International School and Workshop on
Electronic Crystals ECRYS-2014

Cargèse, France August 11-23 2014

Trajectories through phase transitions in electronically ordered systems:

Topological defect dynamics and hidden states of matter

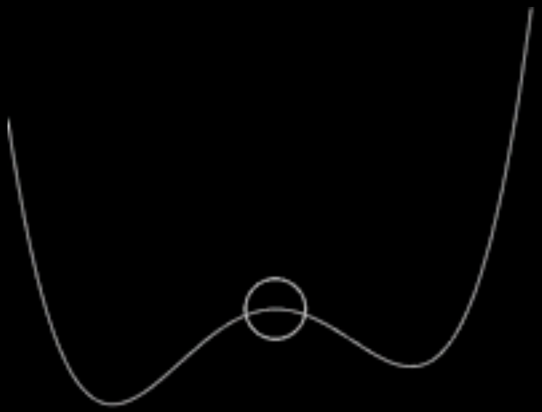
Dragan Mihailovic

Jozef Stefan Institute, Ljubljana, Slovenia
Nanocenter - Center of Excellence for Nanoscience and Nanotechnology
University of Ljubljana, Dept. of Physics
Jožef Stefan International Postgraduate School

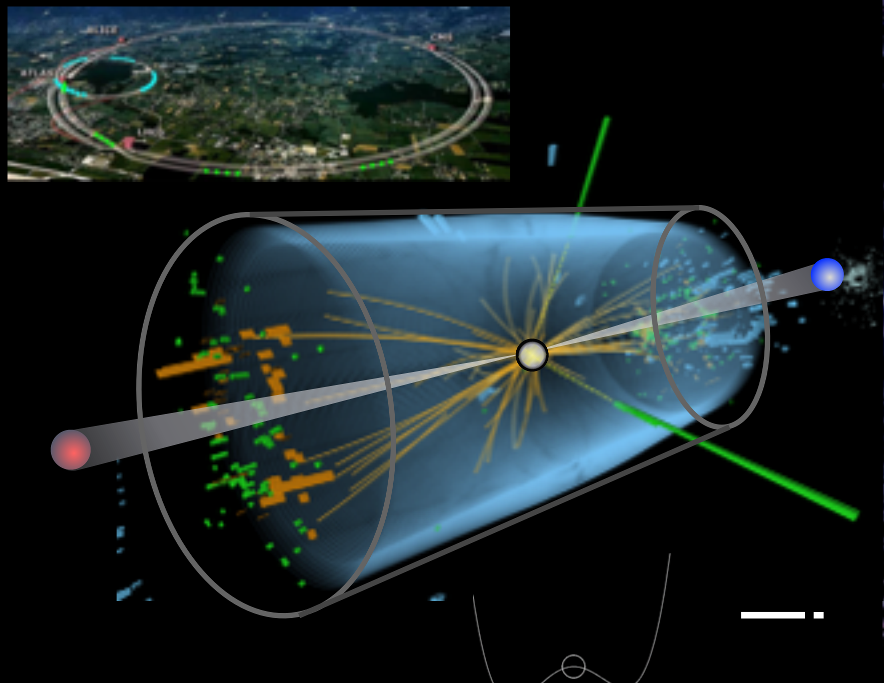
European Research Council
Established by the European Commission

Why do we do it?

Transitions… in time



Stock market crashes



Elementary particle collisions

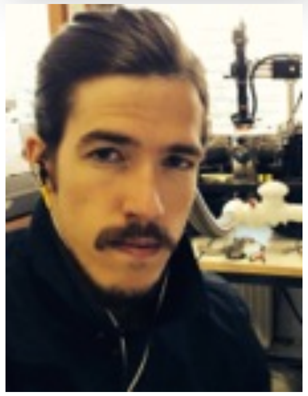
The Big Bang - hidden universes

Optical experiments:
(at JSI)

Ljupka Stojchevska
Igor Vaskivskyi
Tomaz Mertelj
Primoz Kusar
Roman Yusupov

Current switching experiments

Ian Mihailovic



Samples+:

I. Fisher *(Stanford)*
P. Sutar *(JSI)*
H.Berger *(EPFL)*

Lithography:

D.Svetin *(JSI)*

Special thanks to

L.Forro *(EPFL)*

Theory

Serguei Brazovskii
(Univ. Paris Sud Orsay)

TR ARPES

Patrick Kirchman + ZX Shen group
(Stanford)

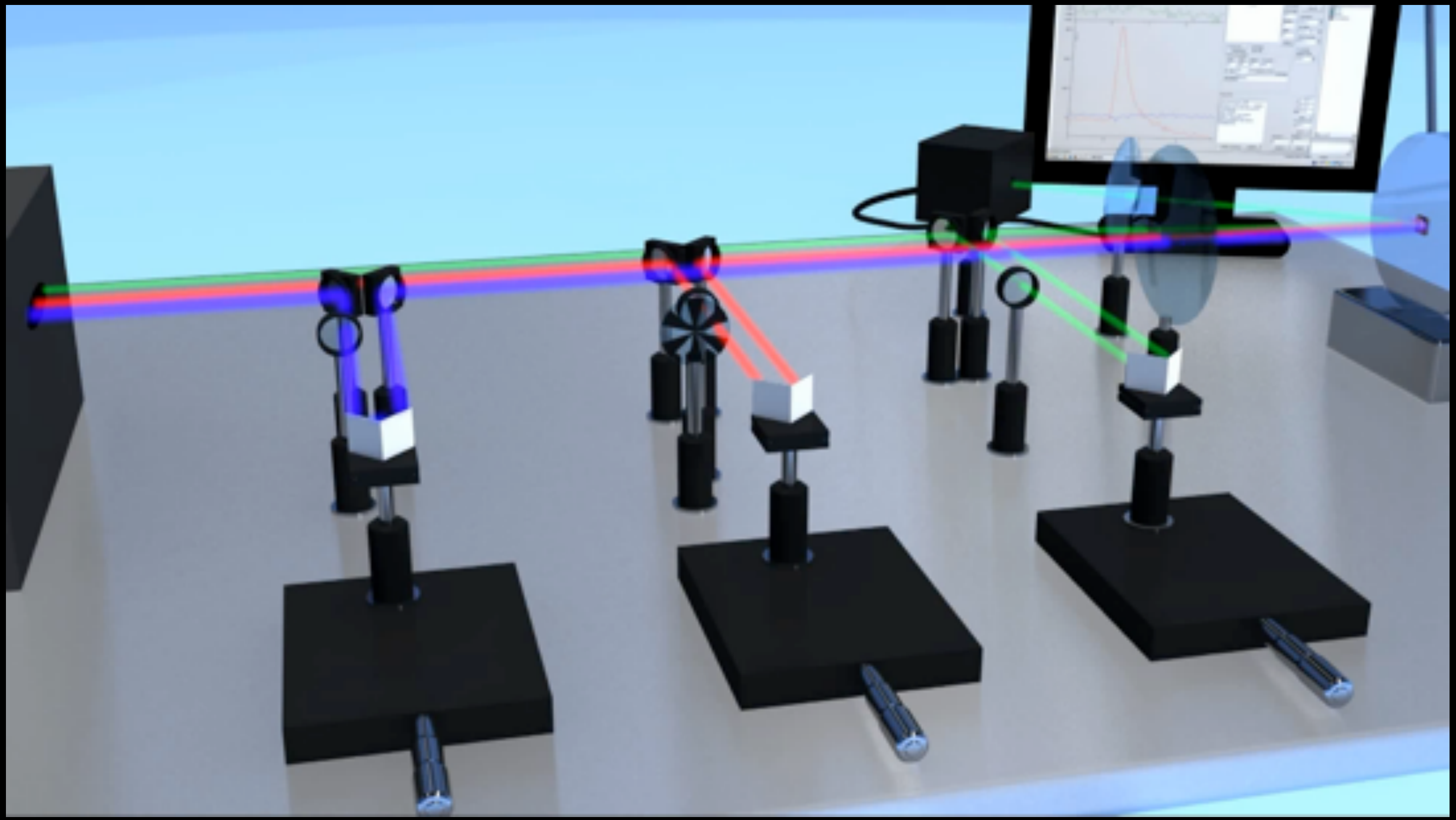
erc
European Research Council
Established by the European Commission

“Cosmic Quench” experiments

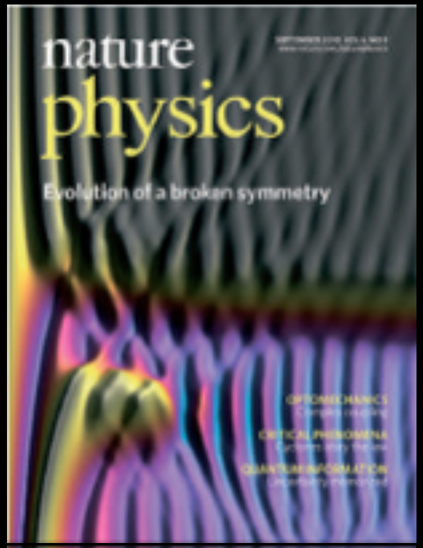
“Cosmology in L^{4}He”, Zurek (1985)

Optical experiments :

- offer high temporal resolution (easily to 7 fs)
- flexibility in probe wavelengths (THz - UV)
- we can probe the symmetry of different states



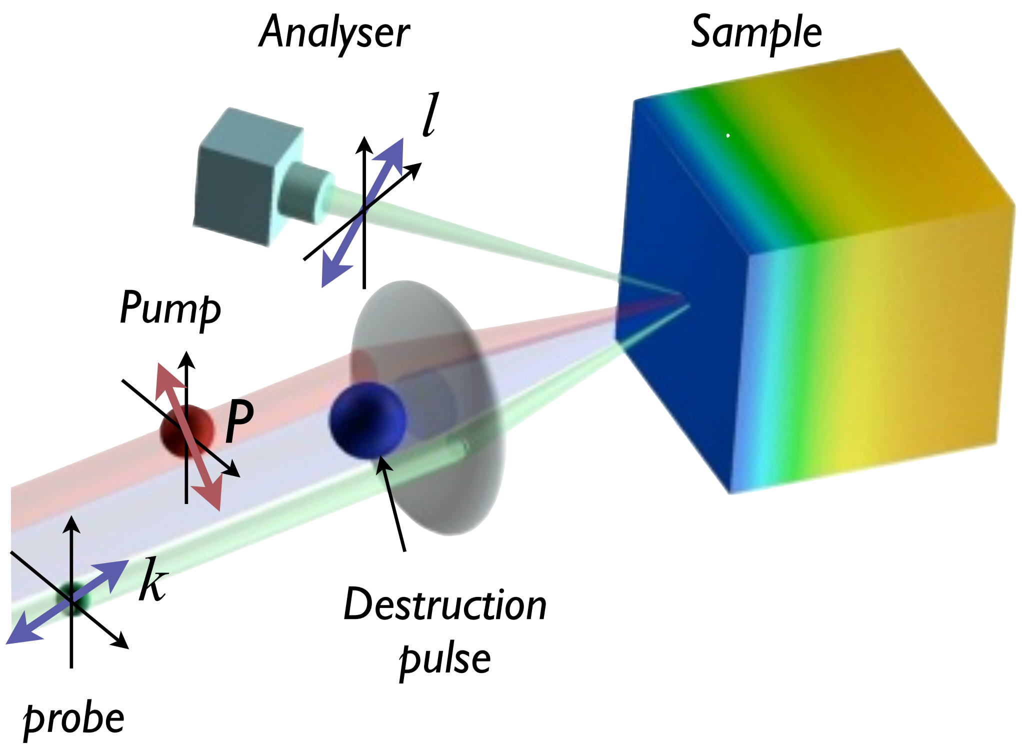
Yusupov, R. *et al. Nat Phys* **6,** 681–684 (2010).



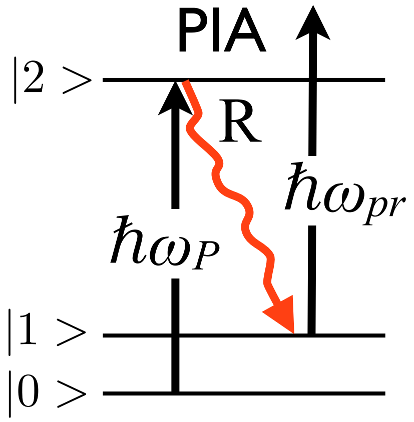
nature physics

Evolution of a broken symmetry

The response of the probe in all-optical experiments



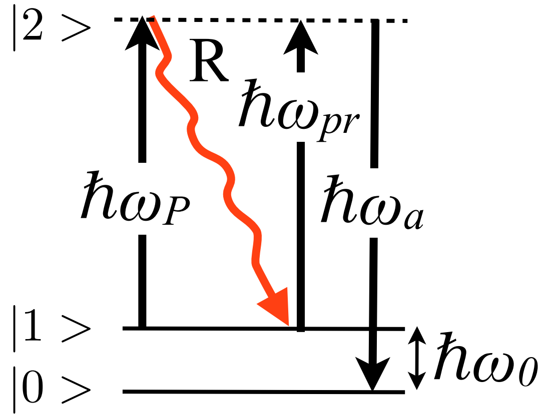
1. Photoinduced absorption (PIA):



The polarisation selection rules are determined by the dielectric tensor

1. Kabanov, V., Demsar, J., Podobnik, B. & Mihailovic, D. *Phys Rev B* **59,** 1497–1506 (1999).
2. Dvorsek, D. *et al.* *Phys Rev B* **66,** 020510 (2002).
3. Mihailovic, D., et al,., *J Phys-Condens Mat* **25,** 404206 (2013).

2. Coherent Raman-like (CRS) process:



The polarisation selection rules are governed by the Raman tensor χ_{kl}

1. Garrett, G., Albrecht, T., WHITAKER, J. & Merlin, R. *Phys Rev Lett* **77,** 3661–3664 (1996).
2. Stevens, T. E., Kuhl, J. & Merlin, R. *Phys Rev B* **65,** 144304 (2002).

CRS and PIA probe processes can be distinguished by polarisation selection rules

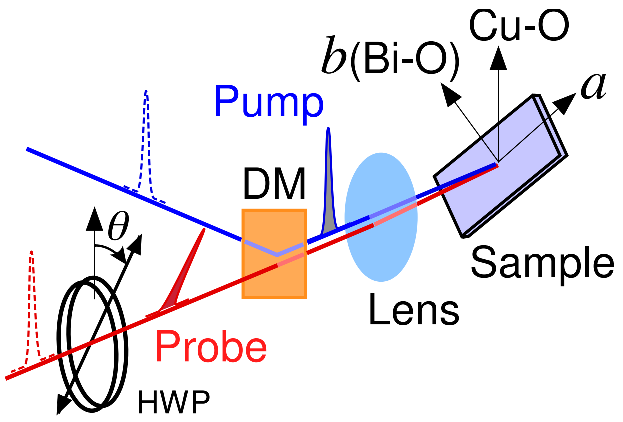
Dynamics of broken symmetry nodal and anti-nodal excitations in $Bi_2Sr_2CaCu_2O_{8+\delta}$ probed by polarized femtosecond spectroscopy

Y. Toda and F. Kawanokami
Department of Applied Physics, Hokkaido University, Sapporo 060-8628, Japan.

T. Kurosawa and M. Oda
Department of Physics, Hokkaido University, Sapporo 060-0810, Japan.

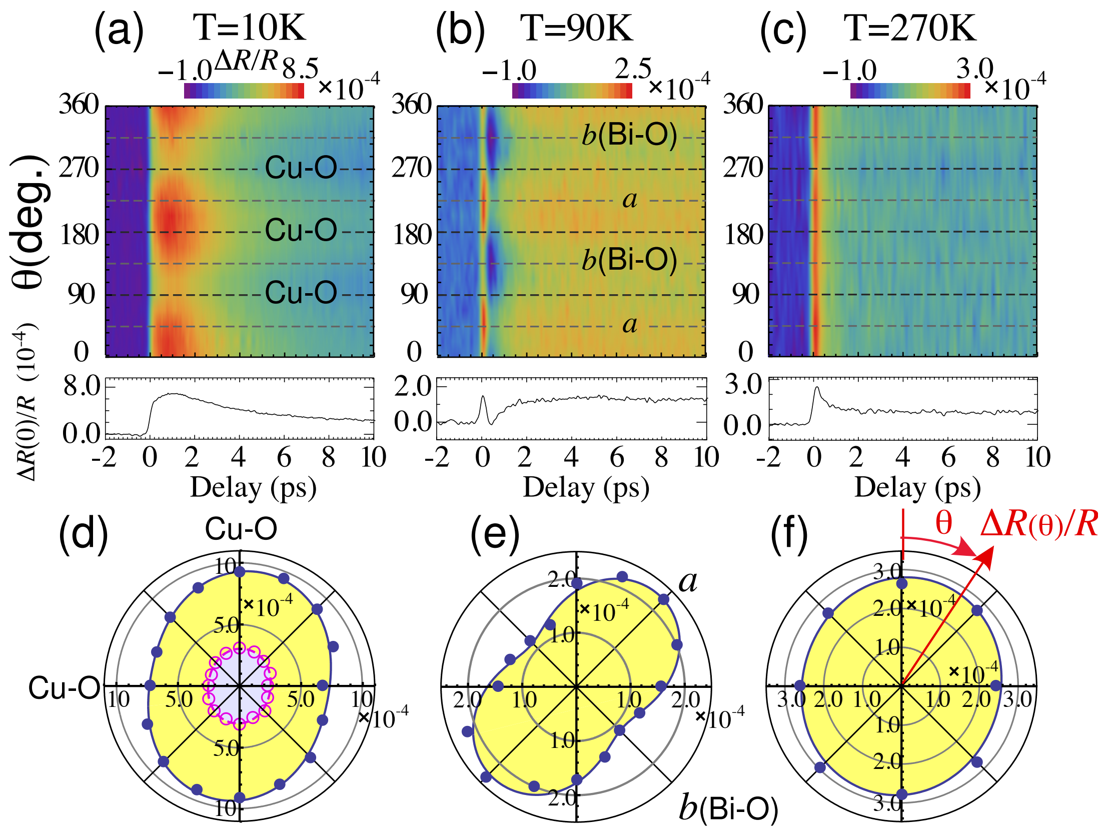
I. Madan, T. Mertelj, V. V. Kabanov, and D. Mihailovic
Complex Matter Dept., Jozef Stefan Institute, Jamova 39, Ljubljana, SI-1000, Slovenia

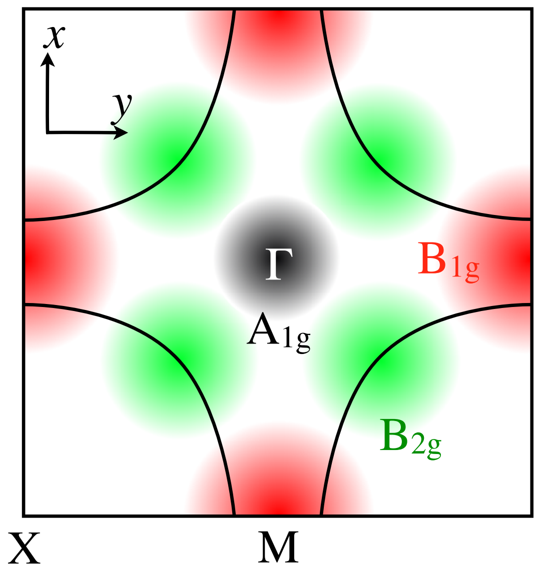
(Dated: January 29, 2014)

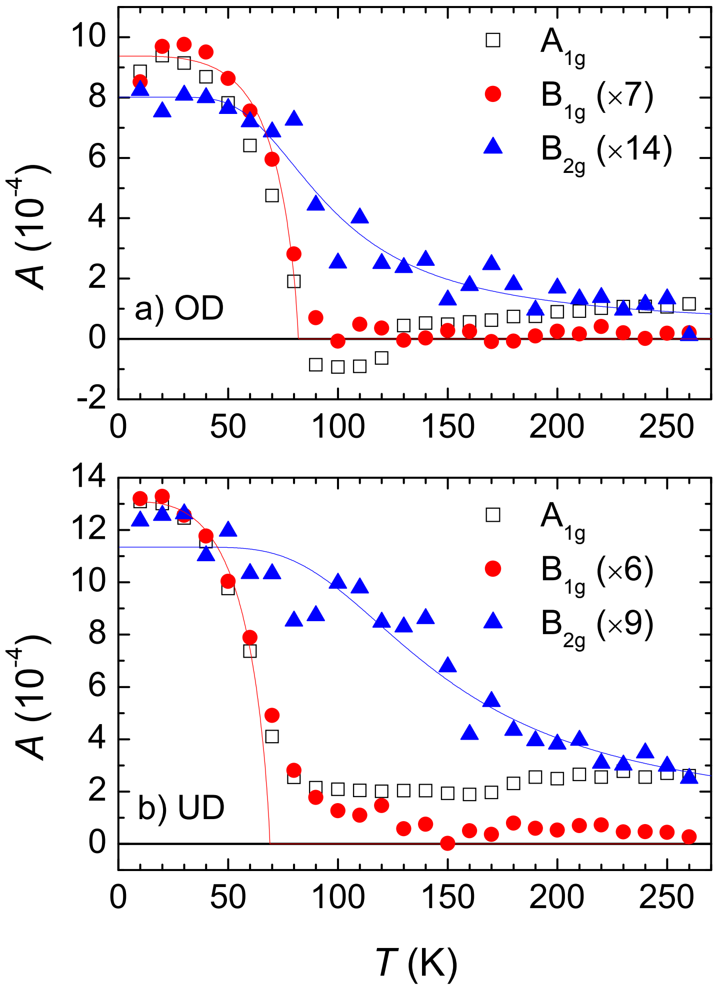


Temperature dependence of different symmetry components, A_{1g}, B_{1g} and B_{2g}:

$$\Delta R(\theta) = \frac{\partial R}{\partial \epsilon_1}\left[\Delta\epsilon_1^{A_{1g}} + \Delta\epsilon_1^{B_{1g}}\cos(2\theta) + \Delta\epsilon_1^{B_{2g}}\sin(2\theta)\right] + \frac{\partial R}{\partial \epsilon_2}\left[\Delta\epsilon_2^{A_{1g}} + \Delta\epsilon_2^{B_{1g}}\cos(2\theta) + \Delta\epsilon_2^{B_{2g}}\sin(2\theta)\right] \quad (2)$$







arXiv: Toda et al., (2013)

