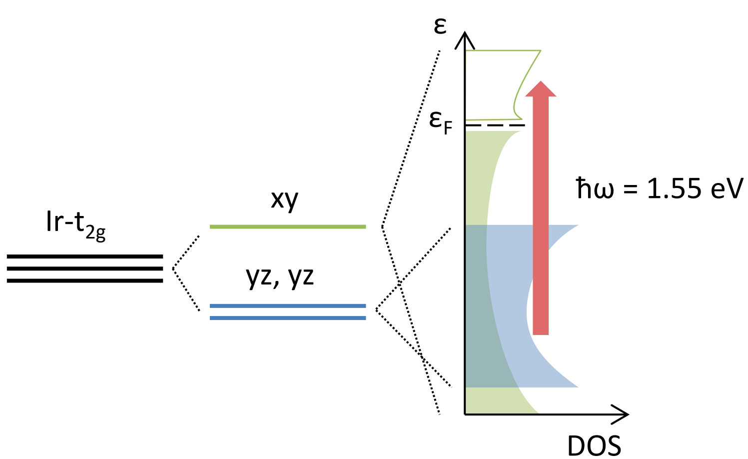
# Orbitally Induced Peierls State

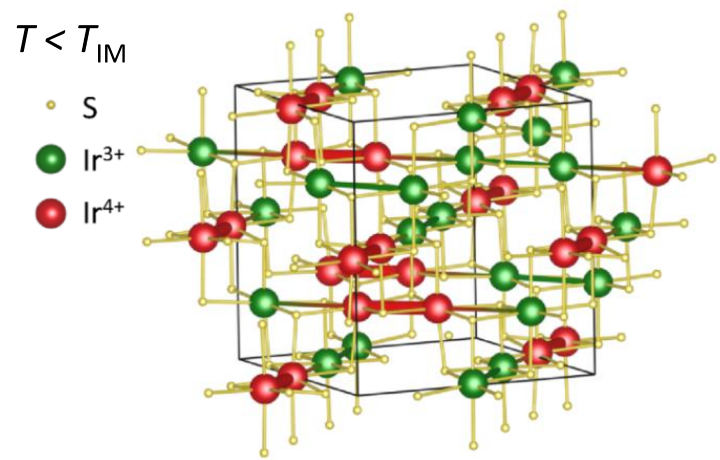
Edge sharing octahedra chains along <110> directions



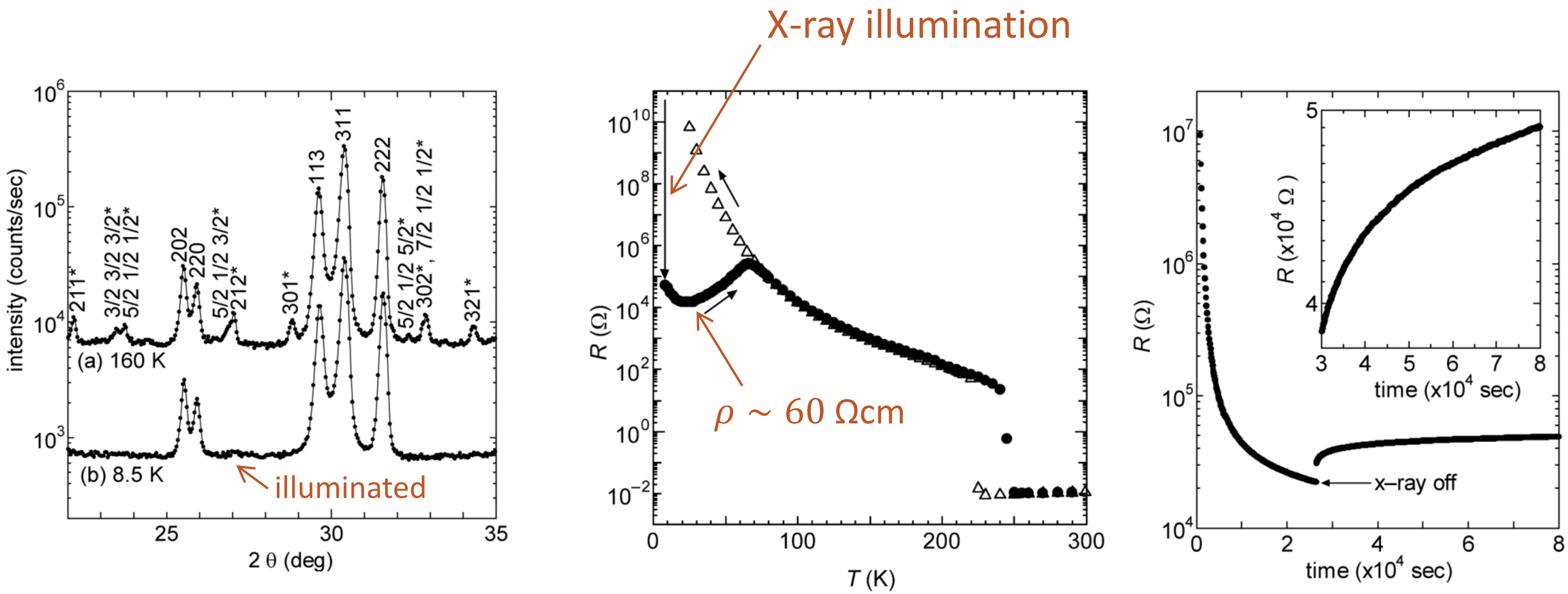





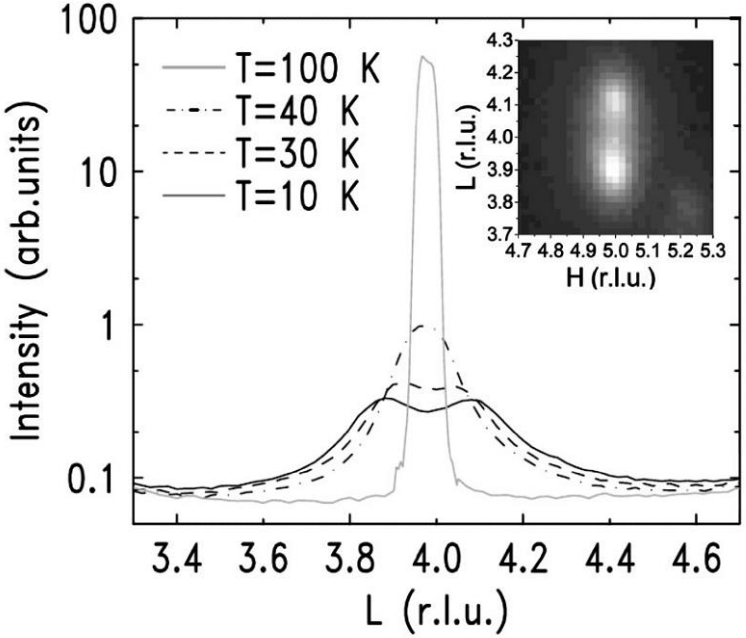

Khomskii, Mizokawa, PRL **94**, 156402 (2005)