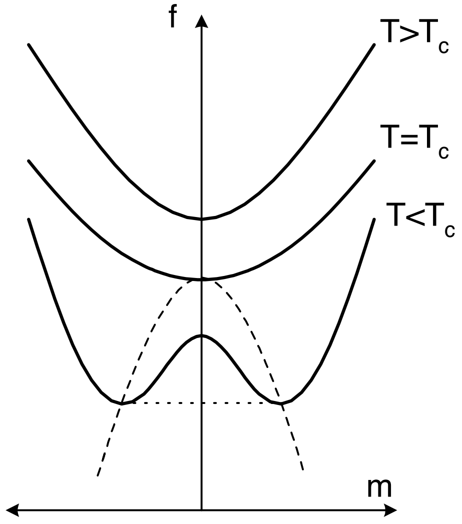
The non-linear energy functional

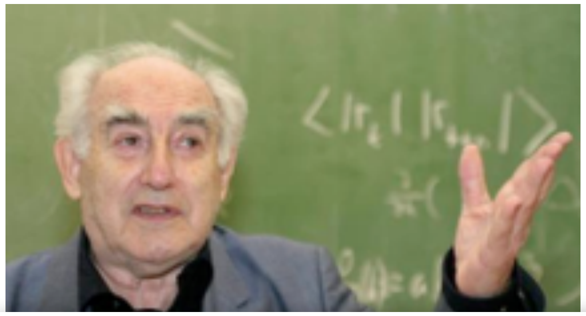
The Landau non-linear energy functional originally written to describe a **structural phase transition**:

$$F = \alpha\Psi^2 + \beta\Psi^4 + H\Psi \quad \text{where} \quad \alpha = \alpha_0(T - T_c)$$

The Ginzburg-Landau equation for a **superconductor**:

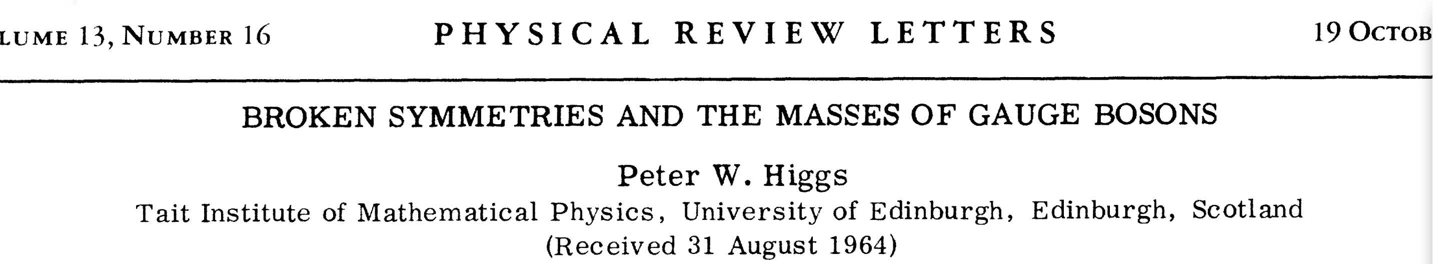
$$F = F_0 + \alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \frac{1}{2m}|(-i\hbar\nabla - 2e\mathbf{A})\psi|^2 + \frac{|\mathbf{B}|^2}{2\mu_0}$$





Complex order parameter

$$\Psi = \Delta\, e^{i\phi}$$



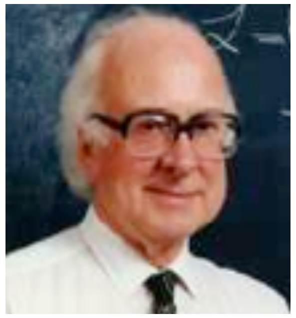
LUME 13, NUMBER 16 PHYSICAL REVIEW LETTERS 19 OCTOB

BROKEN SYMMETRIES AND THE MASSES OF GAUGE BOSONS

Peter W. Higgs

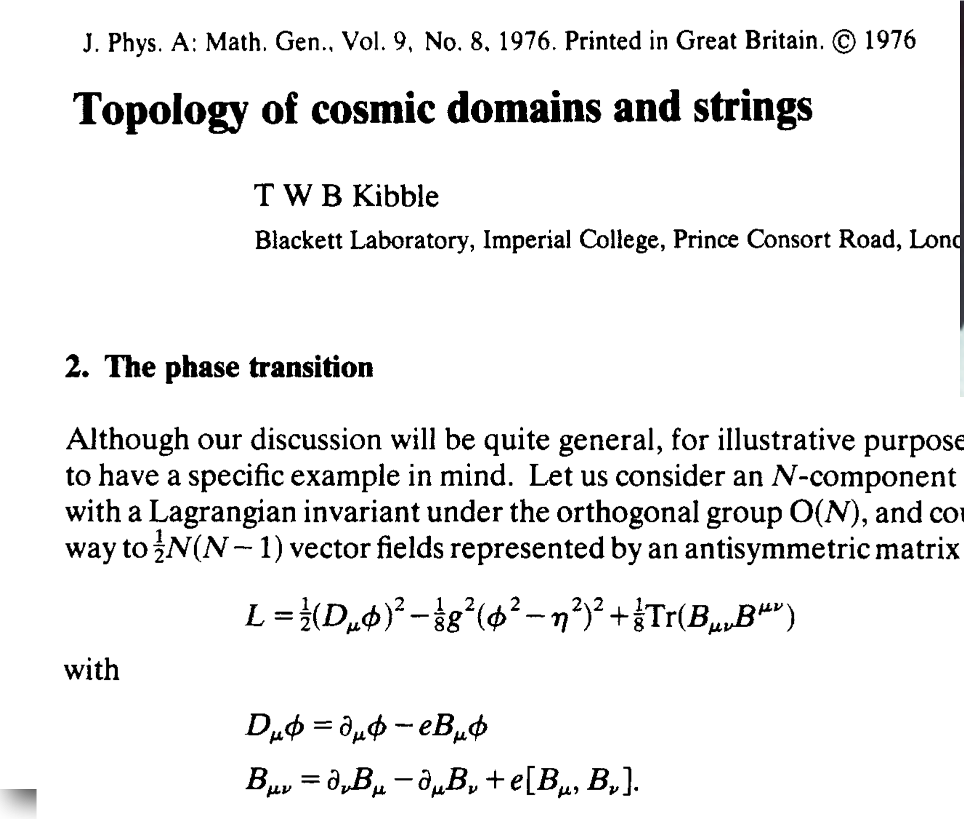
Tait Institute of Mathematical Physics, University of Edinburgh, Edinburgh, Scotland

(Received 31 August 1964)



Lagrangian density, includes K.E. term

$$L(\varphi) = \partial_\mu\varphi^*\partial^\mu\varphi - \alpha\varphi^*\varphi - \frac{\beta}{2}|\varphi^*\varphi|^2$$



J. Phys. A: Math. Gen., Vol. 9, No. 8, 1976. Printed in Great Britain. © 1976

Topology of cosmic domains and strings

T W B Kibble

Blackett Laboratory, Imperial College, Prince Consort Road, Lond

2. The phase transition

Although our discussion will be quite general, for illustrative purposes it is convenient to have a specific example in mind. Let us consider an N-component real scalar field ϕ with a Lagrangian invariant under the orthogonal group O(N), and coupled in the usual way to $\frac{1}{2}N(N-1)$ vector fields represented by an antisymmetric matrix B_μ. We can take

$$L = \tfrac{1}{2}(D_\mu\phi)^2 - \tfrac{1}{8}g^2(\phi^2 - \eta^2)^2 + \tfrac{1}{8}\mathrm{Tr}(B_{\mu\nu}B^{\mu\nu}) \tag{1}$$

with

$$D_\mu\phi = \partial_\mu\phi - eB_\mu\phi$$
$$B_{\mu\nu} = \partial_\nu B_\mu - \partial_\mu B_\nu + e[B_\mu, B_\nu].$$

The time-dependent GLT

Serguei Brazovskii, 2010

The energy of the system can be described in terms of a time-dependent Ginzburg-Landau functional[†]:

$$F = \alpha\Psi^2 + \beta\Psi^4 + H\Psi$$

where instead of the usual temperature dependence (T - T_c), the *first* term is time-dependent:

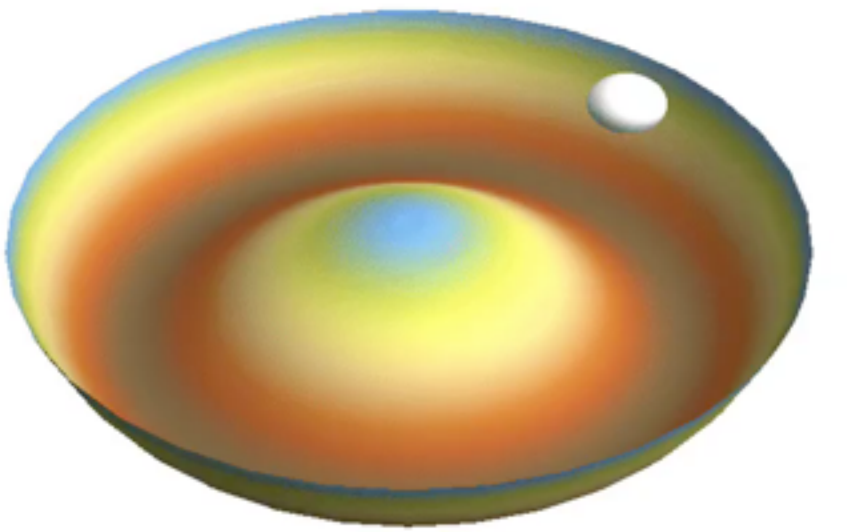
$$\alpha = [1 - \frac{T_e(t,\mathbf{r})}{T_c}]$$

“The quench process”

The equation of motion is obtained via the Euler-Lagrange theorem :

$$\boxed{\frac{1}{\omega_0^2}\frac{\partial^2}{\partial t^2}A + \frac{\alpha}{\omega_0}\frac{\partial}{\partial t}A - (1-\eta)A + A^3 - \xi^2\frac{\partial^2}{\partial z^2}A = 0}$$

The order parameter, $\psi(t) = A(t)e^{i\phi(t)}$

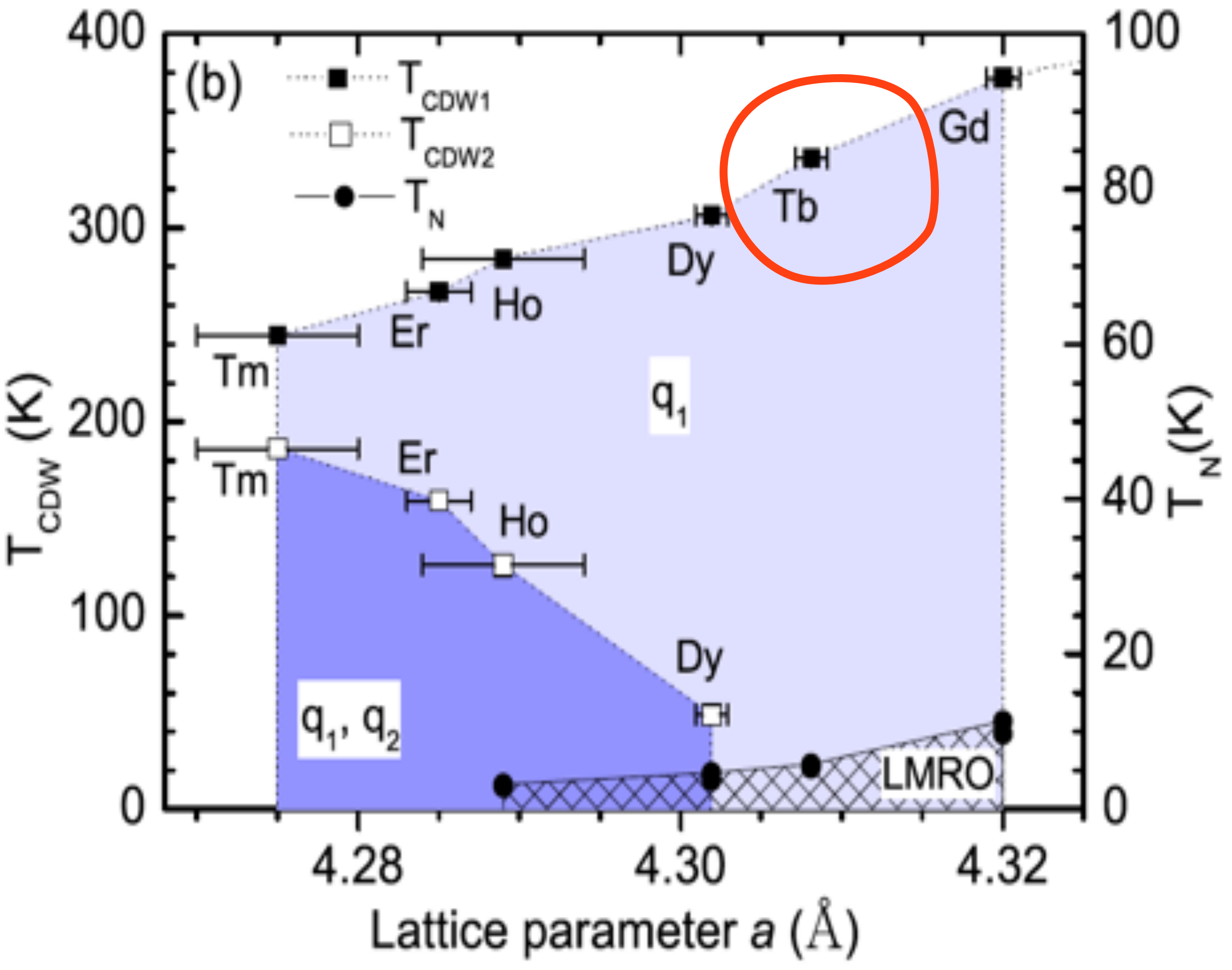


Yusupov et al, Nat Phys. (2010)

[†] Phase fluctuations are assumed to be slow.

1. A system which recovers fully after a rather complex series of events: $TbTe_3$

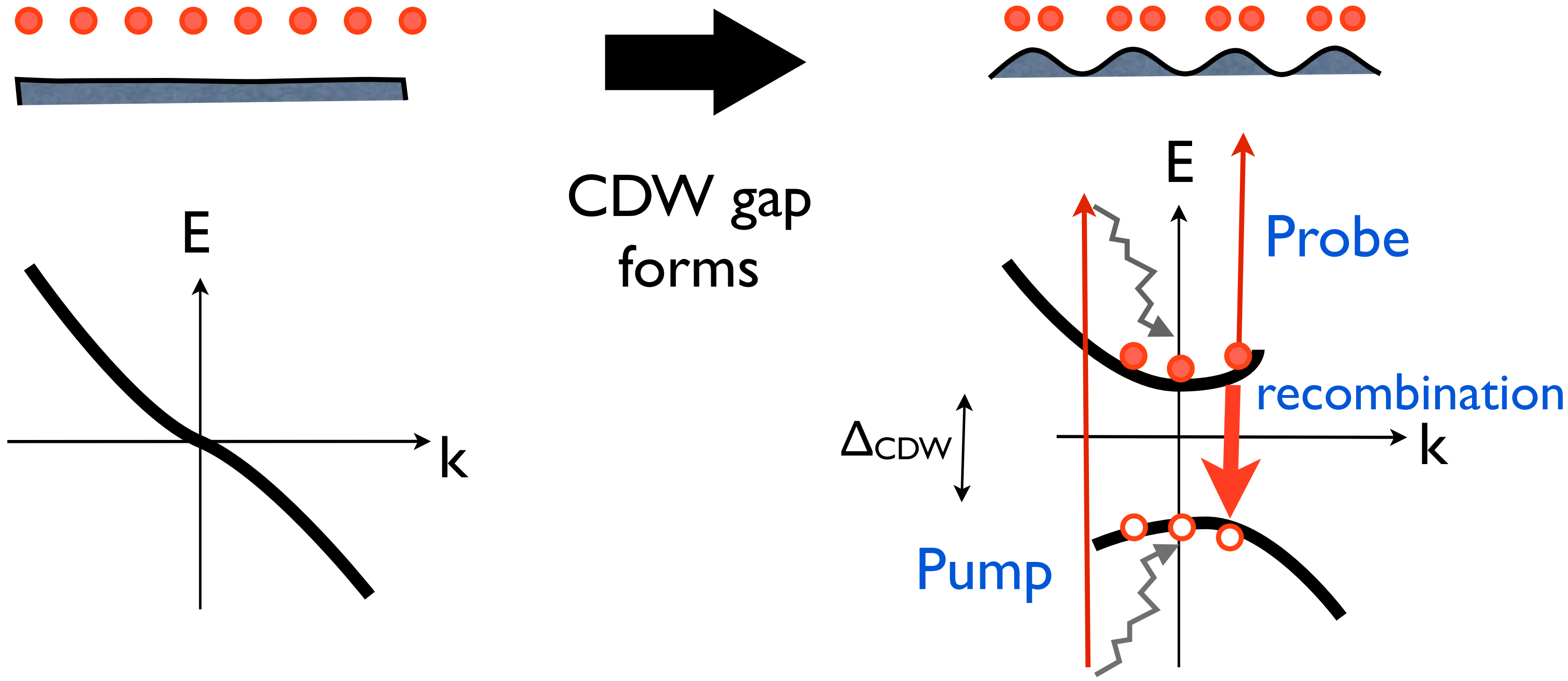
DiMasi ’94,’95, Fisher ’05,’08

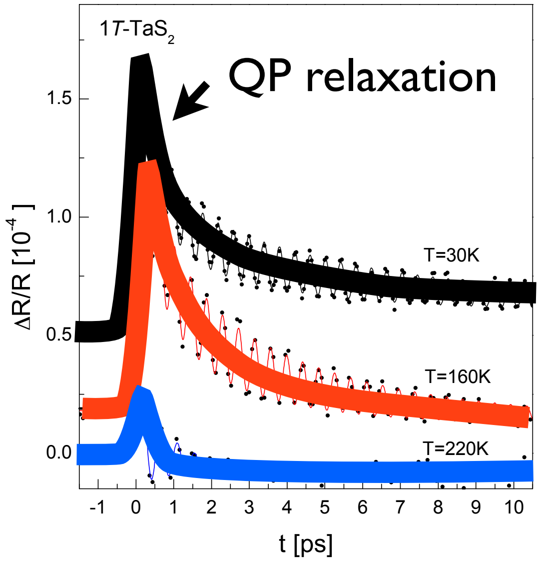


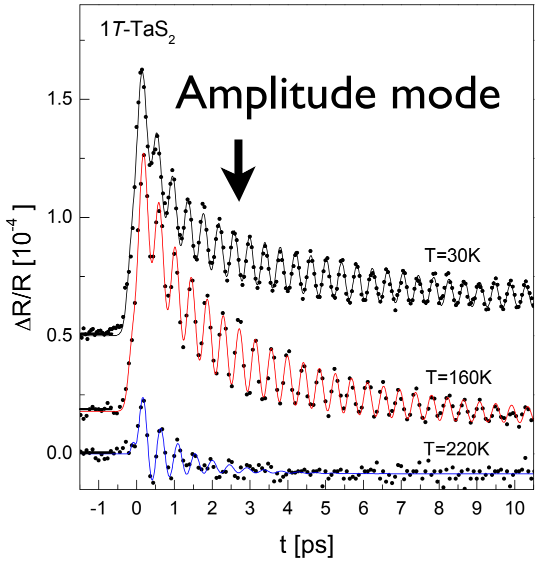
- The tritellurides are layered, strongly 2-dimensional metals with an orthorhombic (pseudo-tetragonal) crystal structure Cmca (D_{2h})
- They exhibit a purely electronically driven 2nd order incommensurate **CDW transition** at T_{c1} = 230~330K
- An **AFM state** exists at low T_{N}, some compounds exhibit another transition at low T_{c2}.
- A **Superconducting** transition exists with Tc = 3.5 K under a pressure of 75 kbar.

Detection of the onset of order in CDW systems: The elementary excitations

1. Detection of the gap through quasiparticle (fermionic) excitations

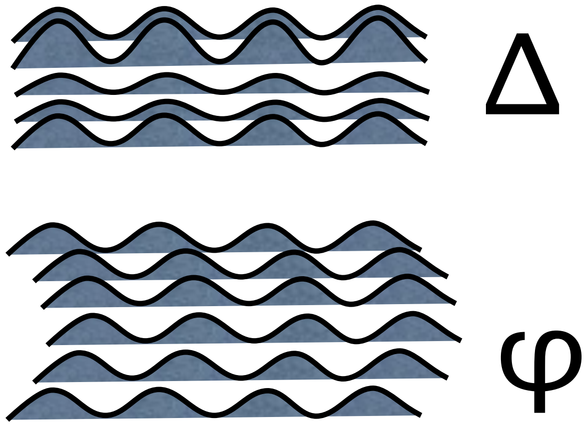






2. Collective mode (bosonic) excitations

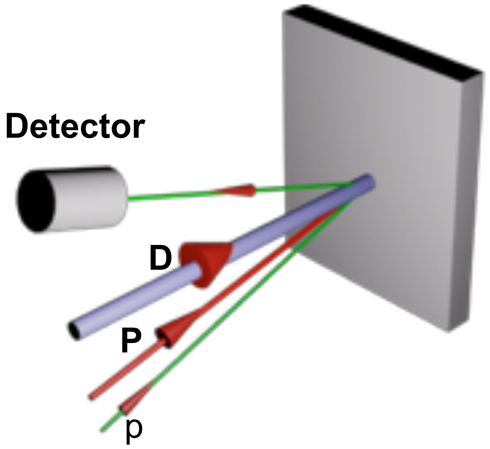
The amplitude and phase modes

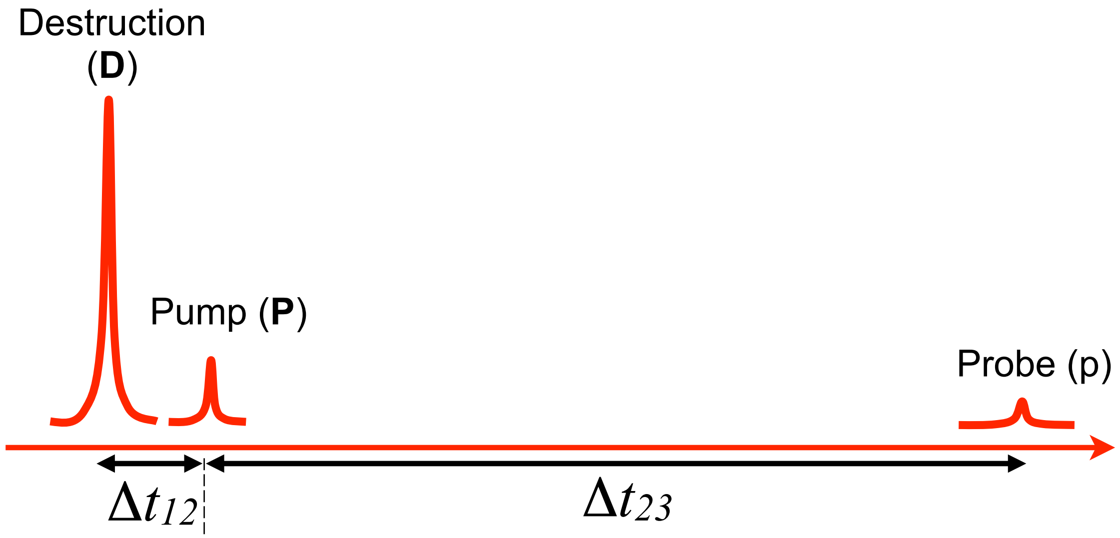


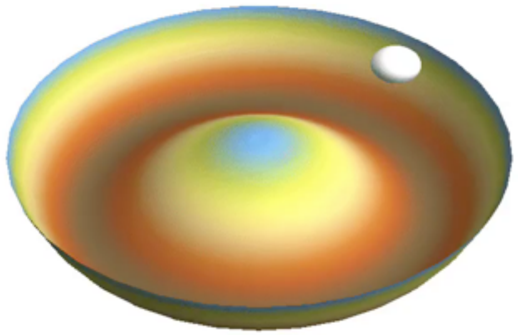
$$\Psi = \Delta e^{i\varphi}$$

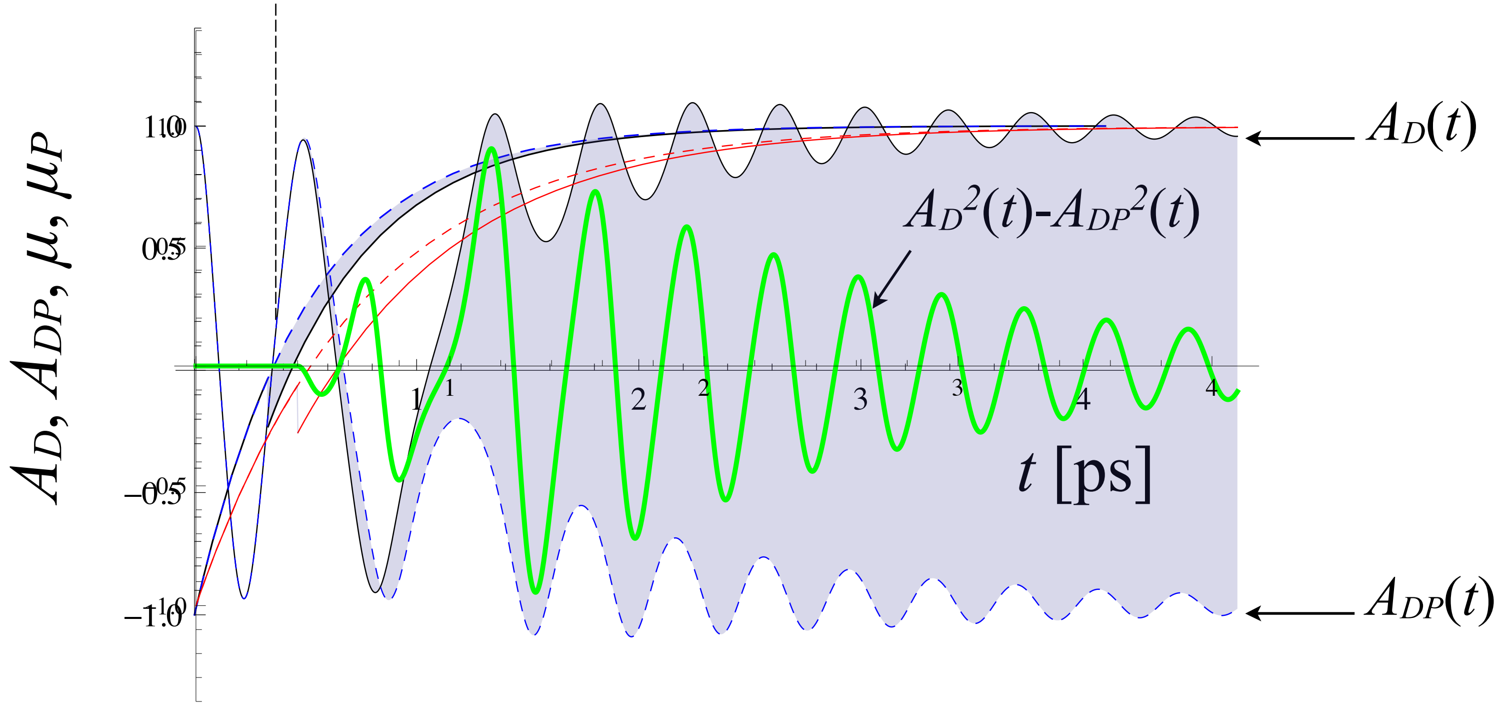
Demsar et al., PRL **83**, 800 (1999).
Demsar, J.,et al, PRB **66**, (2002).
Demsar, et al., PRB **82**, 4918 (1999).
Kusar et al, PRL 101, 227001 (2008)
Yusupov et al.,PRL **101**, 246402 (2008).

The optical response of the **collective mode**



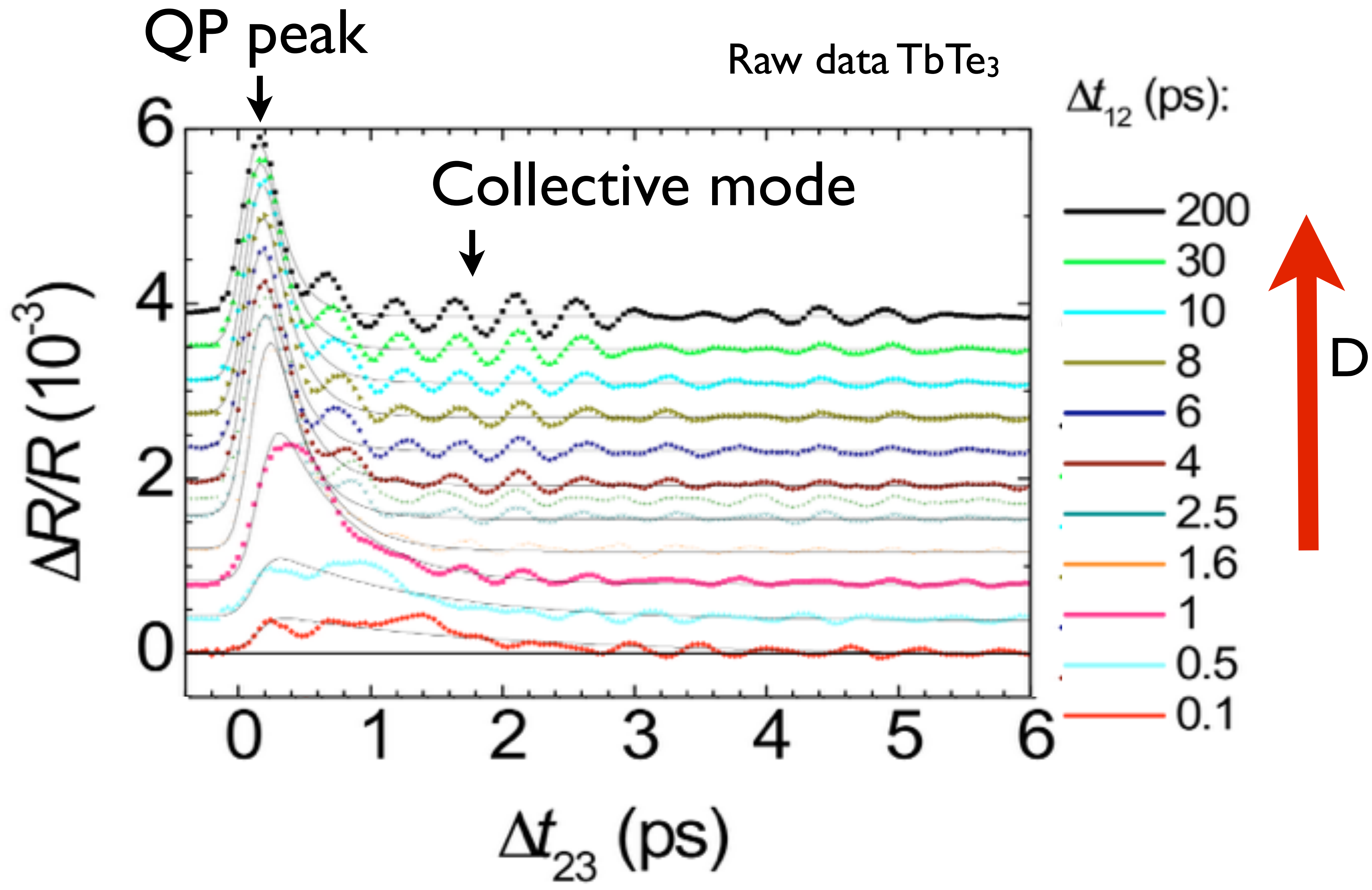






The reflectivity, $\Delta R(t) \propto \left(\frac{\partial R}{\partial \epsilon}\right) \Delta\epsilon \propto \int [A^2_{DP}(t, \mathbf{r}, \Delta t_{12}) - A^2_D(t, \mathbf{r})] e^{-z/\lambda} d^3\mathbf{r}.$

The transient reflectivity ΔR/R after a quench at Δt_{12}=0



QP peak

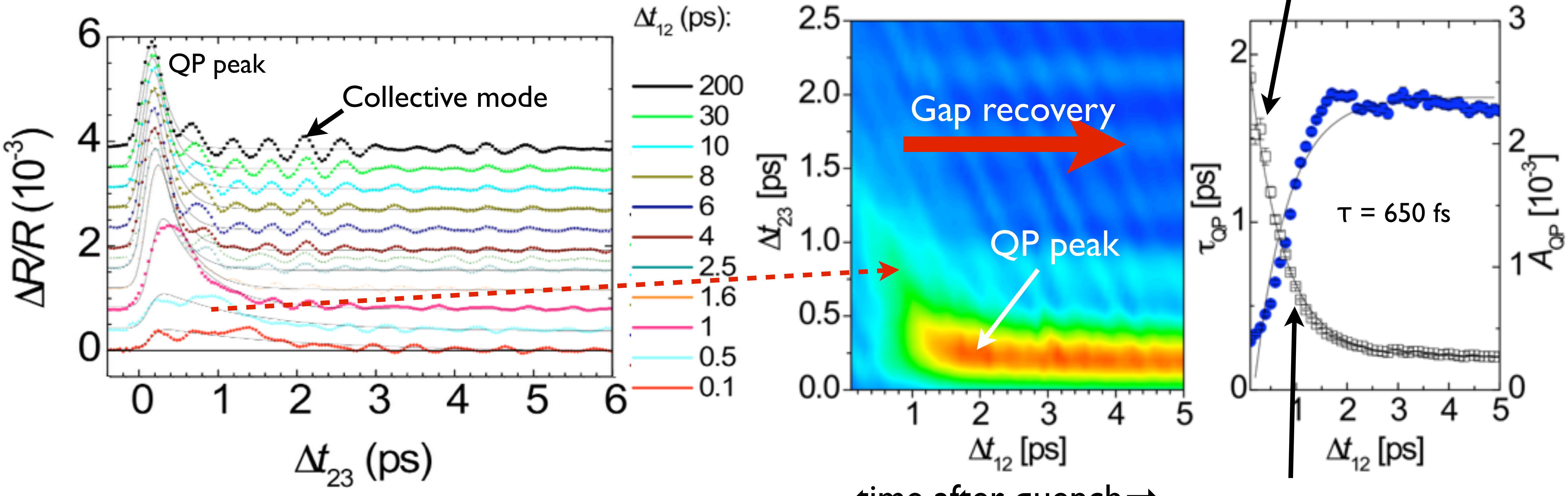
Collective mode

Raw data TbTe3

Delay time after the D pulse

Quasi-particle (Fermion) kinetics: gap recovery

$$\delta R = -\frac{2A\Delta_0^2}{\omega^2} n_p.$$



time after quench→

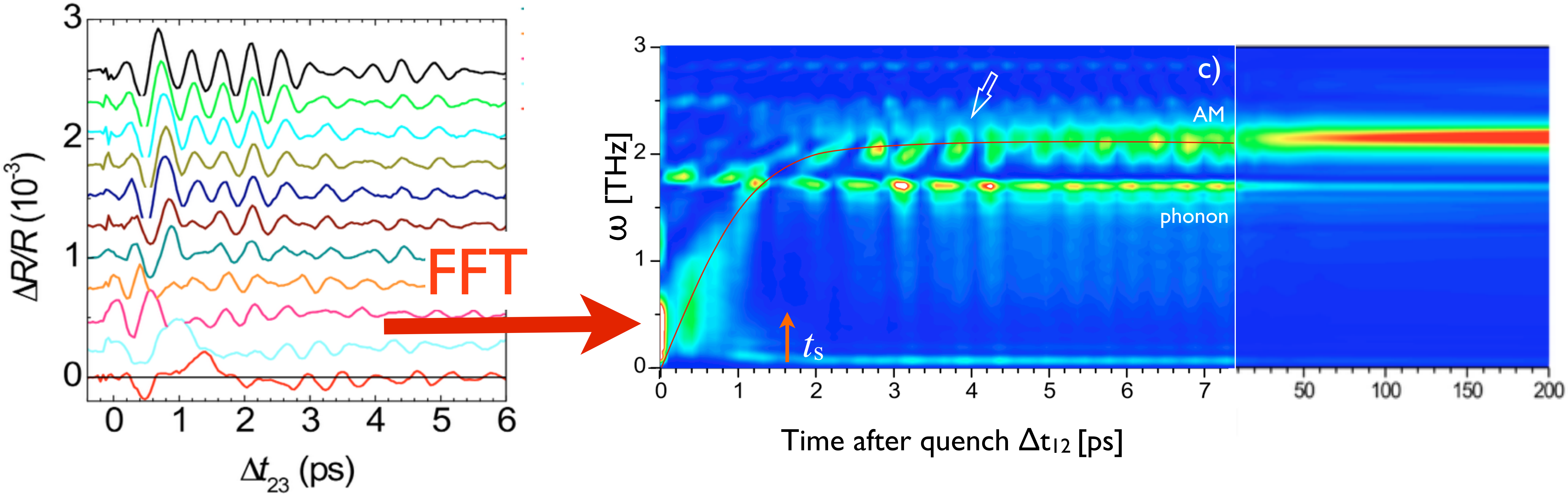
Relaxation time recovery

$$\tau \propto \frac{1}{\Delta}$$

The time-dependence of ΔR/R during the recovery of ψ:

$$\delta R/R \propto \frac{1/(|\psi(t)| + T(t)/2)}{1 + B\sqrt{2T(t)/|\psi(t)|}\exp[-|\psi(t)|/T(t)]}$$

The collective mode spectrum as a function of time after quench



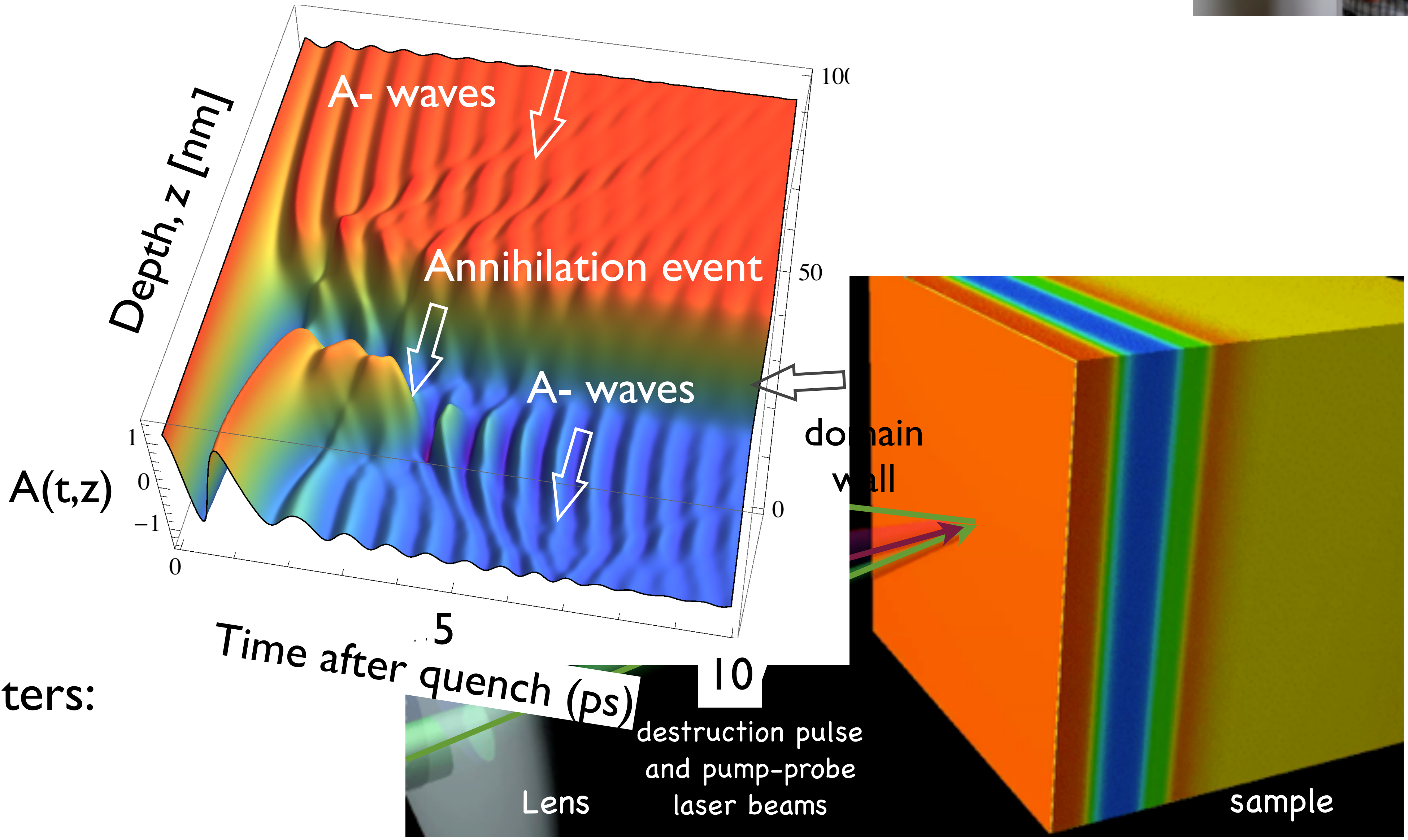
The most obvious feature:
oscillations of intensity of the collective mode

Order parameter calculation

The eq. of motion:

$$\frac{1}{\omega_0^2}\frac{\partial^2}{\partial t^2}A+\frac{\alpha}{\omega_0}\frac{\partial}{\partial t}A-(1-\eta)A+A^3-\xi^2\frac{\partial^2}{\partial z^2}A=0$$

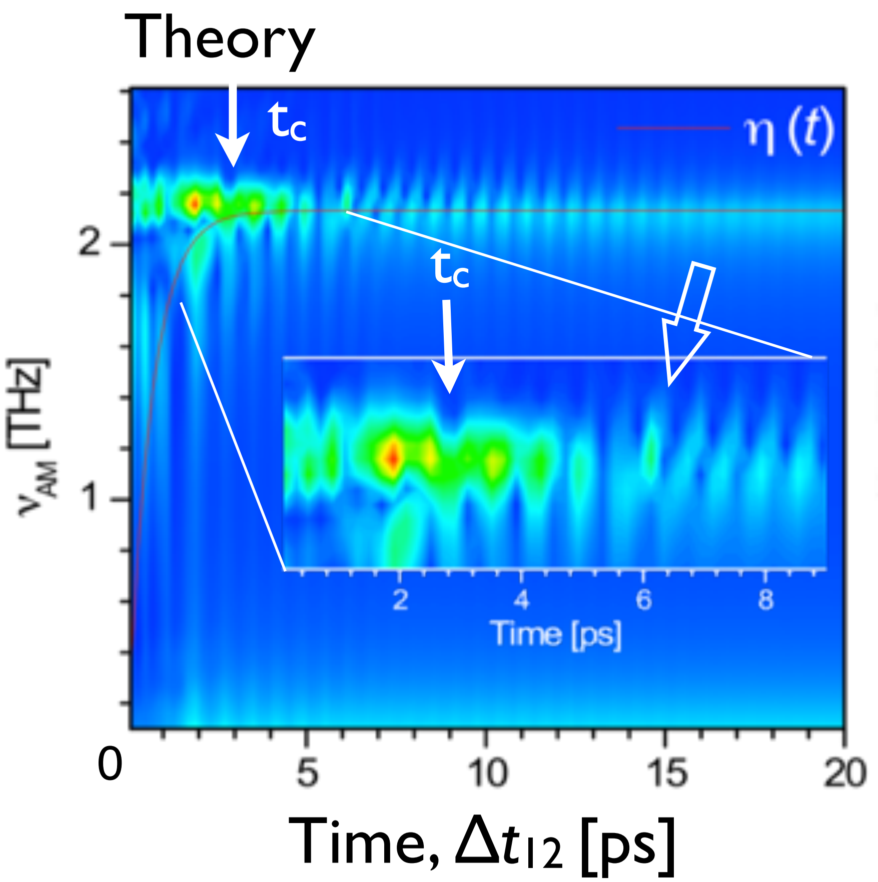
Calculated $A(z,t)$ after quench:

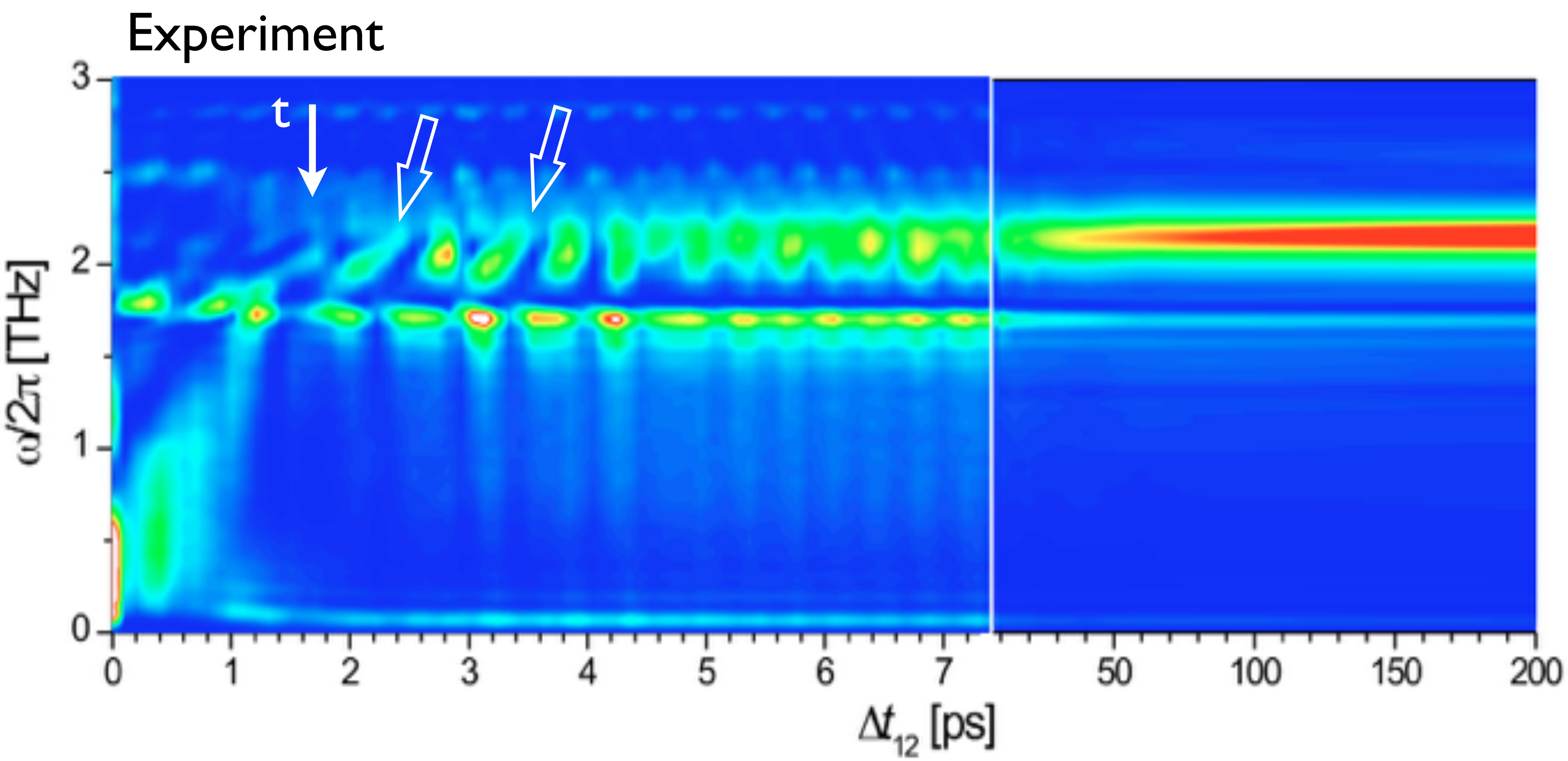


Experimental parameters:

$\tau_{QP} = 650$ fs
$\omega_0/2\pi = 2.18$ THz
$\eta = 2$
$\alpha = 0.1$

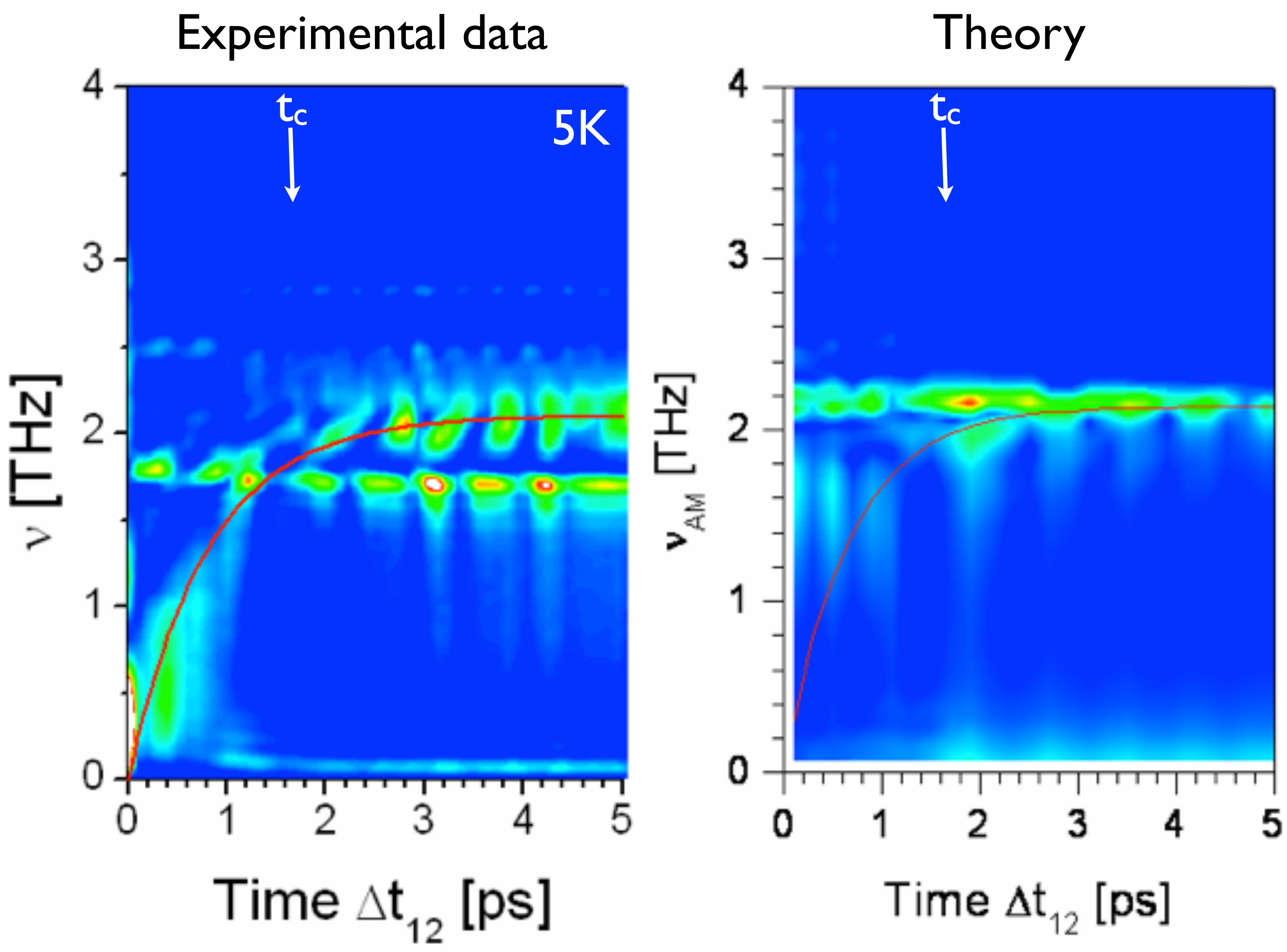
Order parameter dynamics: TDGL theory vs. experiment


Theory


Experiment

Theory predictions:	Experimental observations
Oscillations of Δ or |Ψ|	Intensity oscillations
Critical slowing down	
(Collective mode softening)	Softening of ω
Domain annihilation	
Ψ field (Higgs) waves	Distortions in ω-t spectra

Critical dynamics near t_c


Experimental data

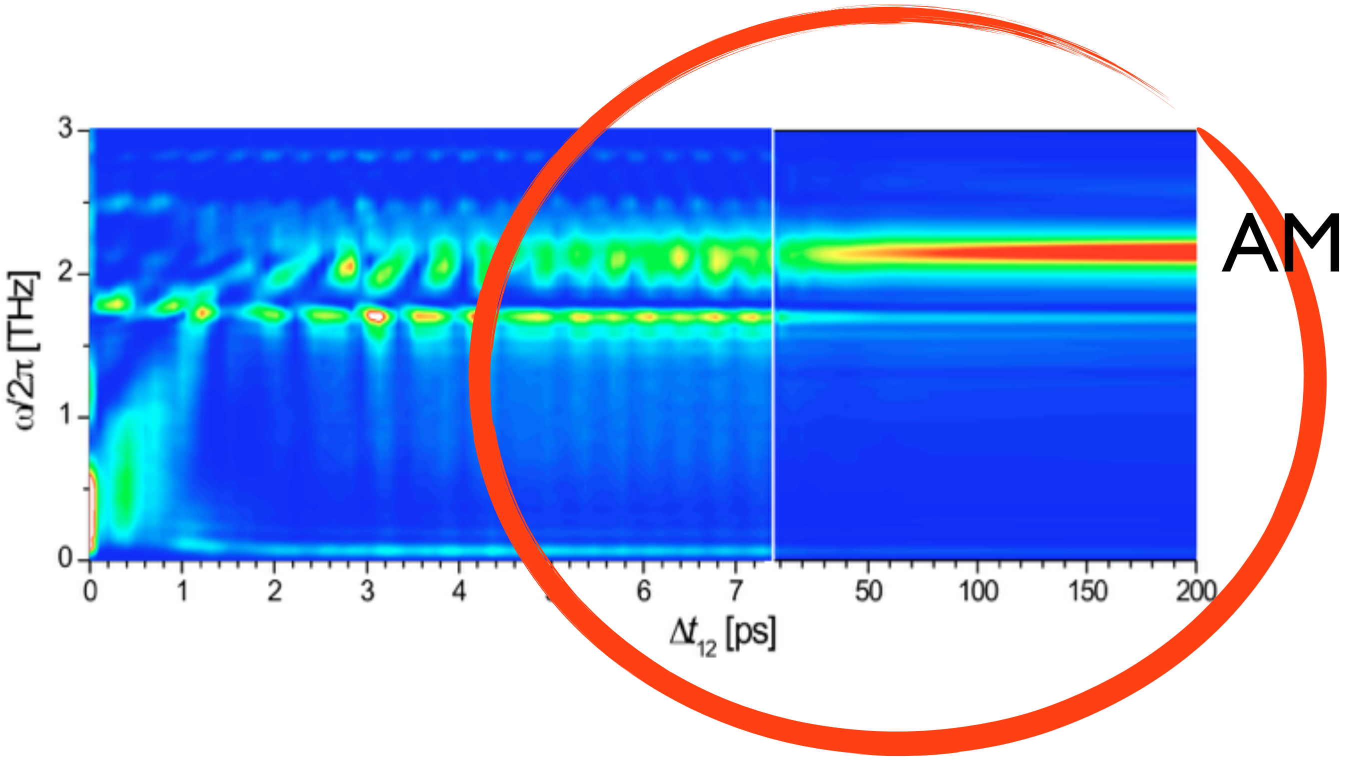
Theory

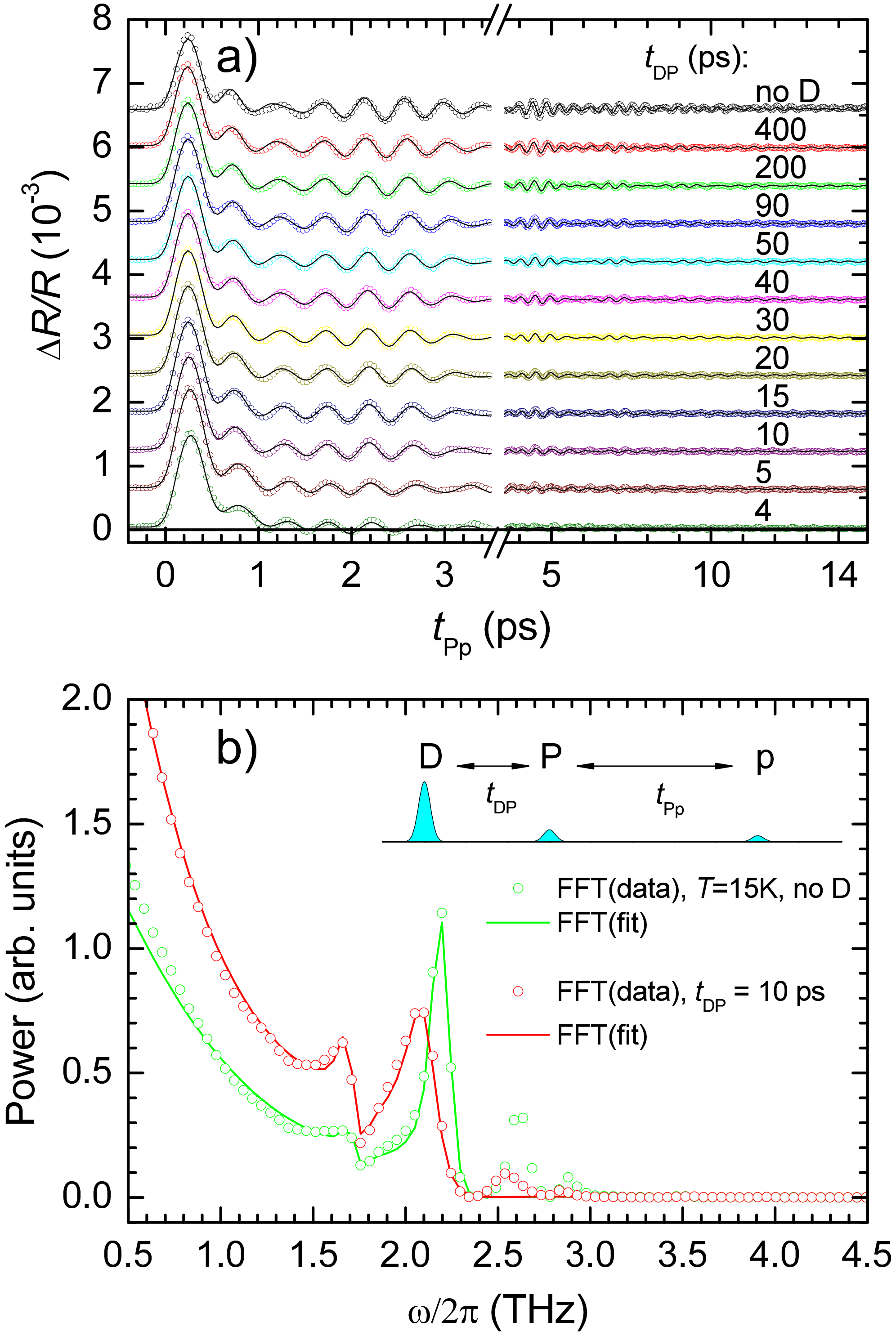
ISSUES NOT ADDRESSED:

- Initial energy relaxation
- fluctuation phenomena
- Bottleneck dynamics
- microscopic details
- ...

Pre-transition behaviour: not great agreement

Incoherent topological defect dynamics: collective mode broadening for $\Delta t_{12} > 7$ ps



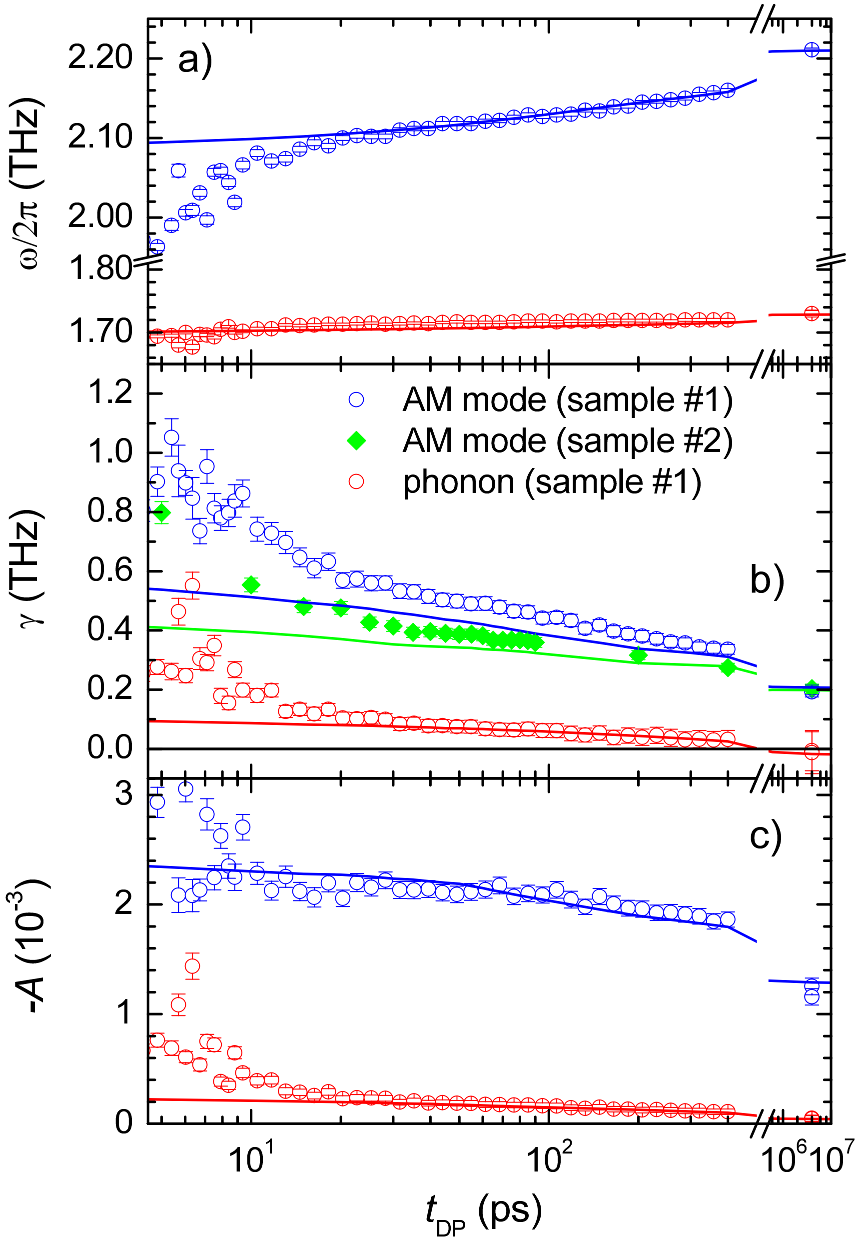


Raw data fit

FFT of data, fit

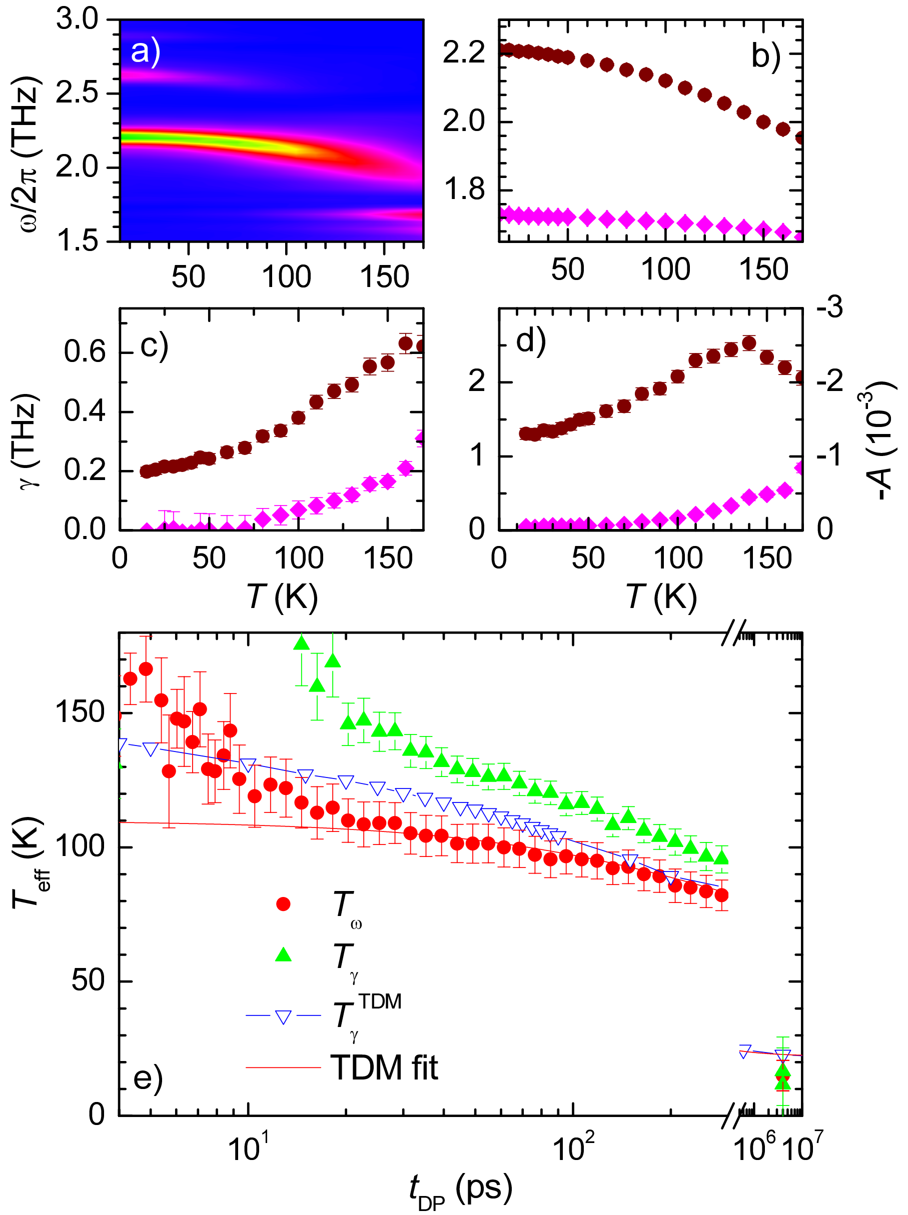
Mertelj, T. *et al.* Incoherent Topological Defect Recombination Dynamics in TbTe_{3}. *Phys Rev Lett* **110,** 156401 (2013).