# X-ray induced weakly conducting disordered (WCD) phase




T. Furubayashi et al., *Solid State Communications* **126,** 617–621 (2003).

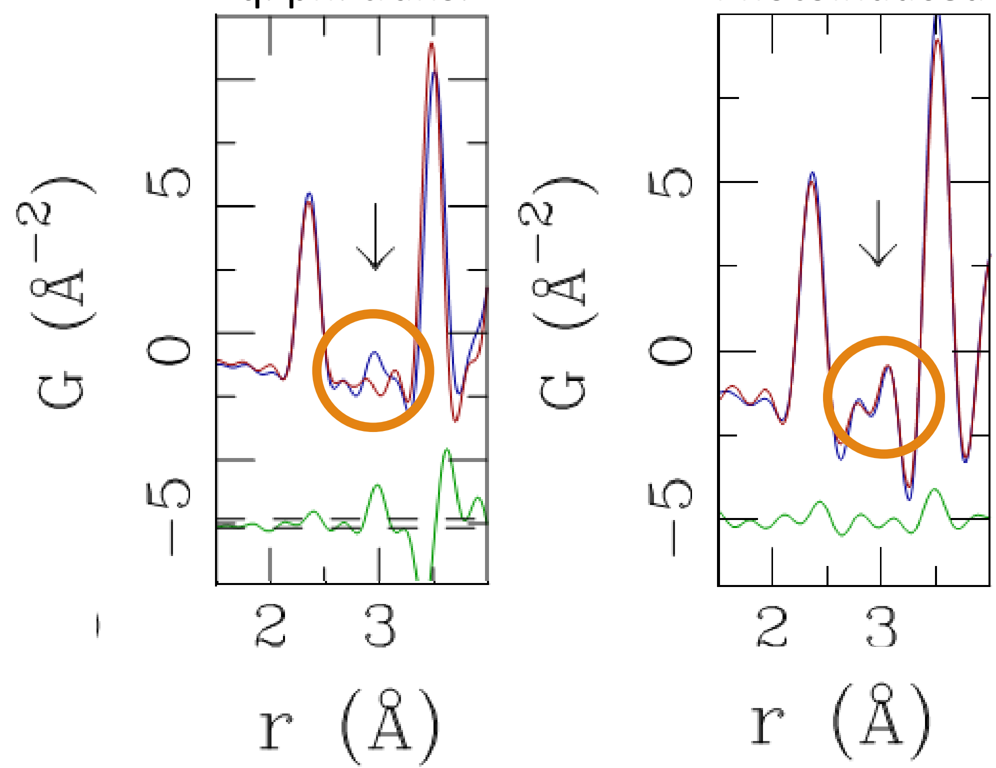
# Local $Ir^{4+}$ pairs persist in the WCD phase




V. Kiryukhin et al., PRL **97**,225503 (2006).

Eq. ph. trans.