Distinguishing incoherent topological defect dynamics in $TbTe_3$ from thermal dynamics

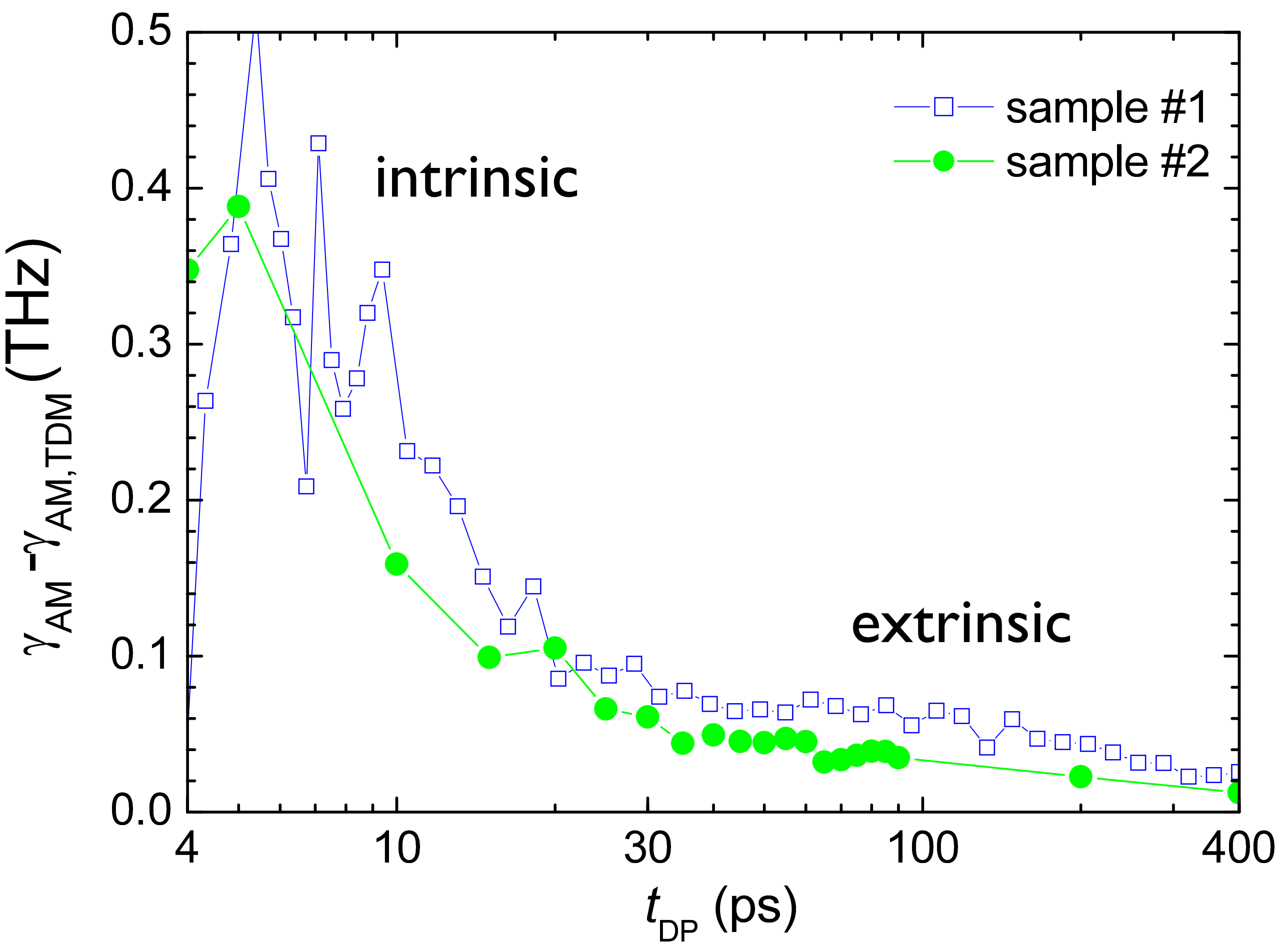


Mertelj, T. *et al.* Incoherent Topological Defect Recombination Dynamics in TbTe_{3}. *Phys Rev Lett* **110,** 156401 (2013).

Temperature reference calibration



Intrinsic (incoherent) and extrinsic topological defect dynamics in $TbTe_3$

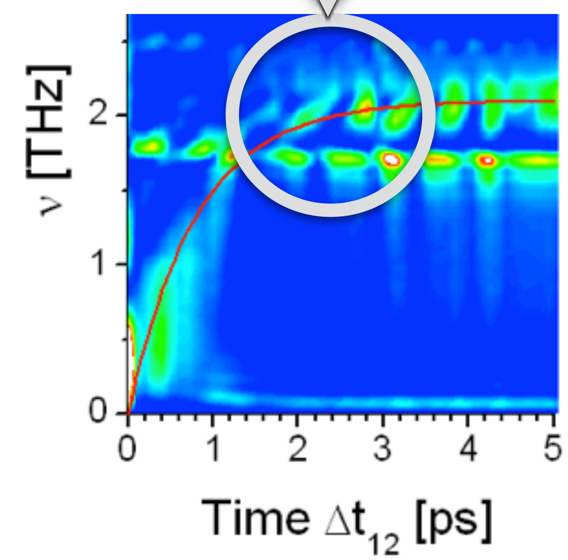


The collective mode linewidth reflects the presence of domain walls

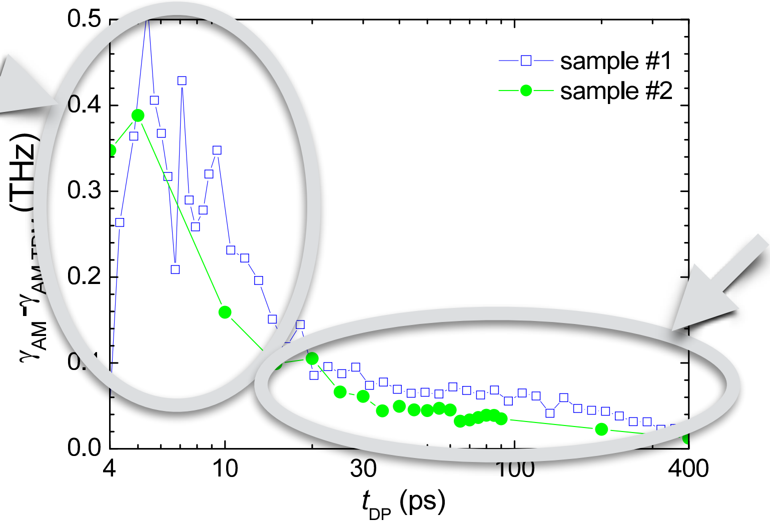
Mertelj, T. *et al.* Incoherent Topological Defect Recombination Dynamics in TbTe_{3}. *Phys Rev Lett* **110,** 156401 (2013).

Topological defect dynamics: timescales

1 ~ 5 ps: Coherent defect annihilation

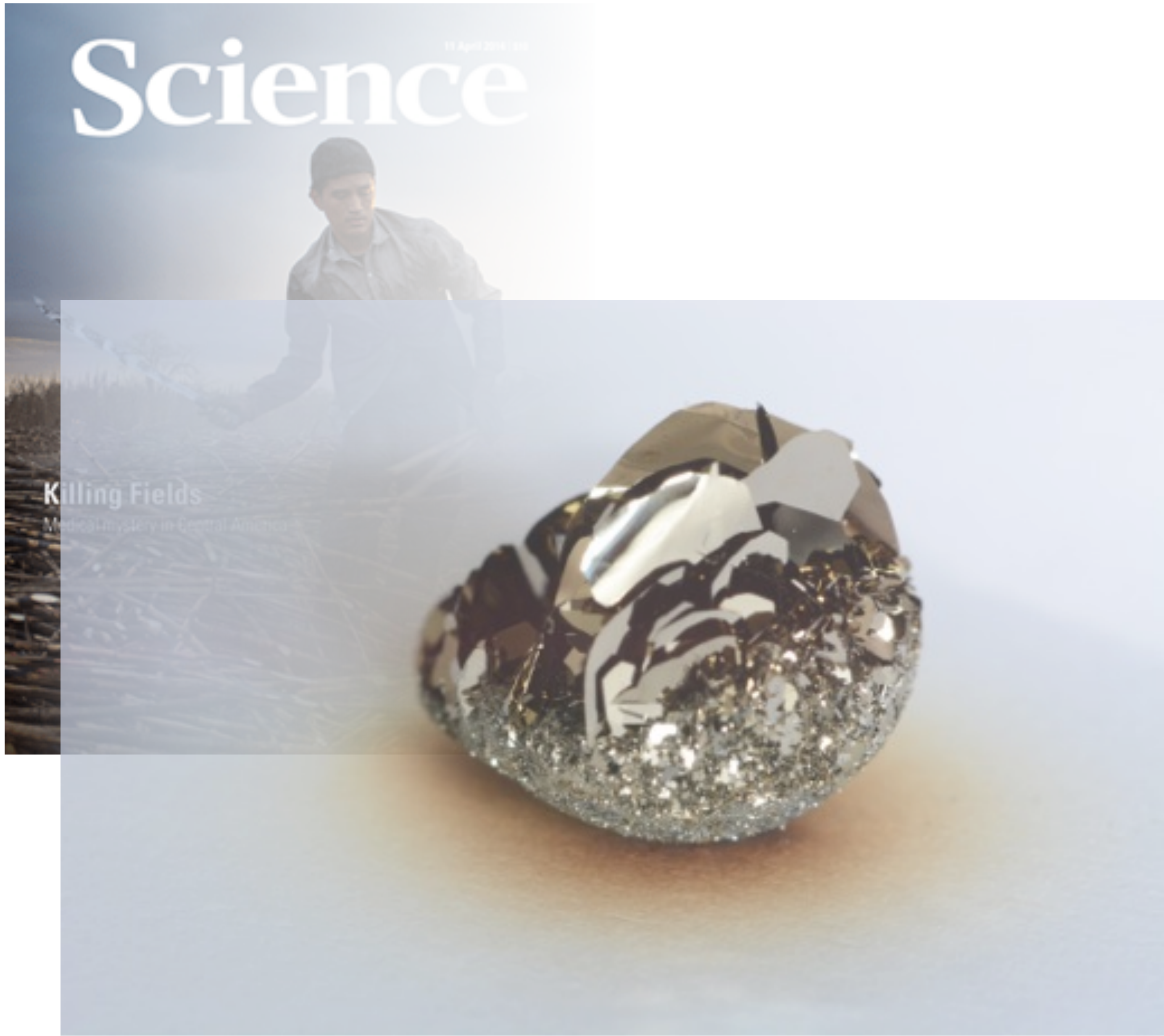


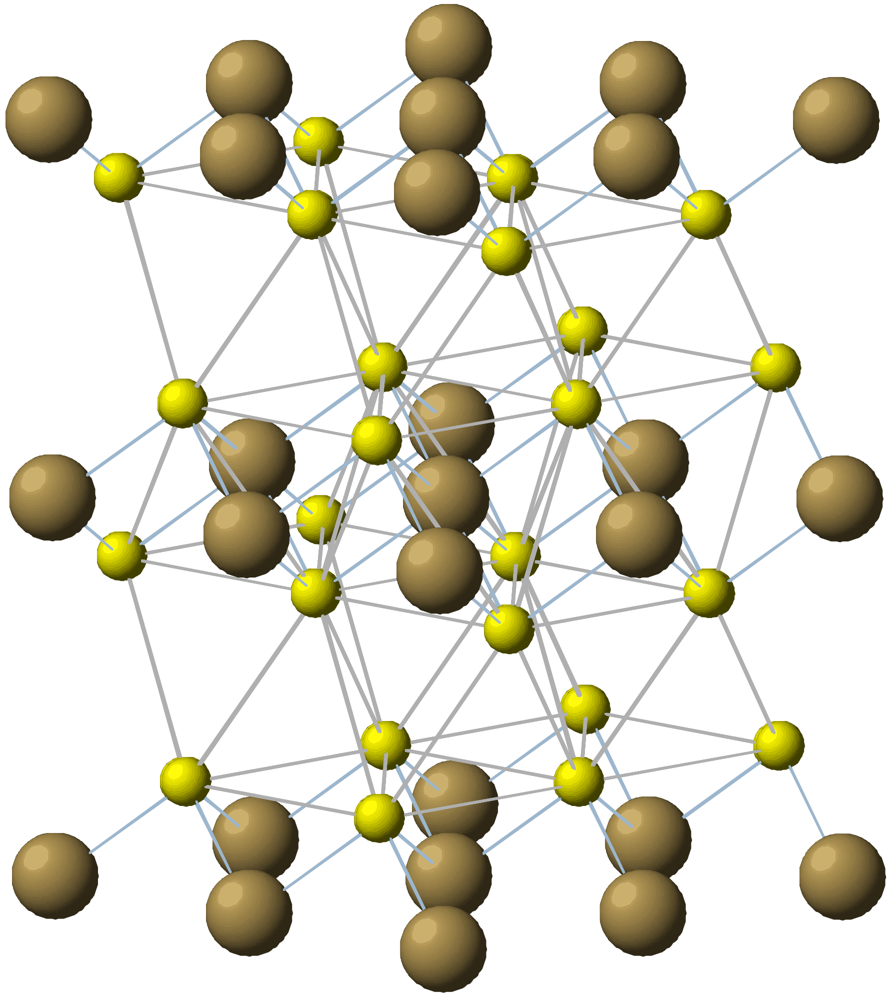
~5-30 ps: incoherent (intrinsic) dynamics:



~ 50 ps to > 1 μs: extrinsic defect-related dynamics

2. The trajectory to a hidden state in $1T$-TaS_2



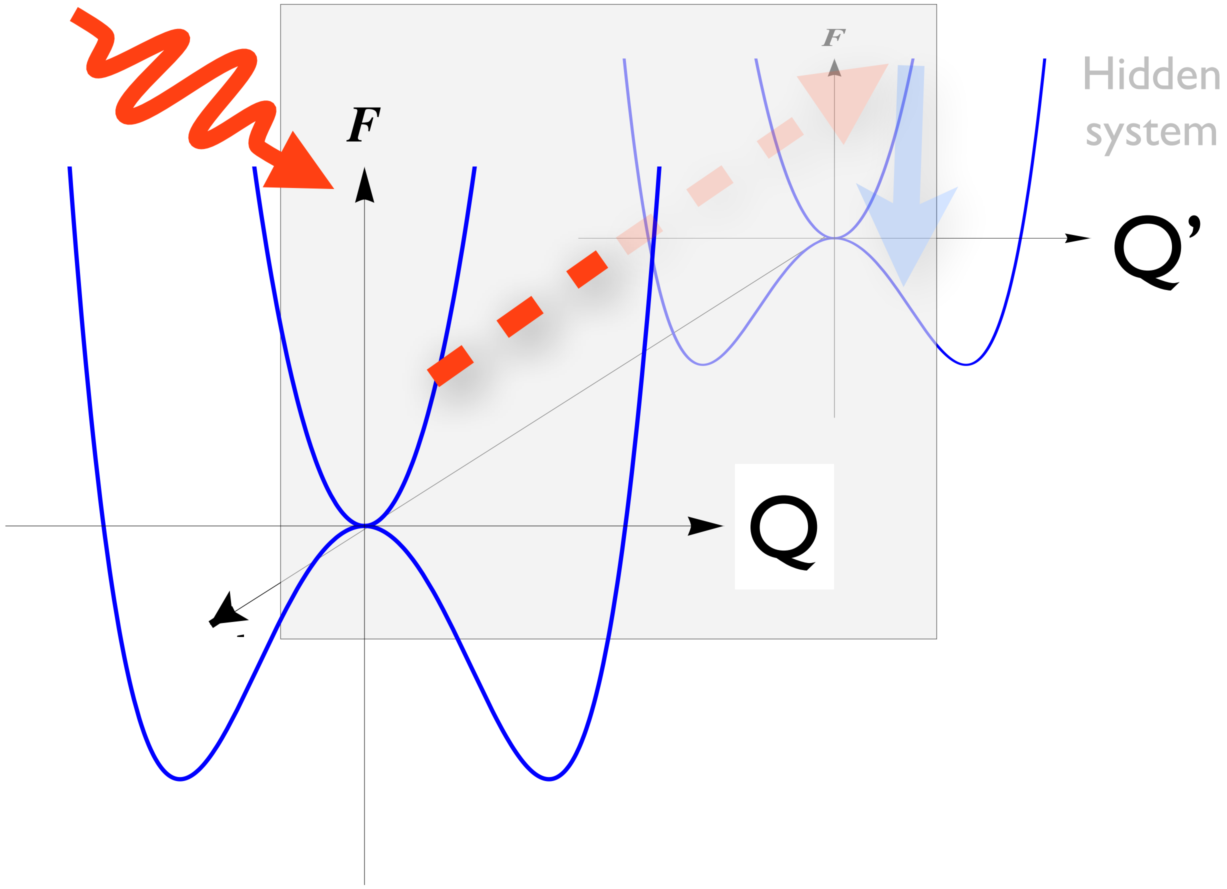


$1T$-TaS_2

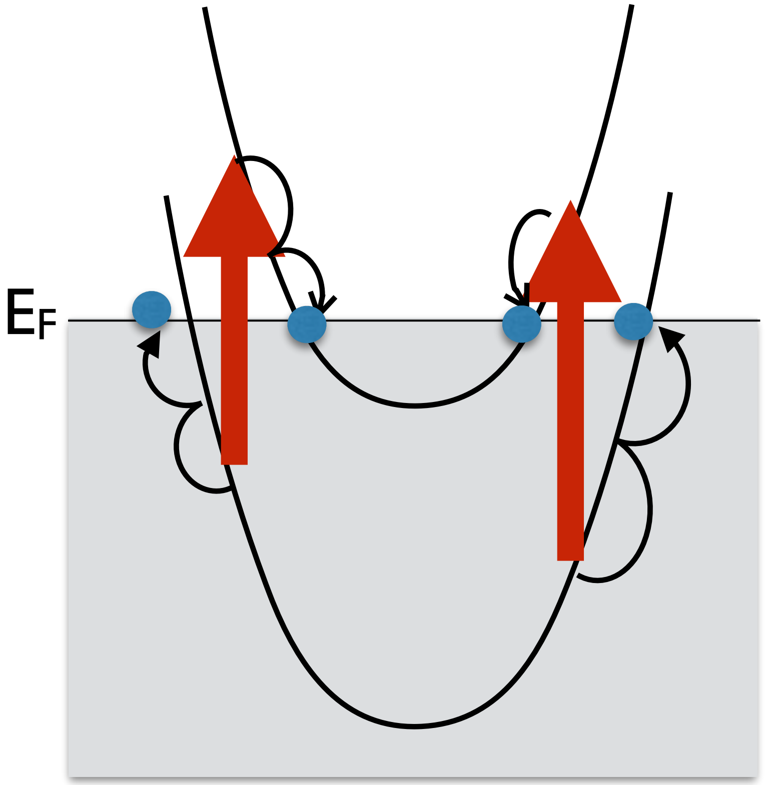
What is a hidden state?

It is a state of matter which cannot be reached under ergodic conditions, by slowly changing *T*, *P*, *EM*-field, etc.

Switching to a hidden state can be achieved by a **non-thermal process** which occurs under highly non-equilibrium conditions of the underlying vacuum

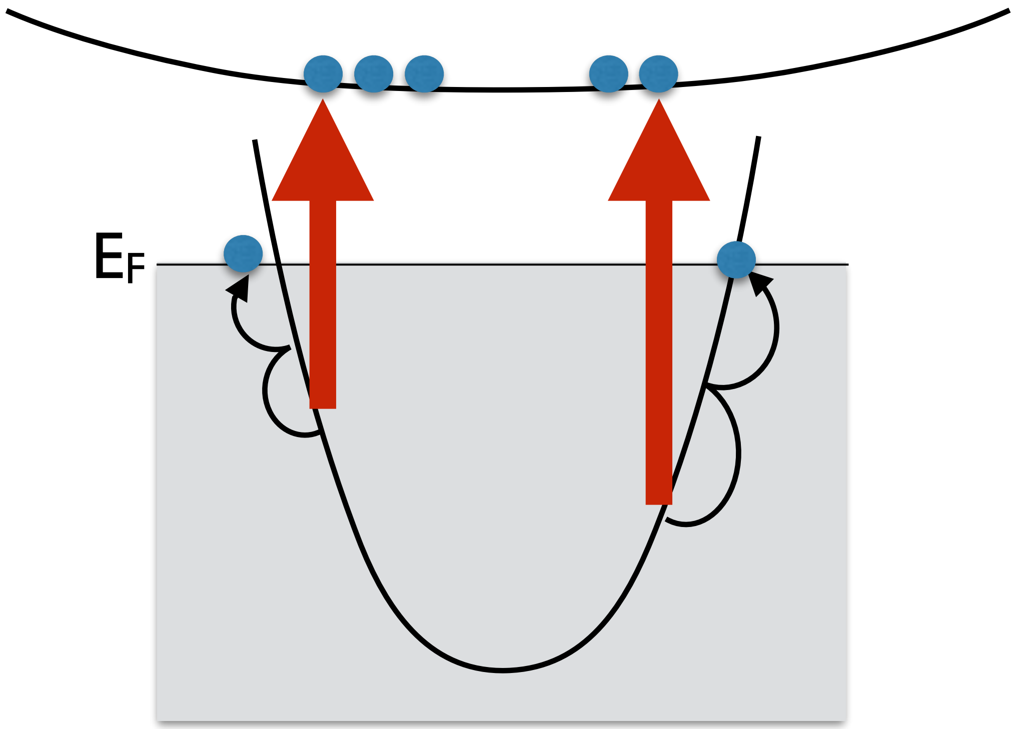


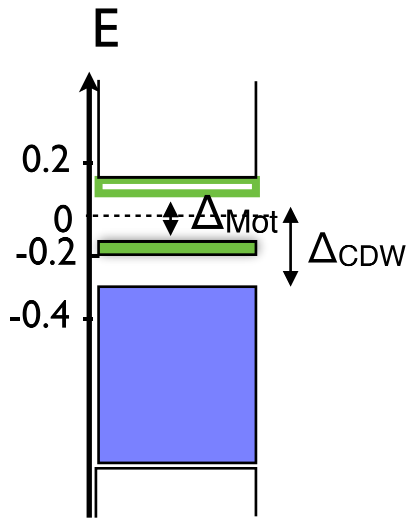
The importance of e-h (a)symmetry for creating photoinduced states



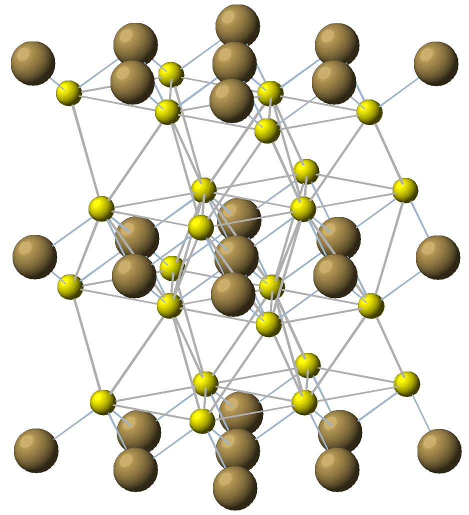
Just heating ($T_e^*=T_L^*=\ldots$).
No doping.

The importance of e-h (a)symmetry for creating photoinduced states



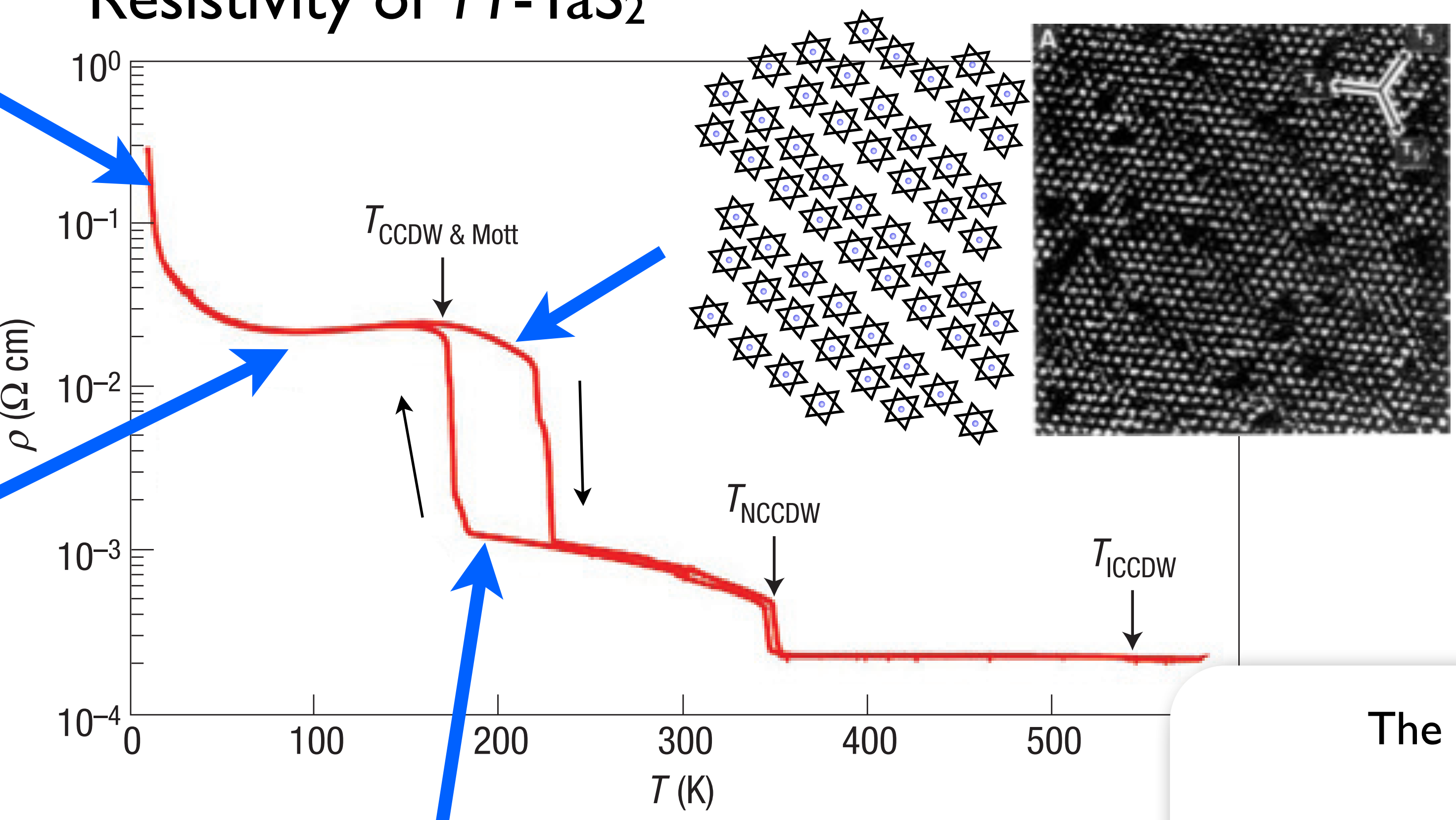


The competing states of *1T*-TaS_2 under equilibrium conditions



Mott state

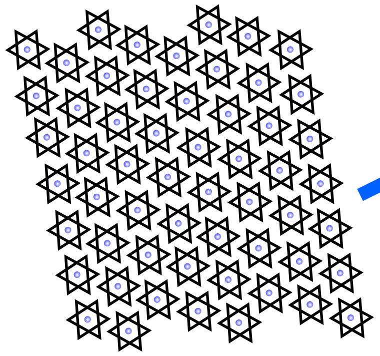
Resistivity of *1T*-TaS_2

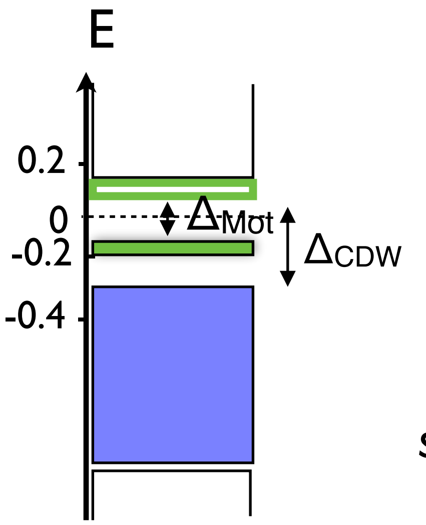


Stripes (on heating)

STM
(Burk et al., 1992)

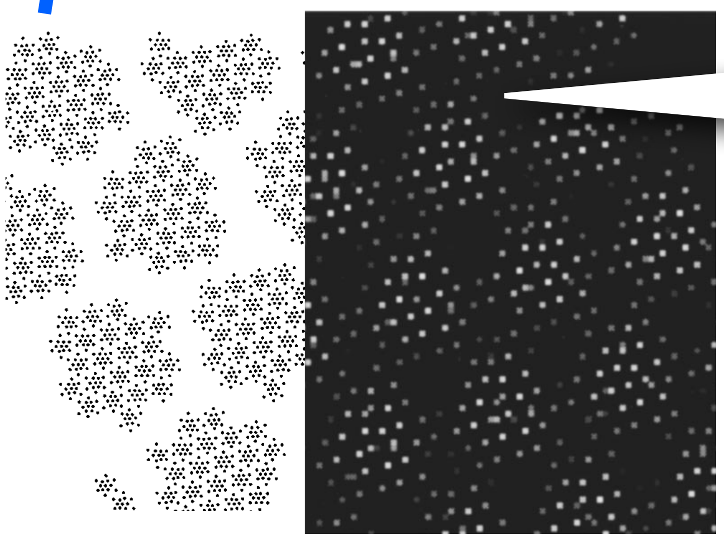
Honeycomb structure
(Commensurate CDW phase)
Tossati and Fazekas (1974)



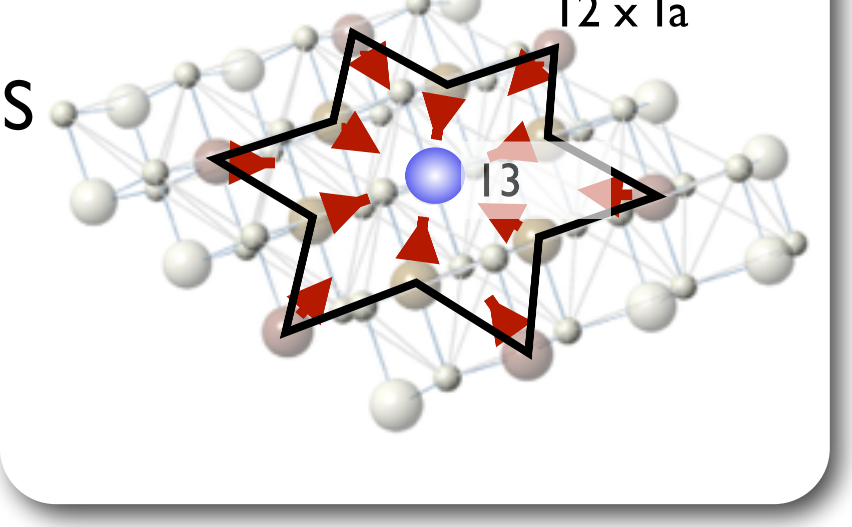


Stretched honeycomb structure of C phase with domain walls in between (Nearly Commensurate CDW phase)

STM

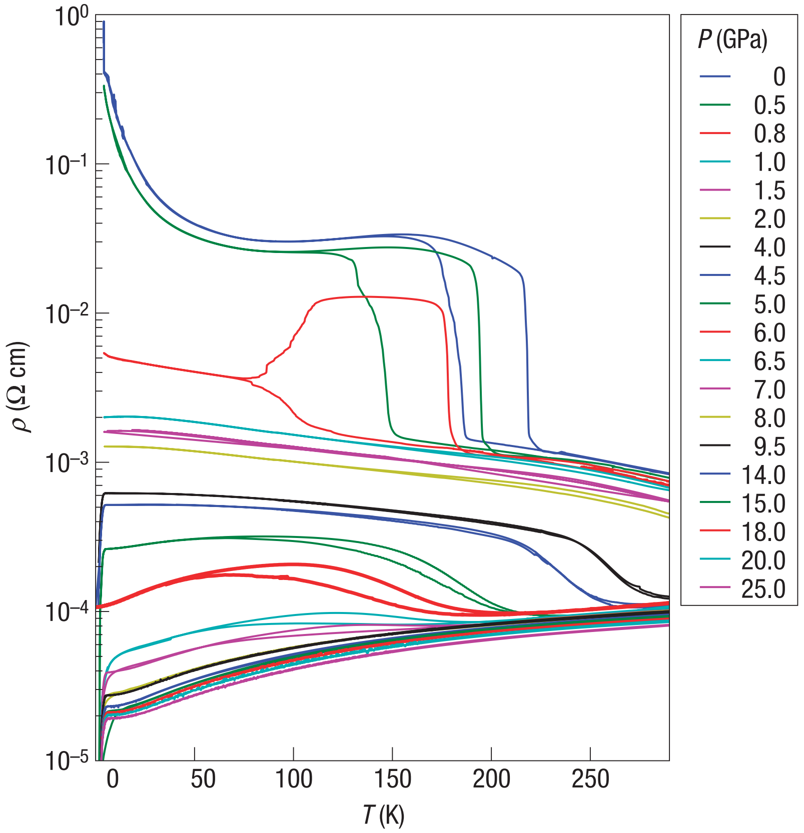


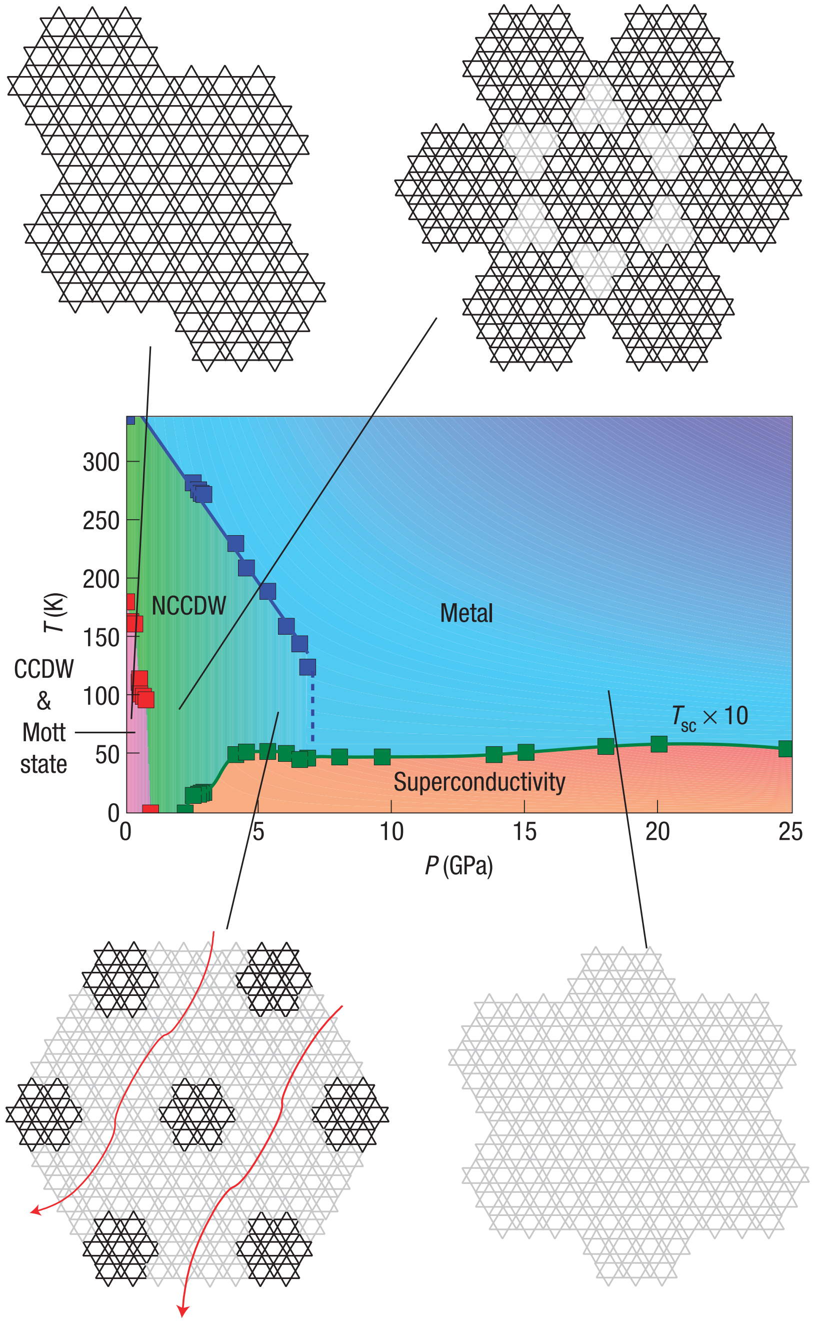
The polaron in *1T*-TaS_2



Other nearby states in 1T-TaS$_2$:
Superconductivity under pressure, or Fe, or Se doping etc.

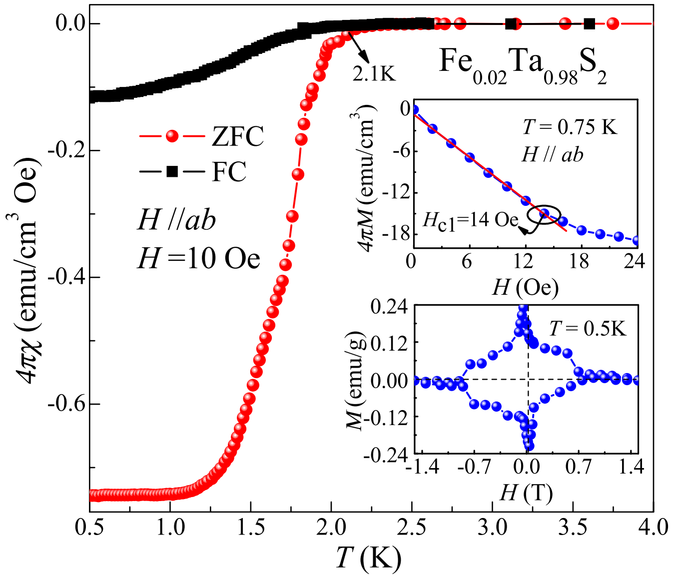
Pressure:

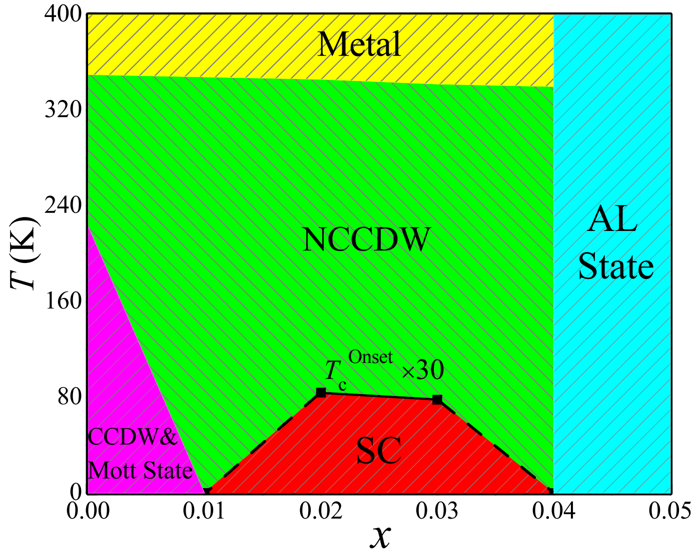




Sipos et al (Nat.Mat. 2008)

Fe doping:

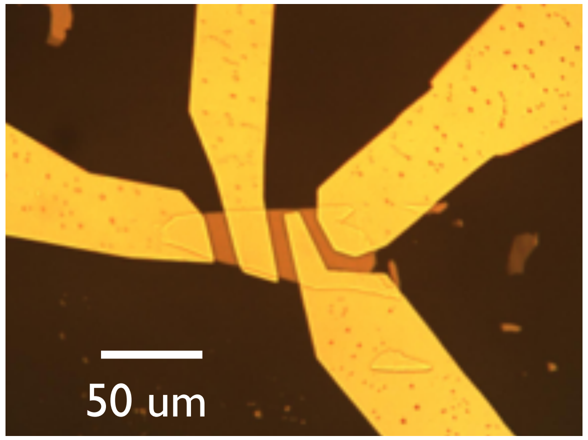




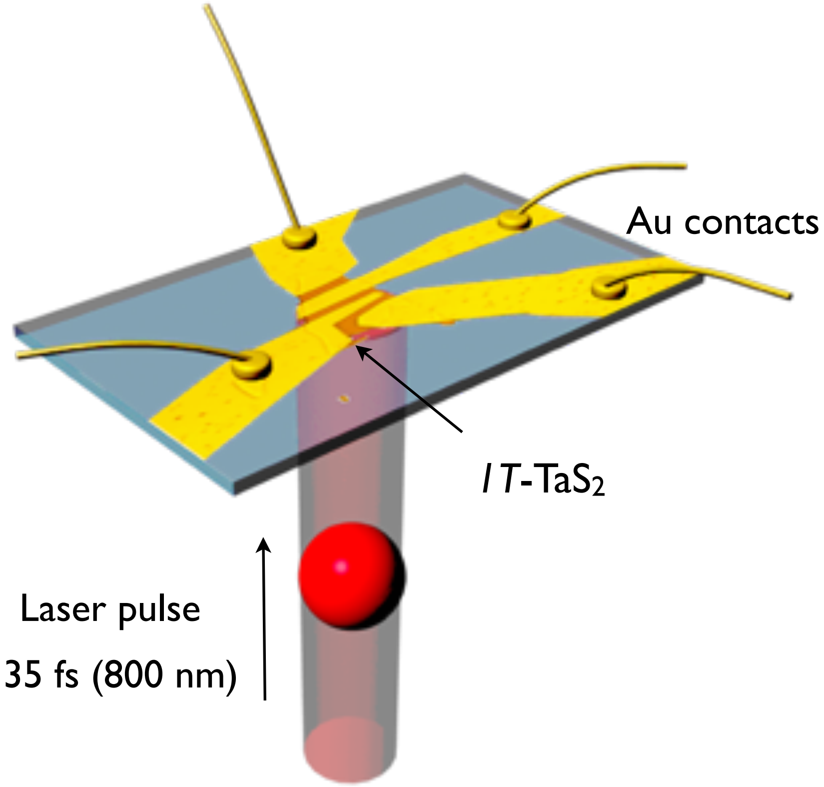
Li et al. EPL 2012

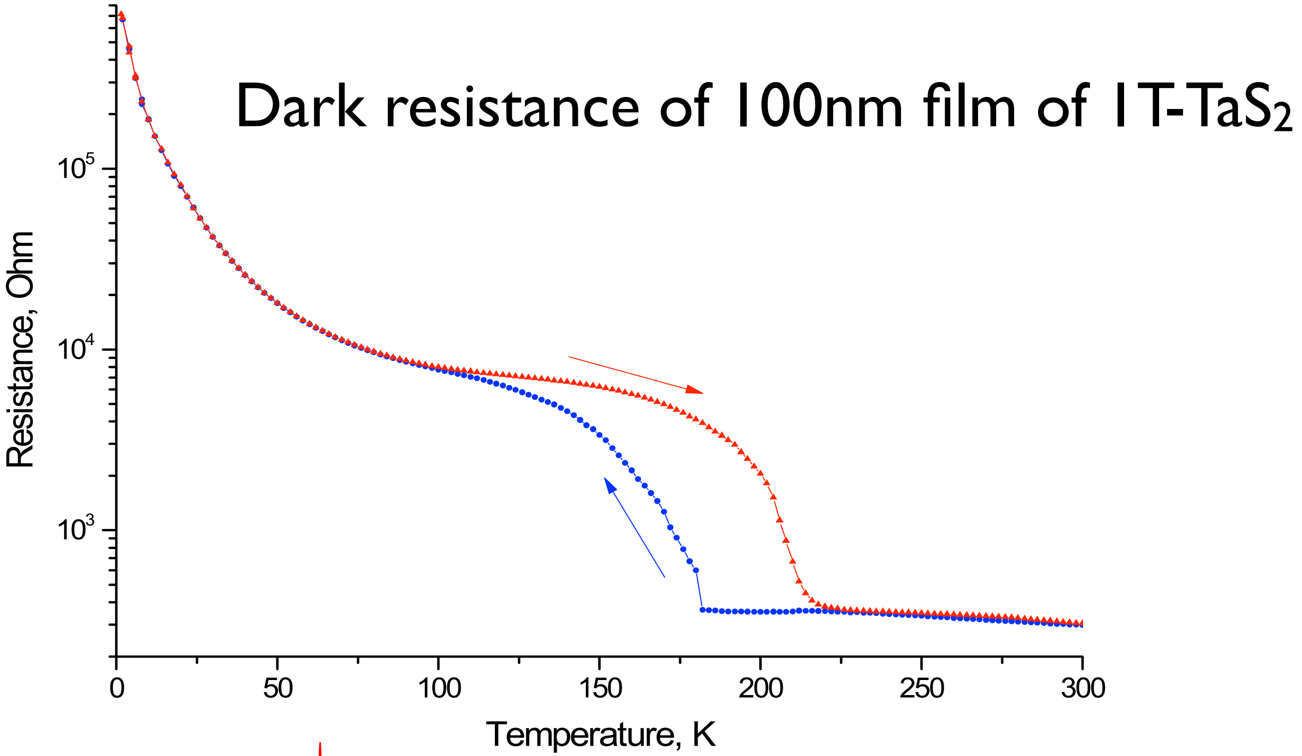
Switching to a hidden state in $1T$-TaS_2 : Resistance change after a (single) 35 fs pulse