Photoinduced

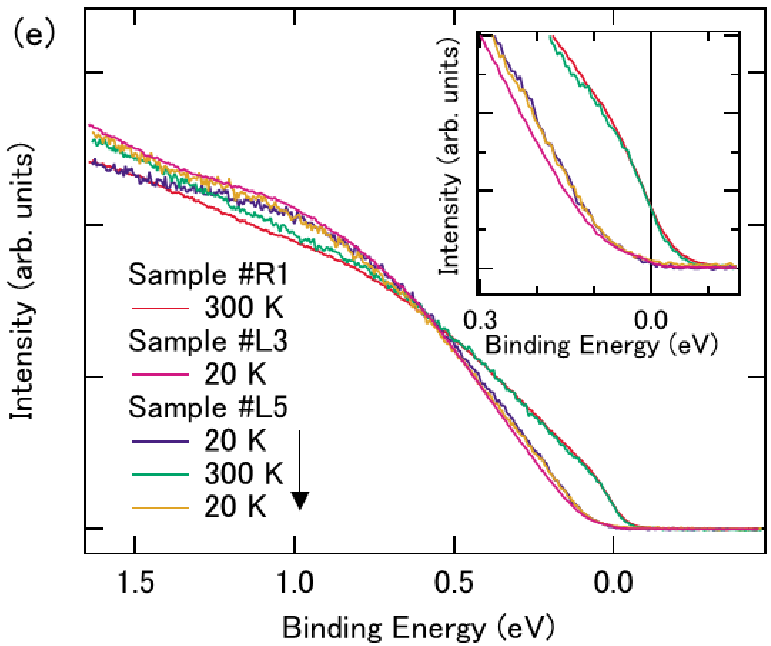


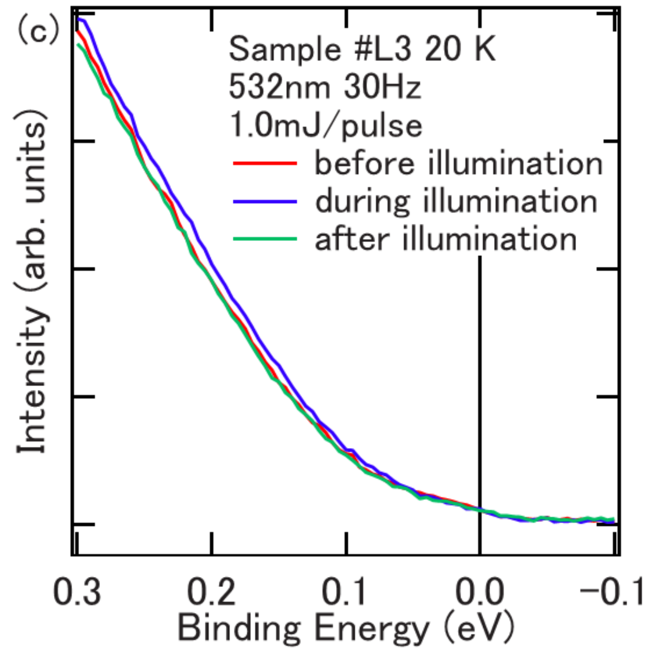

E. Bozin et al., PRL **106**, 045501 (2011)

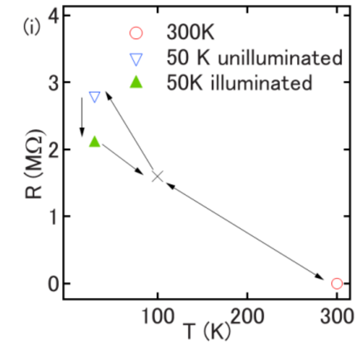
Incommensurate diffuse diffraction

Atomic pair distribution function

# In-gap states in the WCD phase



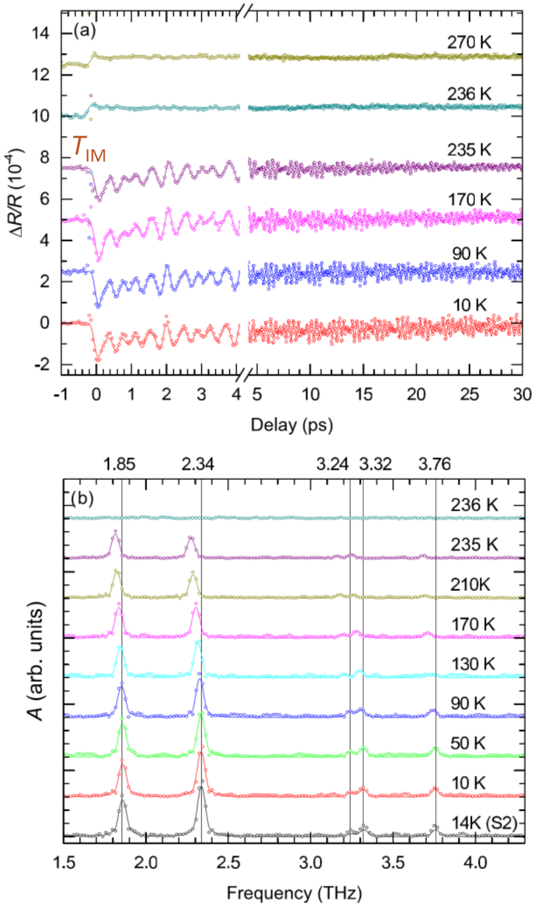



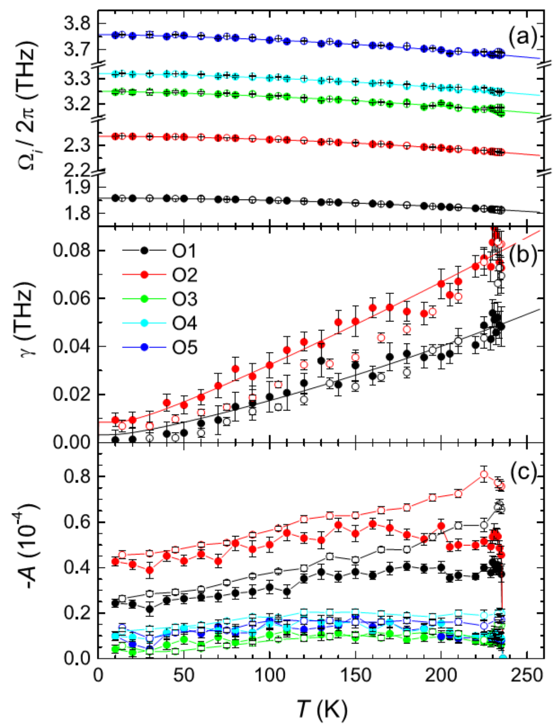



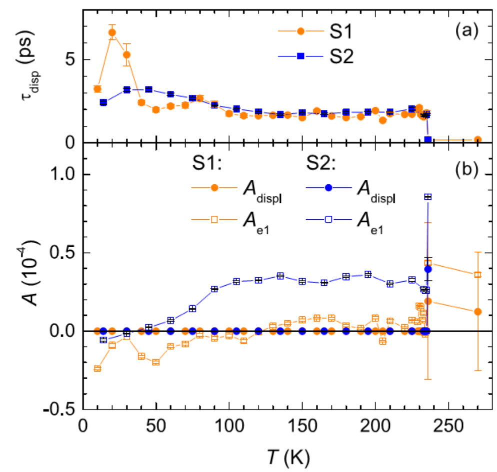

Takubo et al., PRB **78**, 245117 (2008)

# Quasi-equilibrium ultrafast transient reflectivity

## Linear response region ($F \sim 150\ \mu J/cm^2$).



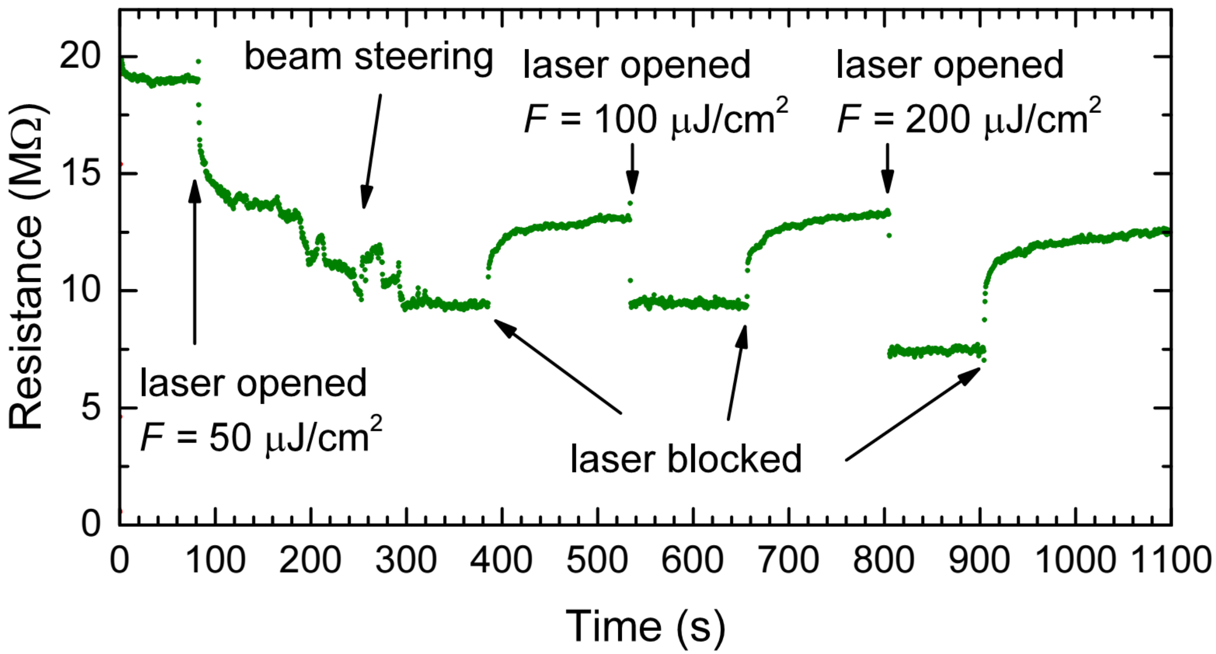



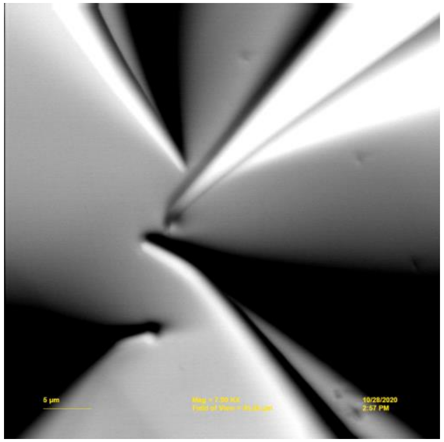

M. Naseska et al., PRB **101**, 165134 (2020).

- Coherent phonons in the insulating broken lattice symmetry phase (Ir and Cu not Raman active in the cubic phase).
- No clear sign of optically induced WCD phase from lattice dynamics despite ~2000 photons/(unit. cell)/s?
- No gap-induced bottleneck due to intragap states (WCD phase?).

# Femtosecond-laser photoinduced WCD phase

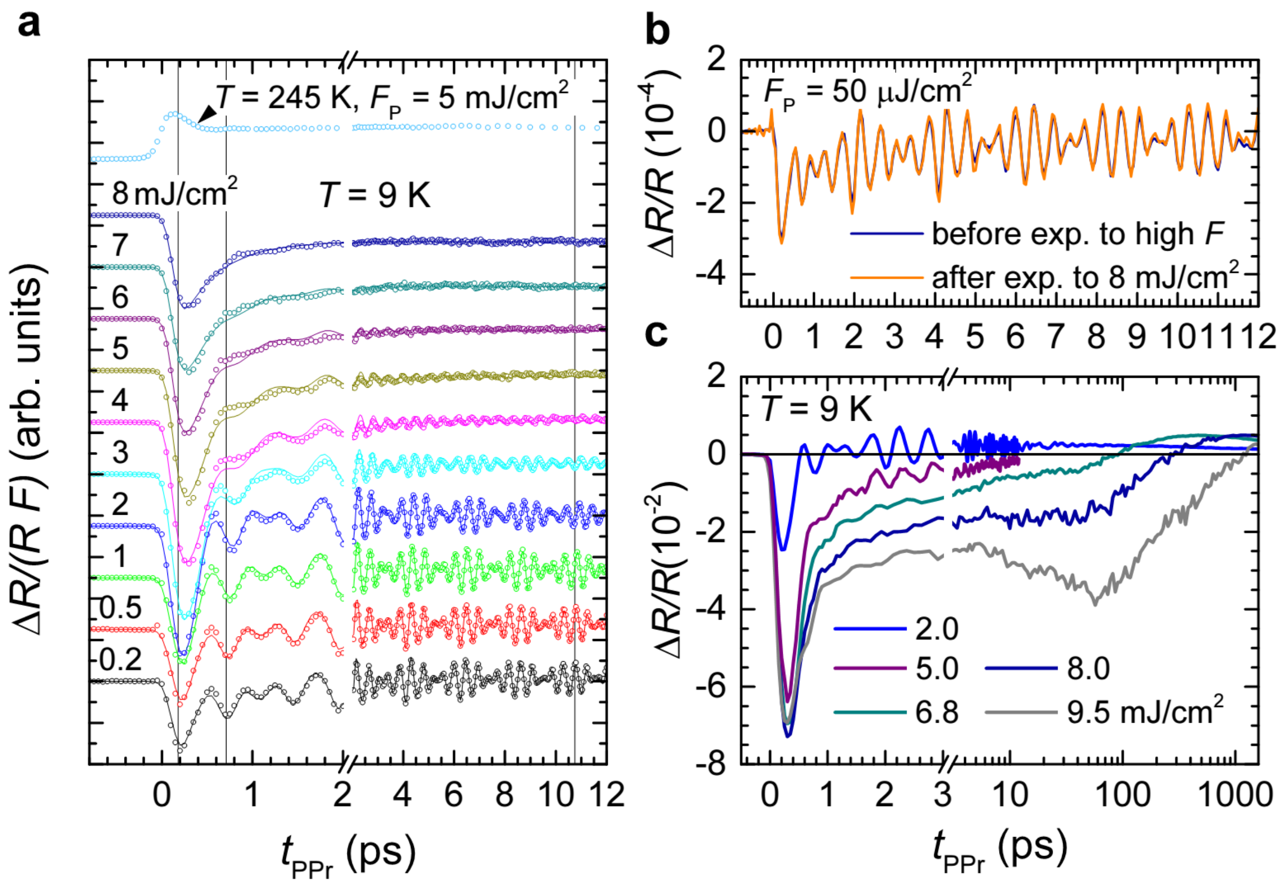



4-tip STM



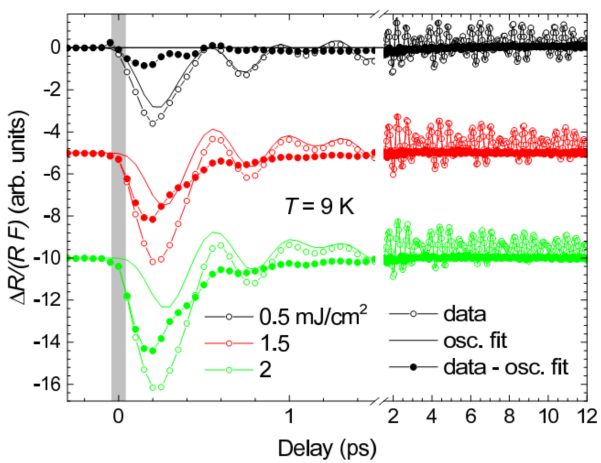
WCD phase “unavoidable” at low $T$ in any transient reflectivity experiment.