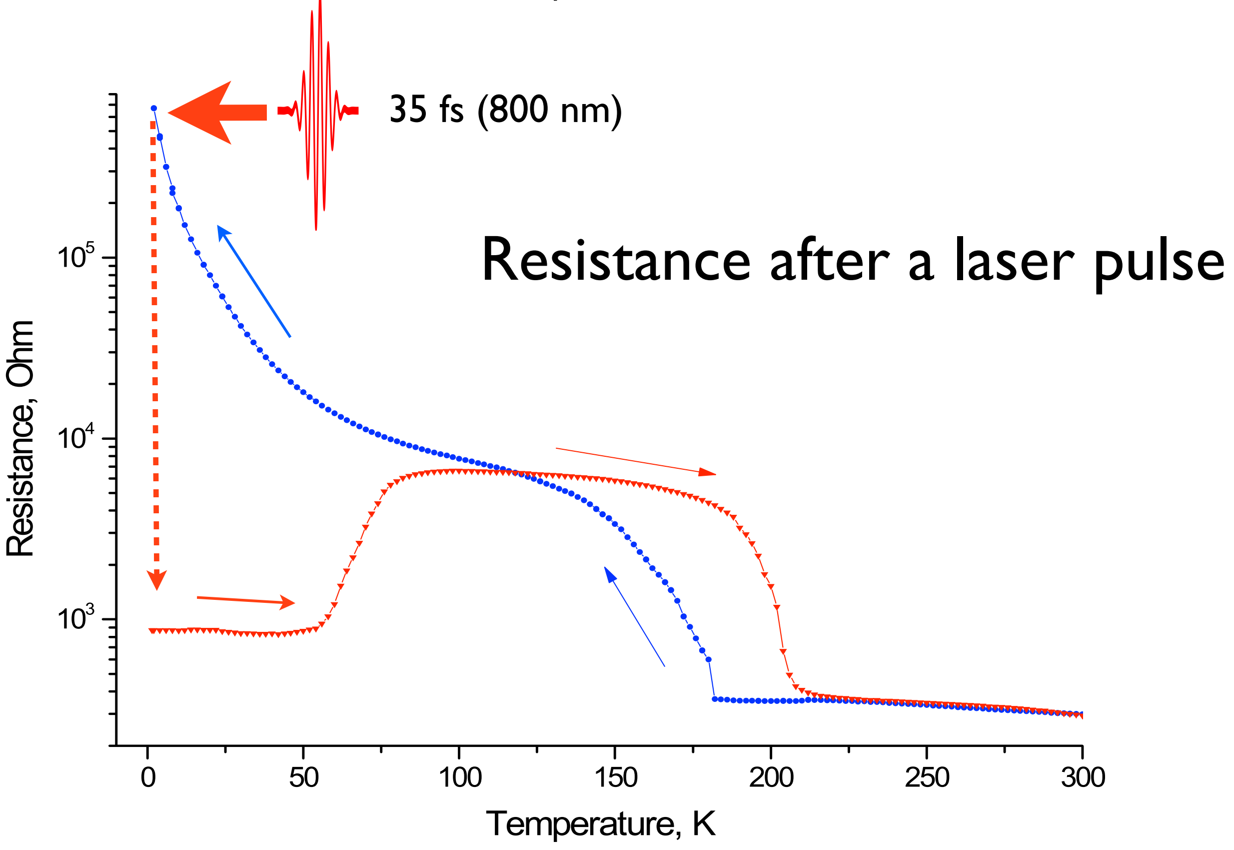

Igor Vaskivskyi



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

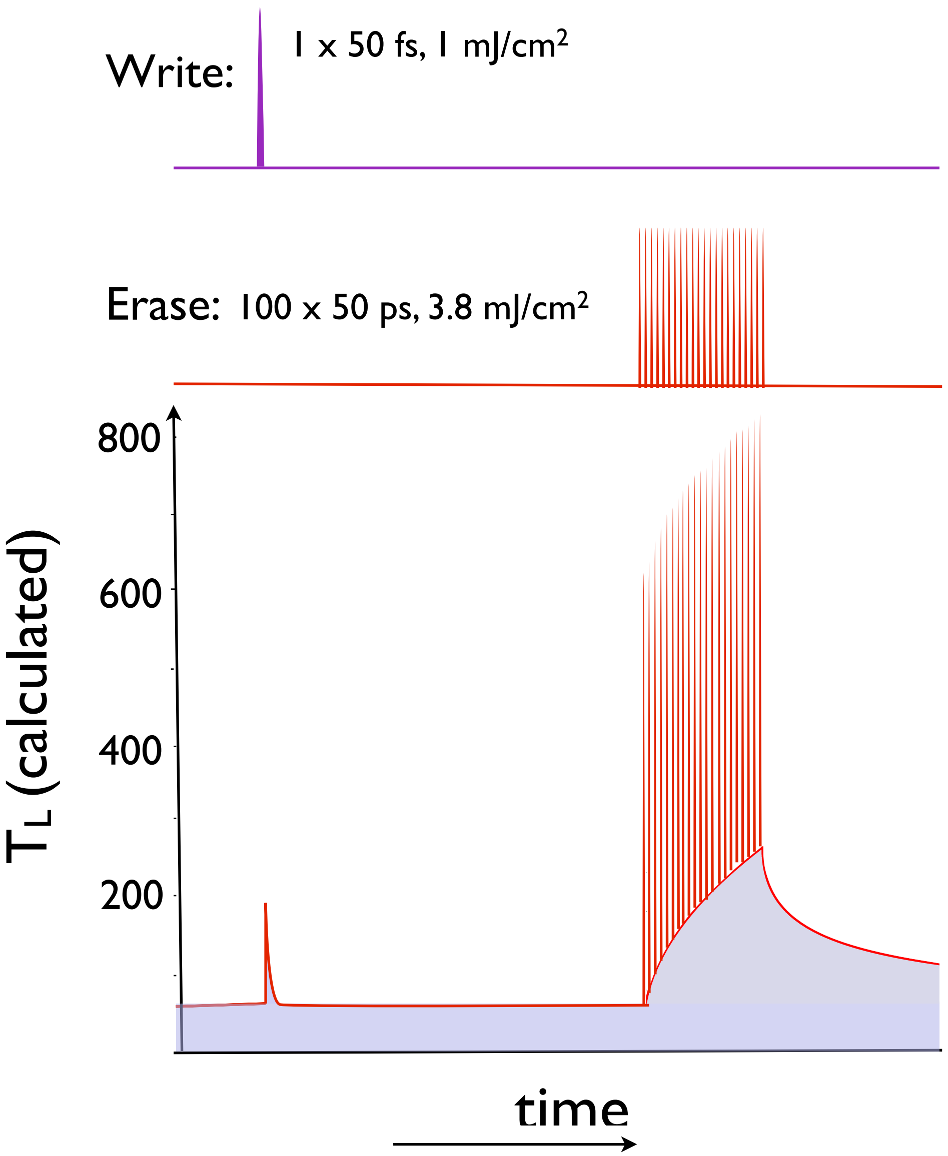


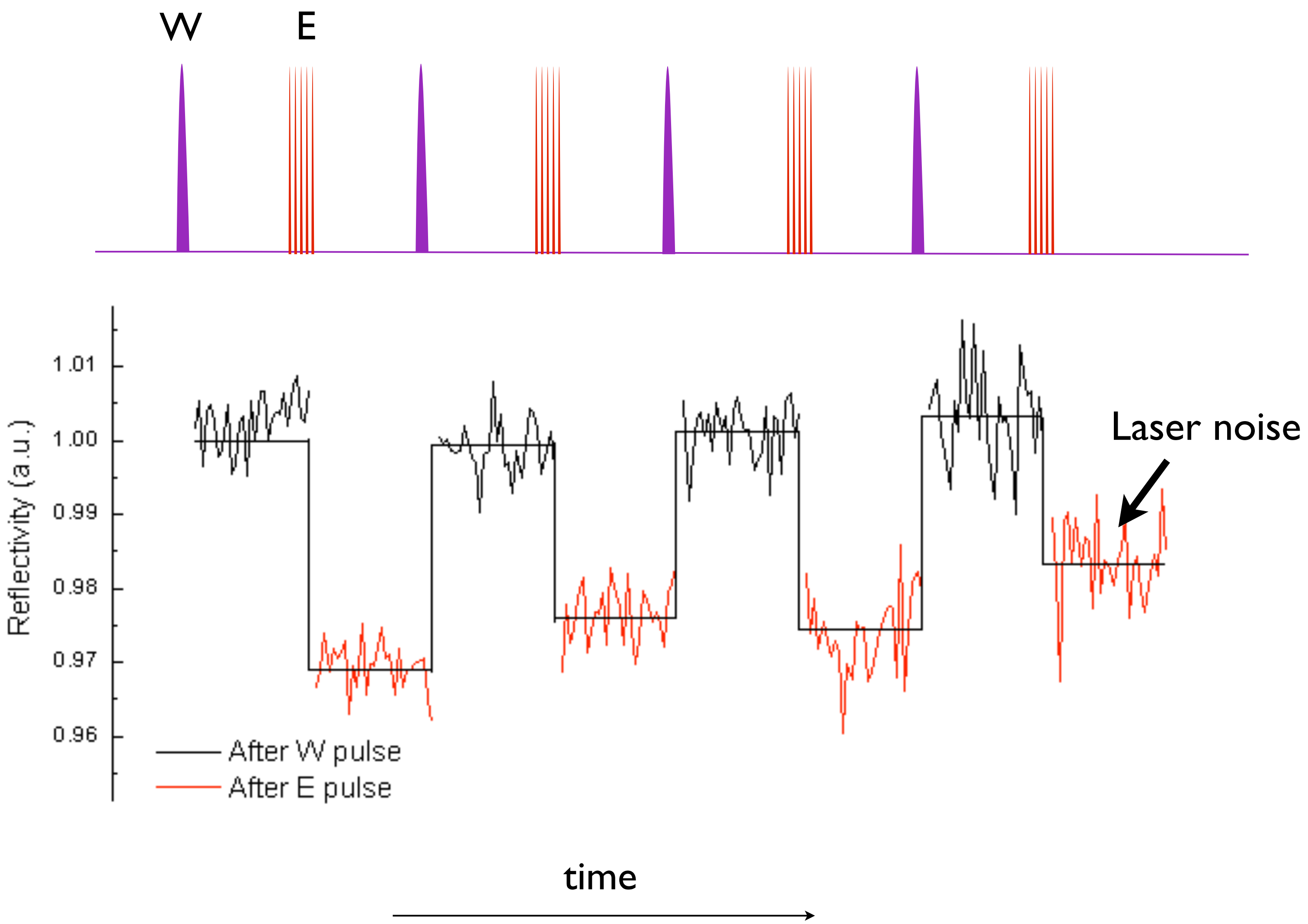

Dark resistance of 100nm film of $1T$-TaS_2


Resistance after a laser pulse

L Stojchevska et al. Science 2014;344:177-180

Reflectivity switching by laser pulses

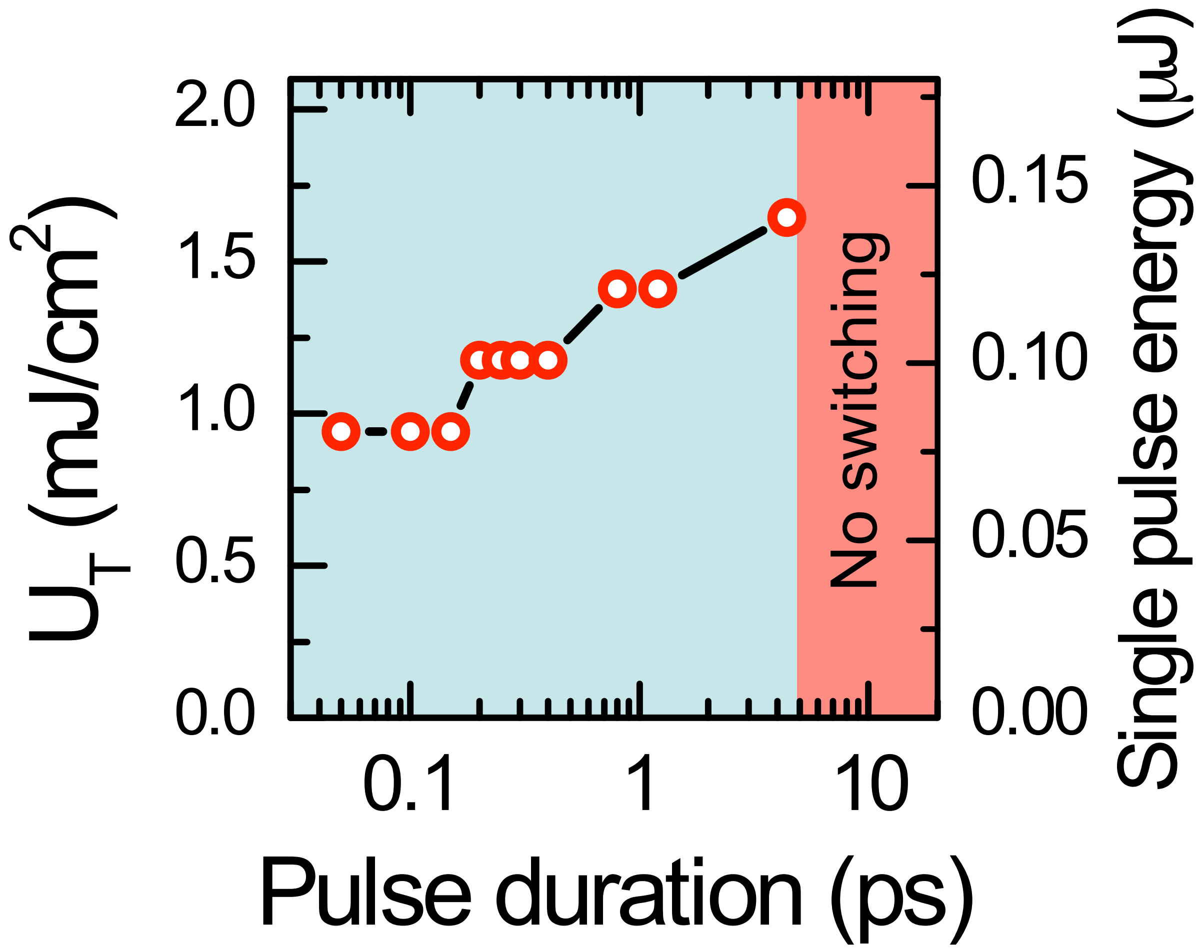




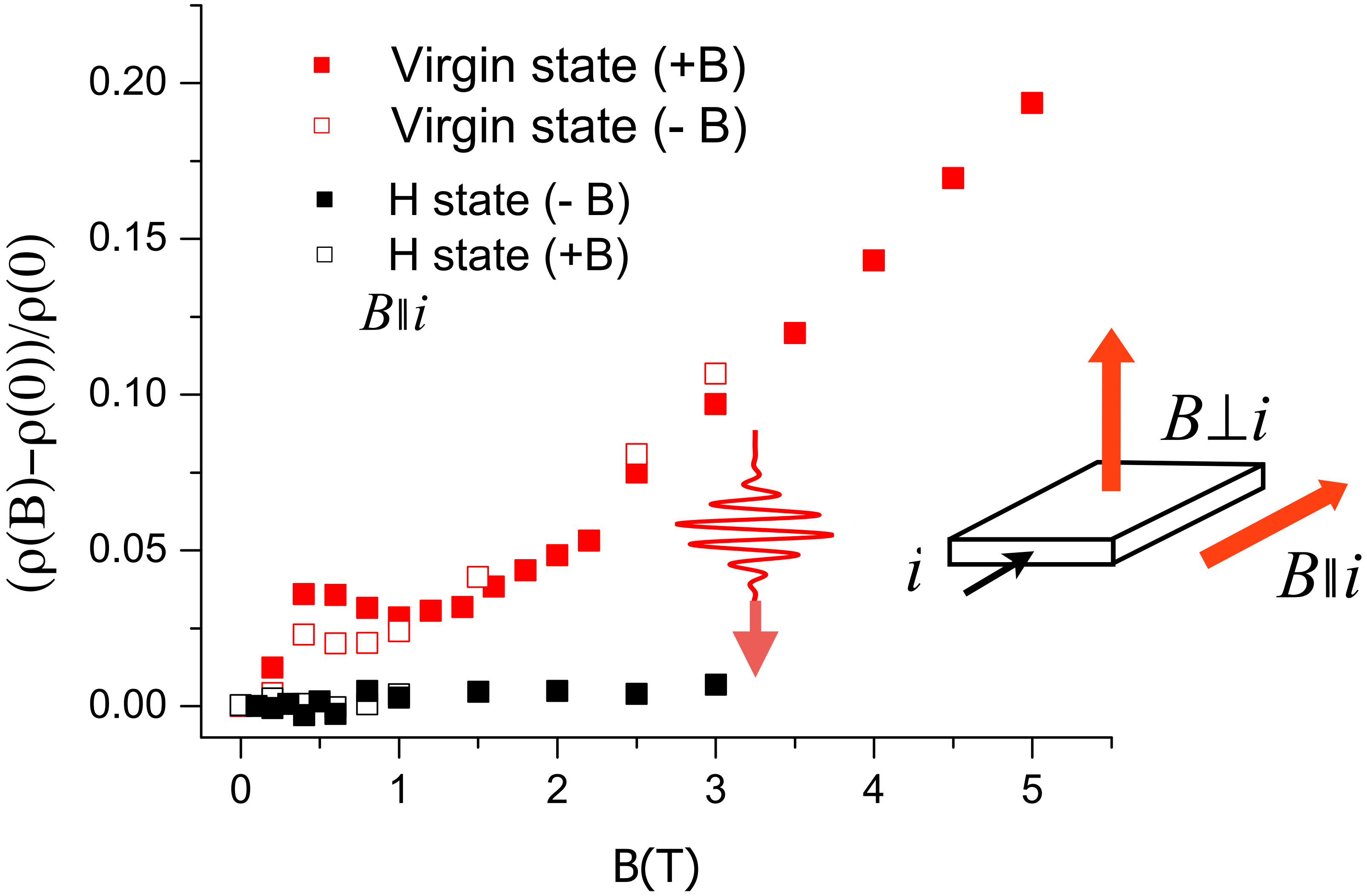
Switching is accompanied by a change in dielectric constant.