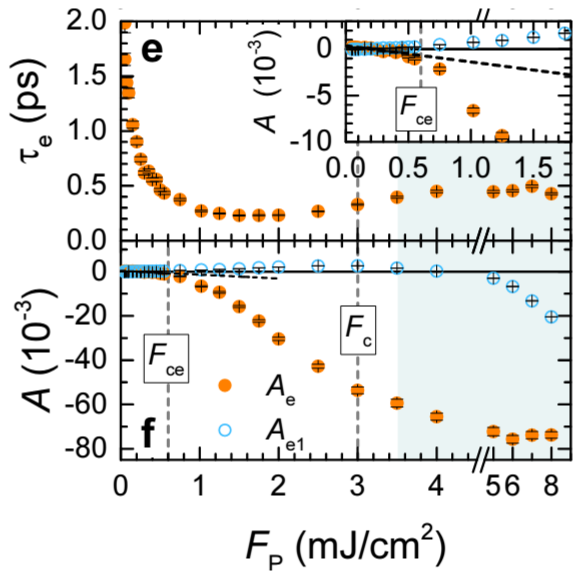
# Strong femtosecond pumping



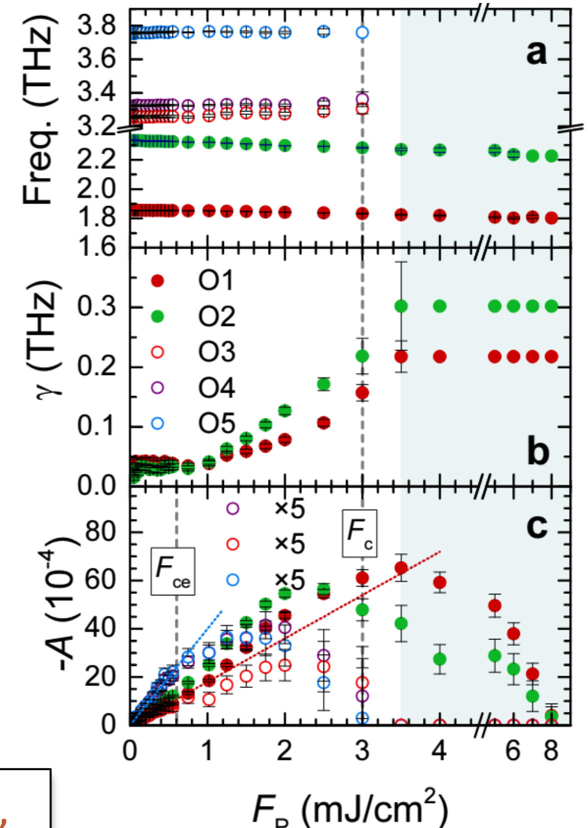

- Suppression of the coherent phonons above $F_c \sim$ 2-3 mJ/cm$^2$.
- Long lived (~50 ps) transient state.
- Reversible, no long lived metastable states (except WCD phase).

# Strong femtosecond pumping - analysis



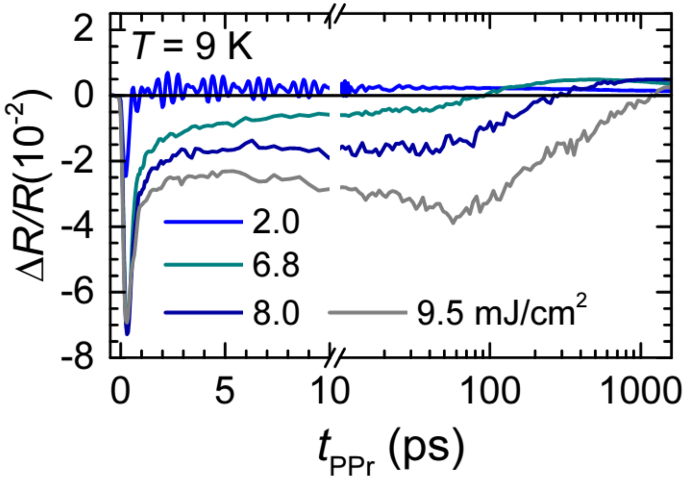

electronic system
(exp. relaxation)

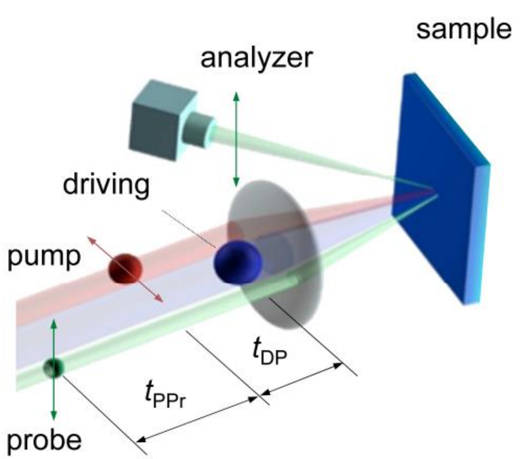


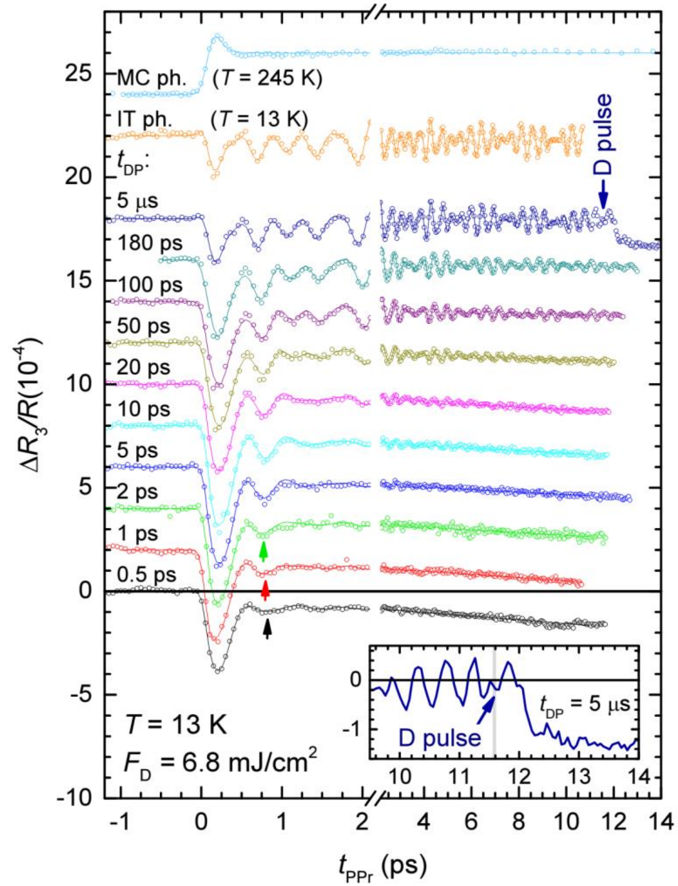

lattice (phonons )

- Different threshold fluences for phonons, $F_c \sim 3$ mJ/cm$^2$, and exponential components, $F_{ce} \sim 0.6$ mJ/cm$^2$.
- Gradual suppresion of the coherent phonons due to the excitation inhomogeneity. (finite penetration depth)

# 3-pulse experiments: highly excited transient state

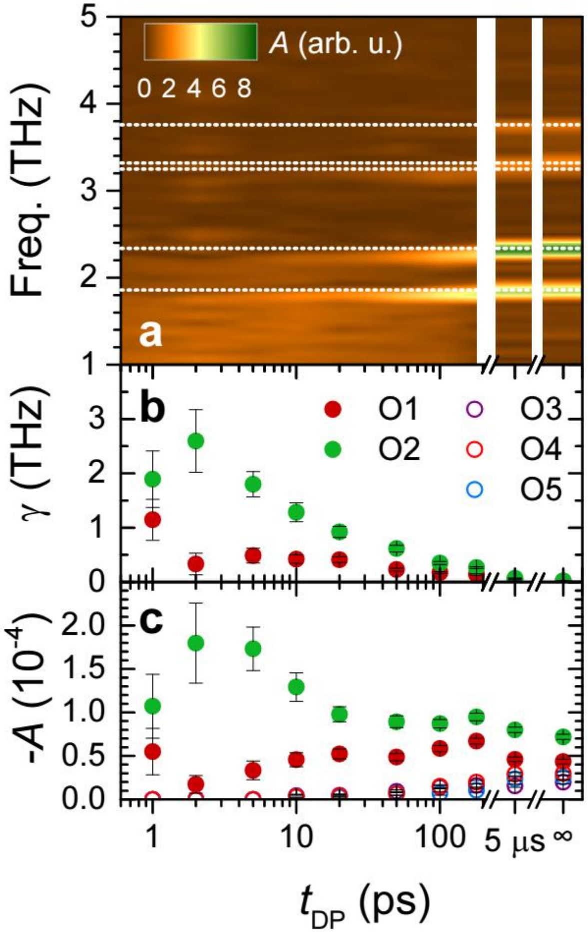


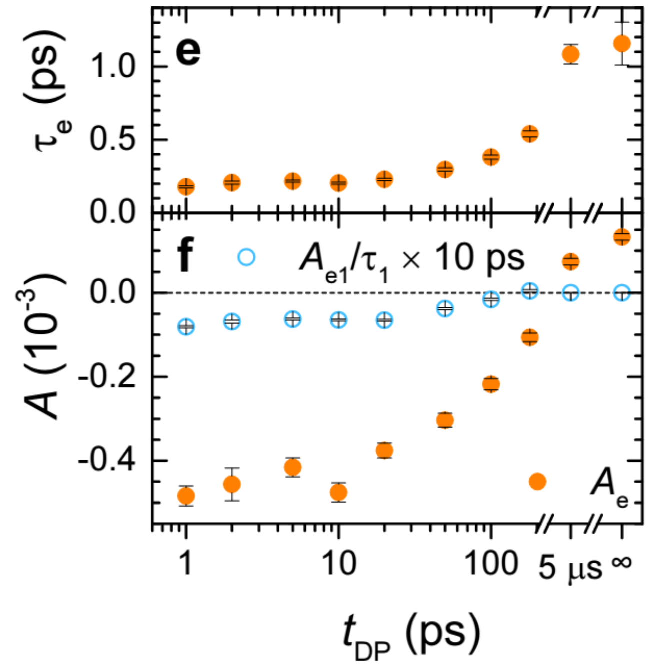




- Strong dephasing, but broken symmetry not suppressed in the highly excited state.
- No evidence for the metallic cubic phase.

# Highly excited transient state - analysis



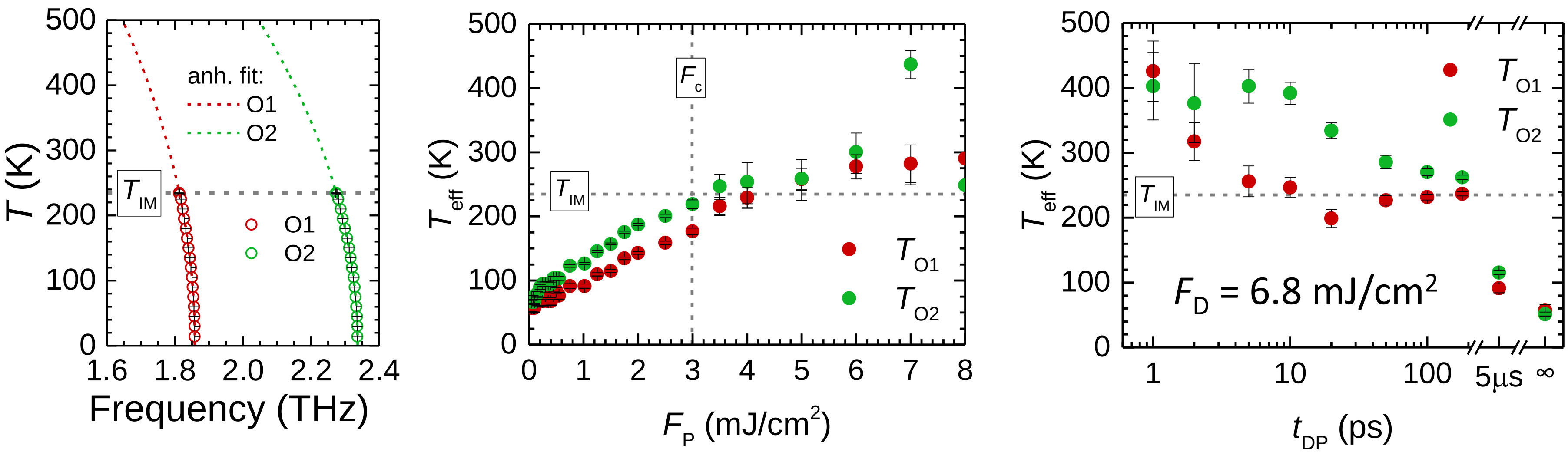

lattice (phonons)




electronic system (exp. relaxation)

- Strong dephasing on a 10-ps timescale.
- The initial phonon amplitude not suppressed. Most of the exc. volume in the (local) broken symmetry state.
- Fast electronic relaxation (~ 200 fs) indicates suppressed gap on the timescale of ~ 100ps.

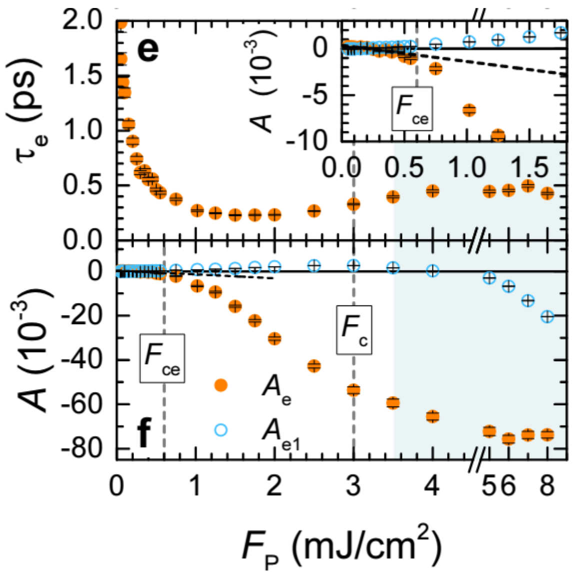
# Thermal considerations




Transient heating estimate from the equlibrium heat capacity and optical constants:

- $F_{c-th} \sim$ 2–3 mJ/cm$^2$ , for thermally heating the excited volume to $T_{IM}$.
- $F_c \sim F_{c-th}$, lattice heated close to $T_{IM}$ at $F_c$.

# Electronic order considerations




$F_{ce} \sim 0.6$ mJ/cm$^2 < F_c$

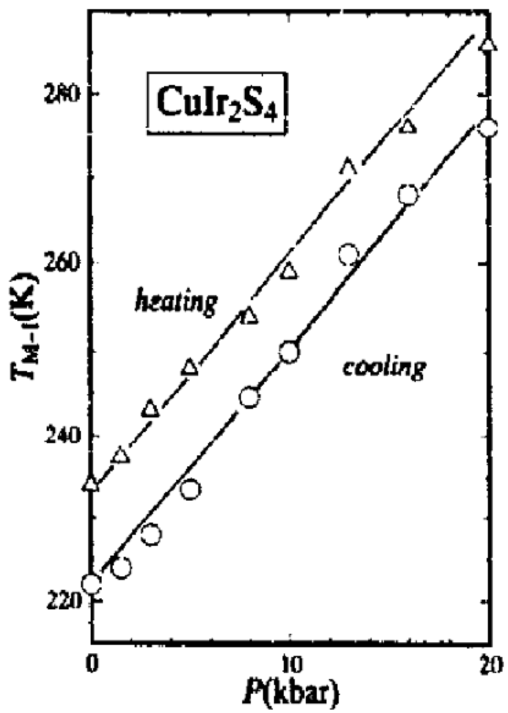
- Electronic ordering (gap) suppressed independently from the lattice order.

Mott transition due to photoexcited carrier screening?

- absorbed photon number density at $F_{ce}$: $\sim 10^{20}$ cm$^{-3}$ .
- photoexcited carrier plasma frequency: $\hbar\omega_p \gtrsim 0.4$ eV $> \Delta_I \sim 0.15$ eV

# Why the cubic symmetry is not (transiently) restored?

Pressure stabilization due to the 0.7% larger densitiy of the surrounding low-*T* monoclinic phase?




G. Oomi et al., JMMM **140**, 157-158 (1995)

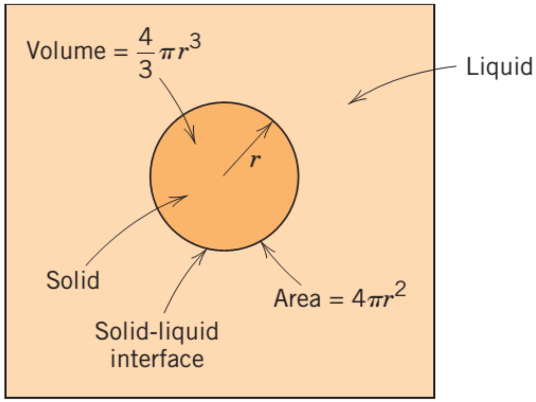
$$\beta = -\frac{1}{V}\frac{dV}{dp} \sim 0.6\ \%/\mathrm{GPa}$$

A.B. Garg et al., Solid State Communications **142**, 369–372 (2007).

$$T_{\mathrm{IM}} \sim 260\ \mathrm{K}\ @\ \frac{\Delta V}{V} = -0.7\%$$

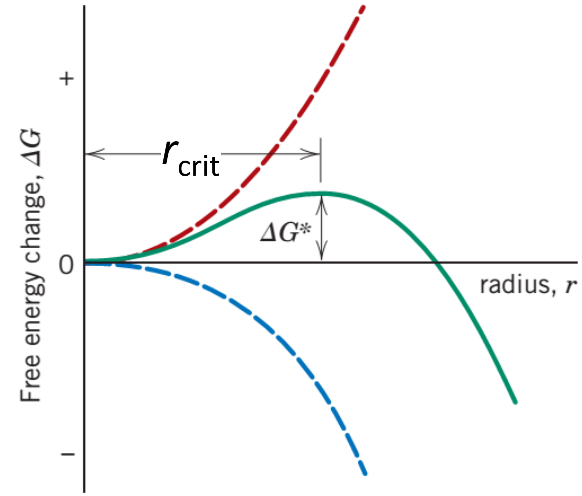
- Could contribute, but the $T_{IM}$ increase is too small.
- Does not explain strong dephasing.

# Nucleation bottleneck




$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

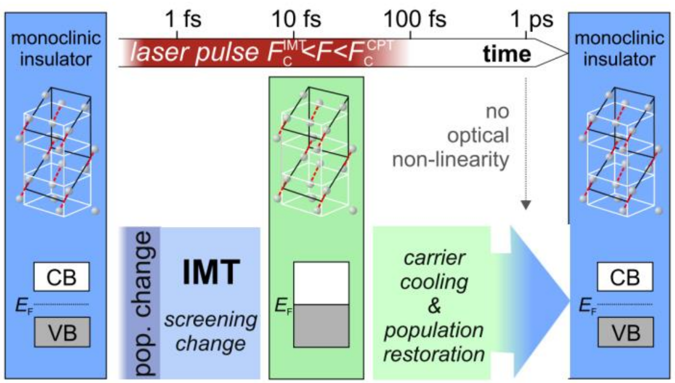
Callister, William D. *Materials science and engineering an introduction*. John Wiley, 2007




Fluctuating droplets of the cubic phase that are too small to grow, but introduce dynamic disorder causing dephasing.

# Comparison to $VO_2$ and $V_2O_3$

## $VO_2$



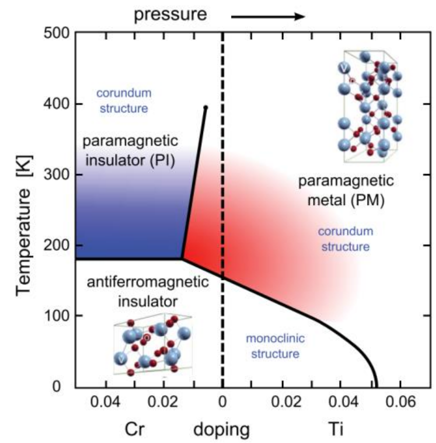

D. Wegkamp, J. Stähler, Progress in Surface Science **90**, 464 (2015)

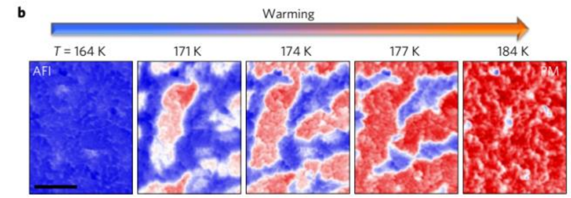
| | I-phase gap (eV) | $\Delta V/V$ (%)[a] |
|---|---|---|
| $VO_2$ | 0.6 [9] | 0.1 [10] |
| $V_2O_3$ | 0.2-0.75 [11] | -1.29 [12] |
| $CuIr_2S_4$ | 0.15 [7] | 0.7 [13] |

[a] Across the IM transition.

Naseska et al., *New Journal of Physics* **23**, 053023 (2021)

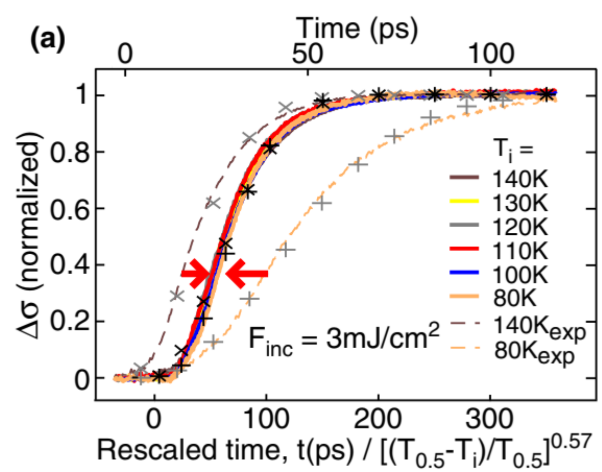
## $V_2O_3$



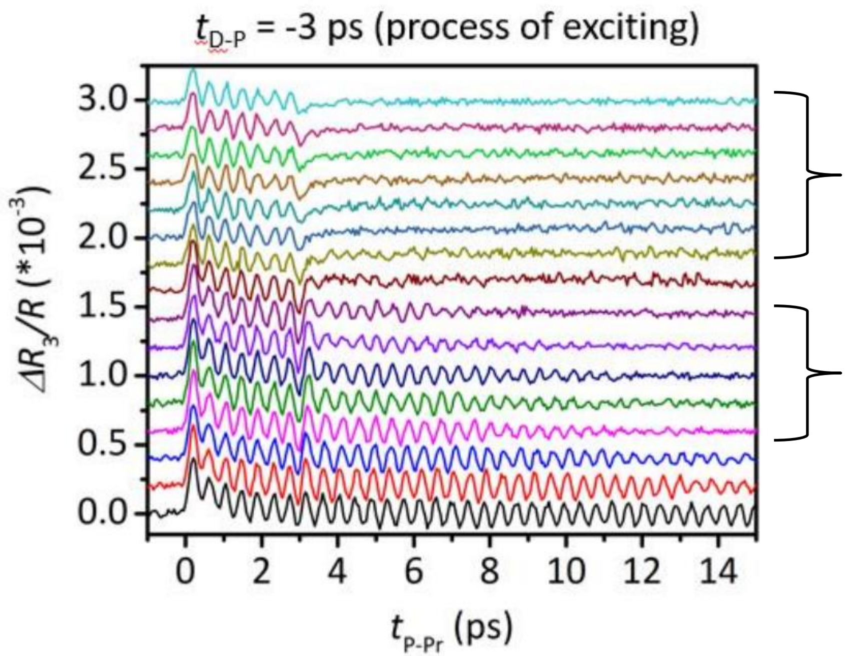

McLeod, A. S., et al., *Nature Physics* **13**, : 80 (2017).

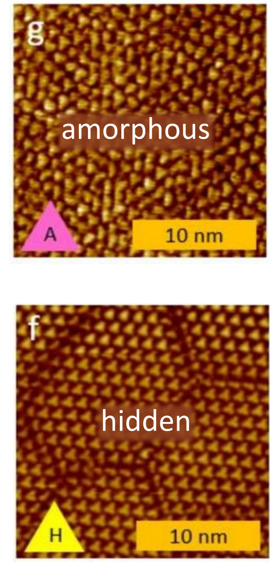
Hansmann et al., Phys. Stat. Sol. B **250**, 1251 (2013)

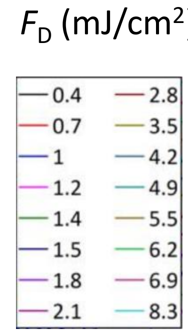



E. Abreu et al., PRB 92, 085130 (2015)

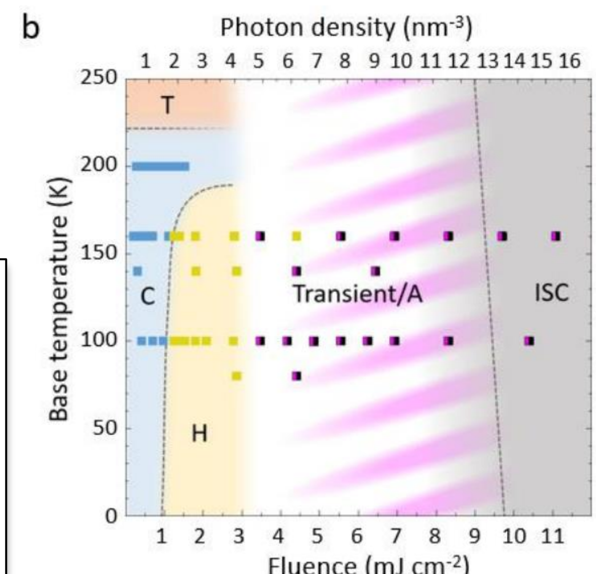
# Comparison to $1T$-$TaS_2$




J. Ravnik et al., Nat. Comm. **12, 1** (2021)




Short timescale:

Behavior above $F_c$ similar to the A phase creation conditions in $1T$-$TaS_2$.

Long timescale:

WCD phase disordered more like A phase in $1T$-$TaS_2$, but without significant gap suppression.

Importance of correlations or stacking in $1T$-$TaS_2$

# Conclusions

- Transient decoupling of the electronic/orbital and lattice orders on a subpicosecond timescale. The gap washed out by a Mott transition.
- Lattice order affected only upon heating close to $T_{IM}$, but no cubic phase forms even well above the treshold.
- Emergence of the cubic phase suppresed by the nucleation kinetics bottleneck.
- No evidence for further metastable phases upon a quench (in addition to the weakly disordered conducting phase).
- Importance of the inter-phase surface energy for ultrafast phase transition kinetics.

# Credits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