ΔR = 5% at 800 nm (1.5 eV)

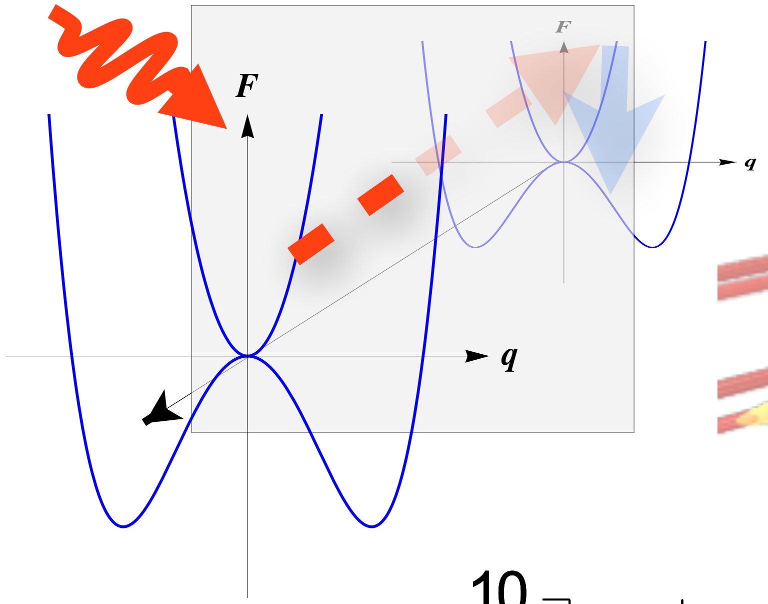
Switching only occurs for short pulses $\tau_L < 4$ ps

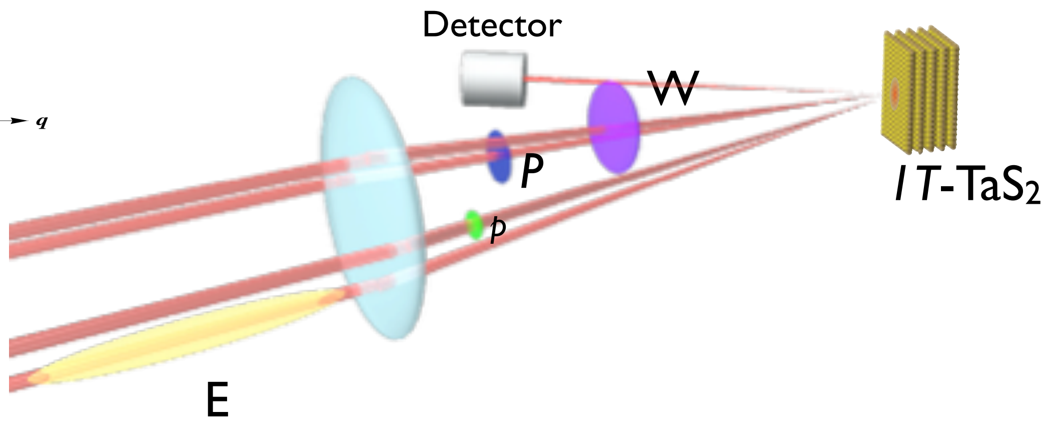


Magnetoresistance switching by a single 35 fs pulse



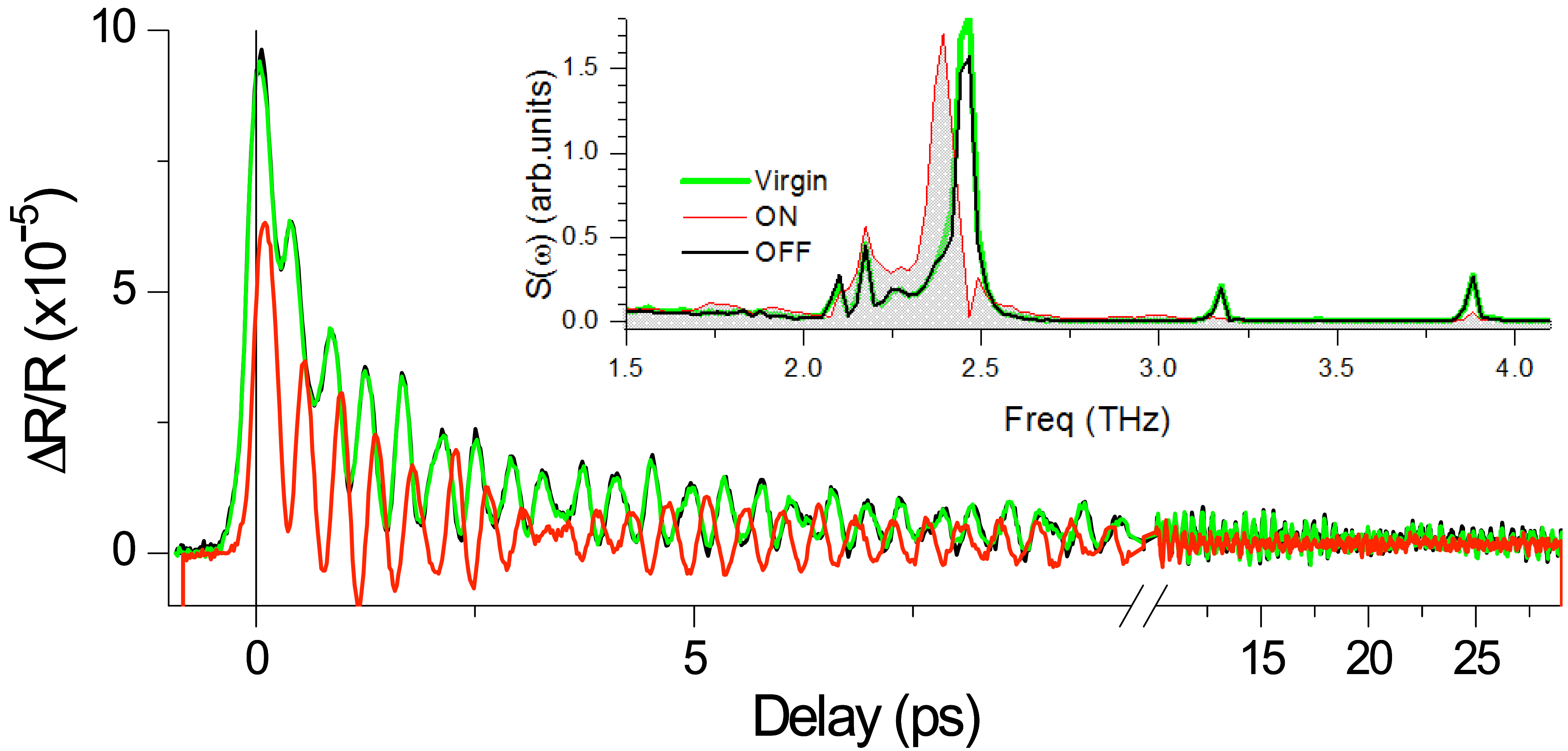
1*T*-TaS$_2$: Collective mode switching





W = 50 fs "write"
E = 50 ps "erase"
P = "pump" (50 fs)
p = "probe" (50 fs)

Ljupka Stojchevska

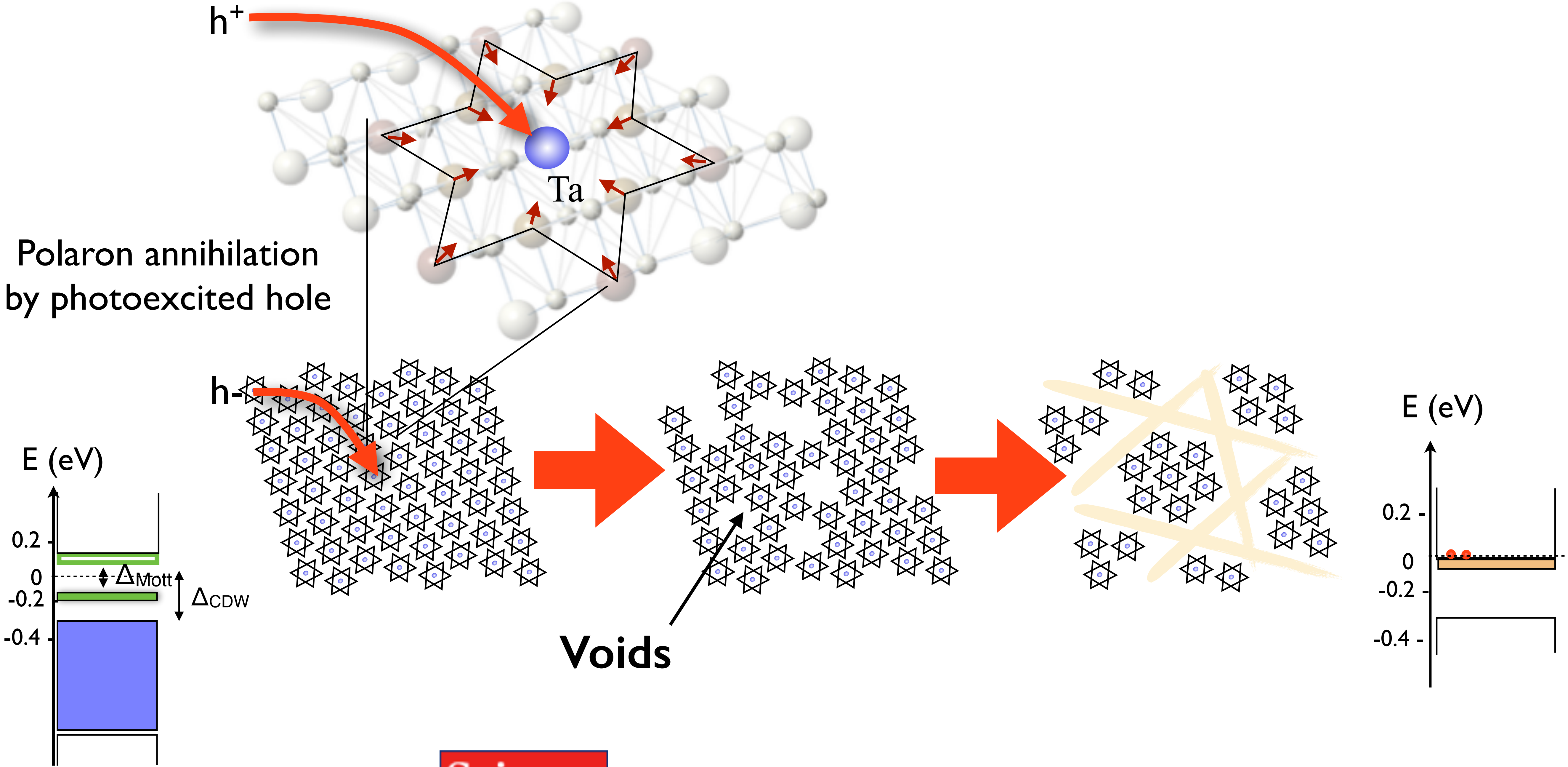


Science AAAS

L Stojchevska et al. Science 2014;344:177-180

Photo”doping” and ordering of voids

The addition of a h+ to the C structure annihilates a polaron, creating a void.



Polaron annihilation by photoexcited hole

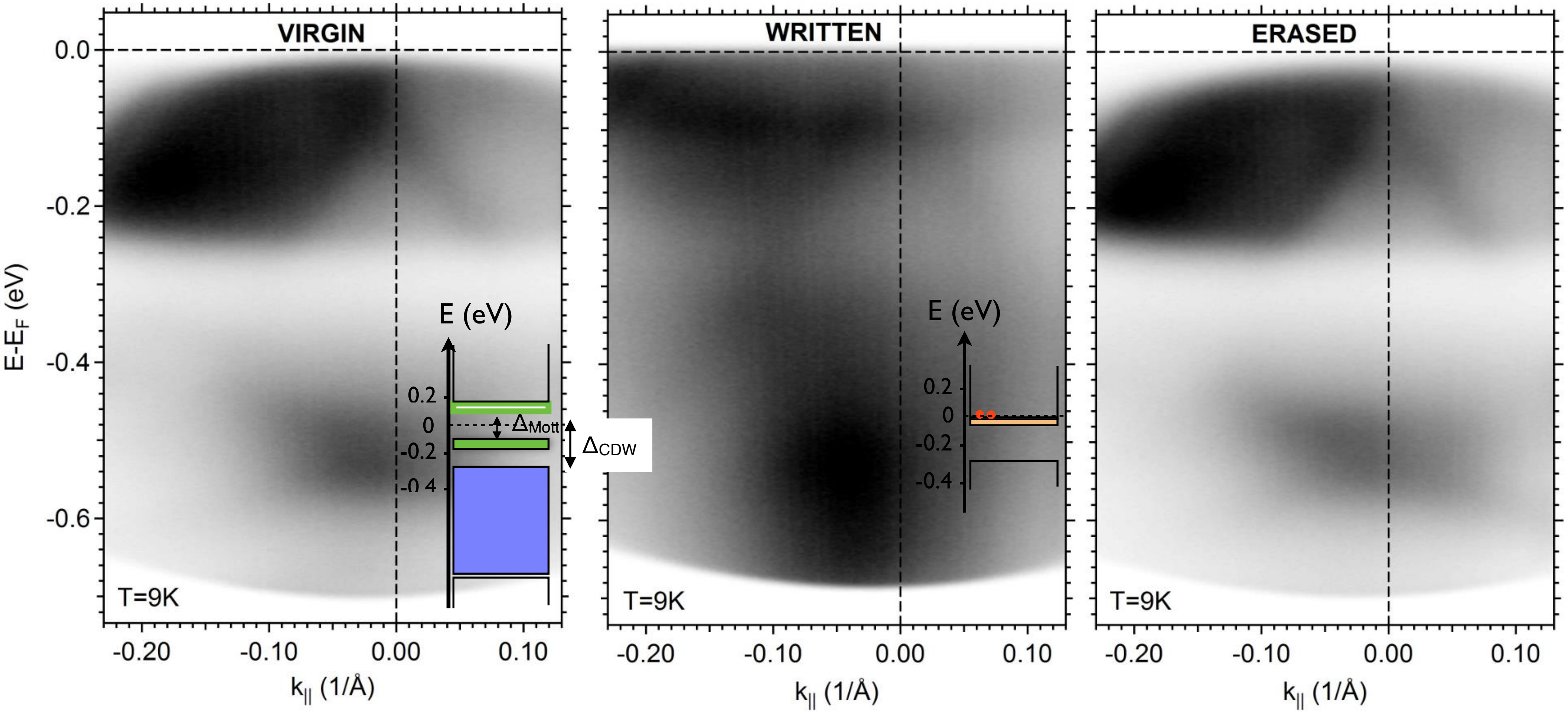
Voids

L Stojchevska et al. Science 2014;344:177-180

What’s happening to the electronic structure?

Patrick S Kirchmann
Stanford Institute for Materials and Energy Sciences (SIMES)
SLAC National Accelerator Laboratory
Menlo Park, CA 94025, USA

Low Temperature ARPES of Switched 1T-TaS$_2$ Overview



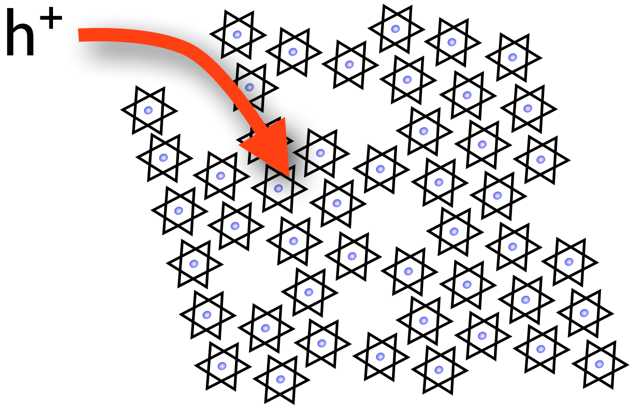
Mott-gapped “VIRGIN” C-state

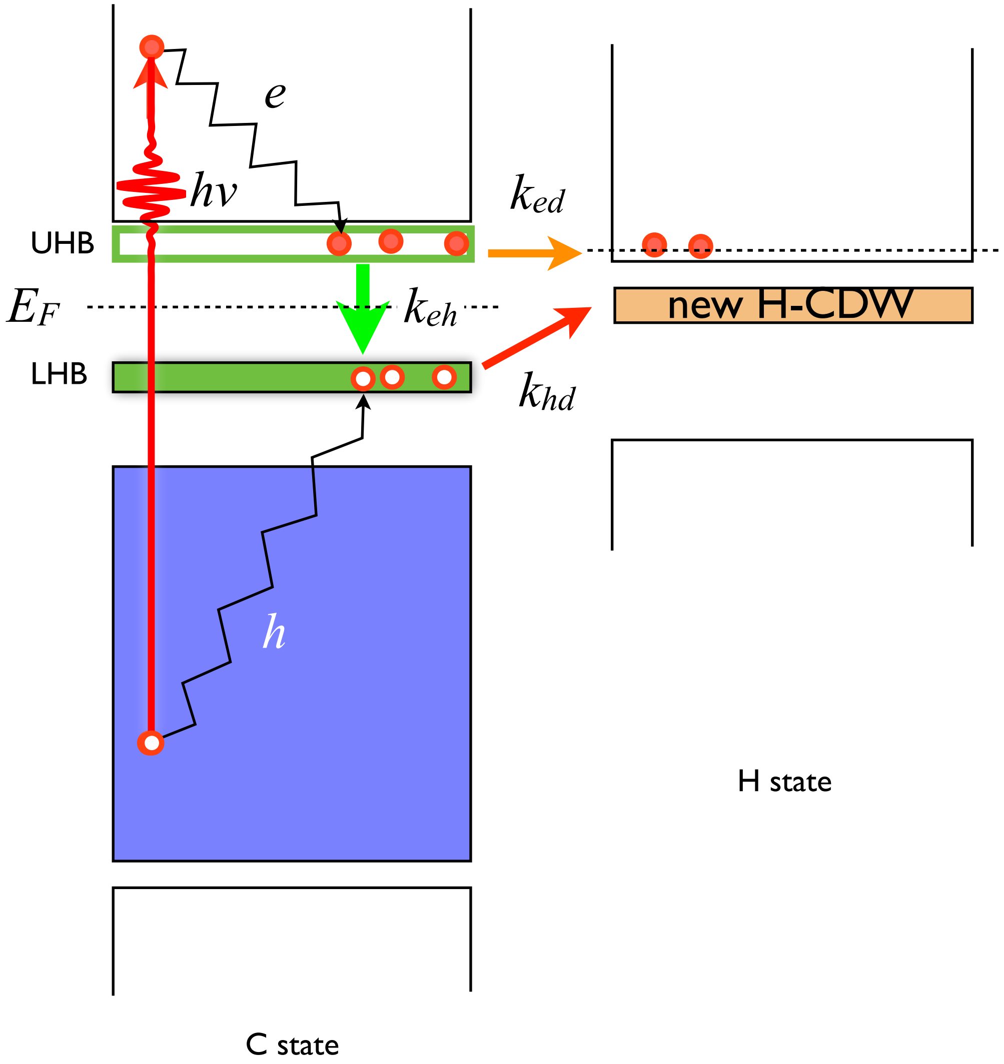
H-state WRITE: single >2mJ/cm^2 pulse changes

1. **ARPES intensity**
2. **Mott gap & bands**
3. **work function**

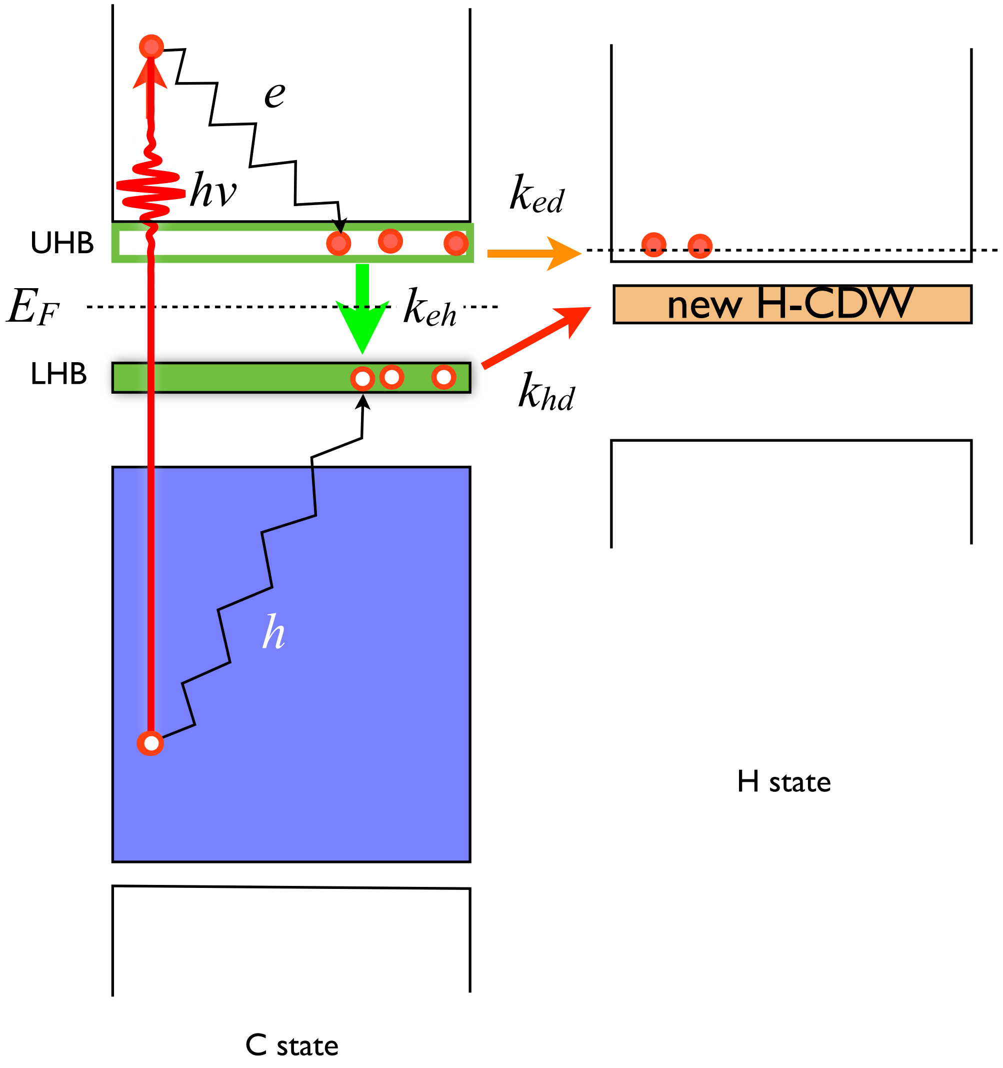
C-state ERASE: multiple ~1μJ/cm^2 pulses or multiple ~1mJ/cm^2 pulses

Kinetics cannot be described in a rigid band approximation





Nonlinear particle kinetics



The kinetic equations for the electrons and holes:

$$\frac{dn_h}{dt} = -k_{eh}n_e n_h(\mu_e + \mu_h) - k_{hd}n_h(\mu_h - \mu_d) \ +P(t)$$
$$\frac{dn_e}{dt} = -k_{eh}n_e n_h(\mu_e + \mu_h) - k_{ed}n_e(\mu_e + \mu_d) \ +P(t)$$

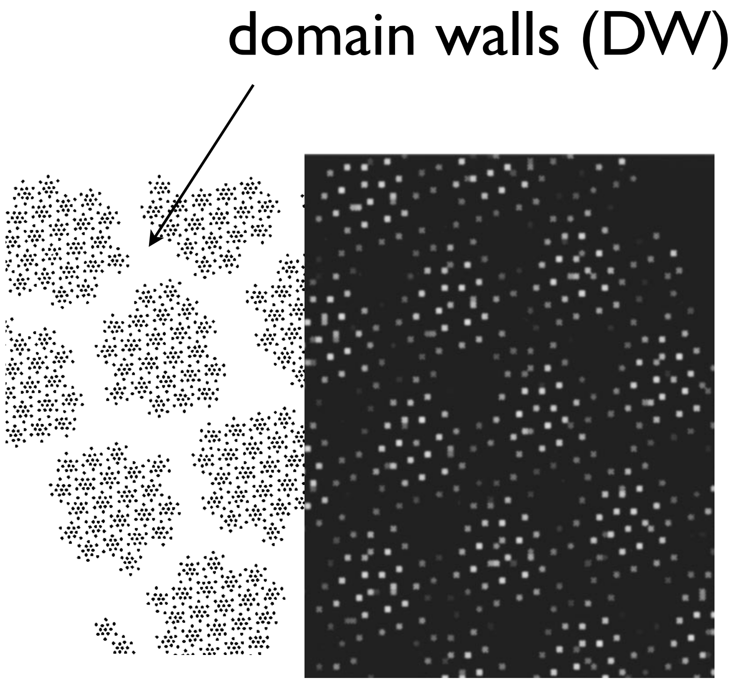
Subject to conservation of charge

$$n_e - n_h = n_v - n_i = n_d.$$

μ_i are time-dependent, and *P(t)* is the laser pulse

The nearly-commensurate state of *1T*-TaS$_2$

McMillan (1975), Nakanishi et al (1977), Serguei Brazovskii, (2013)

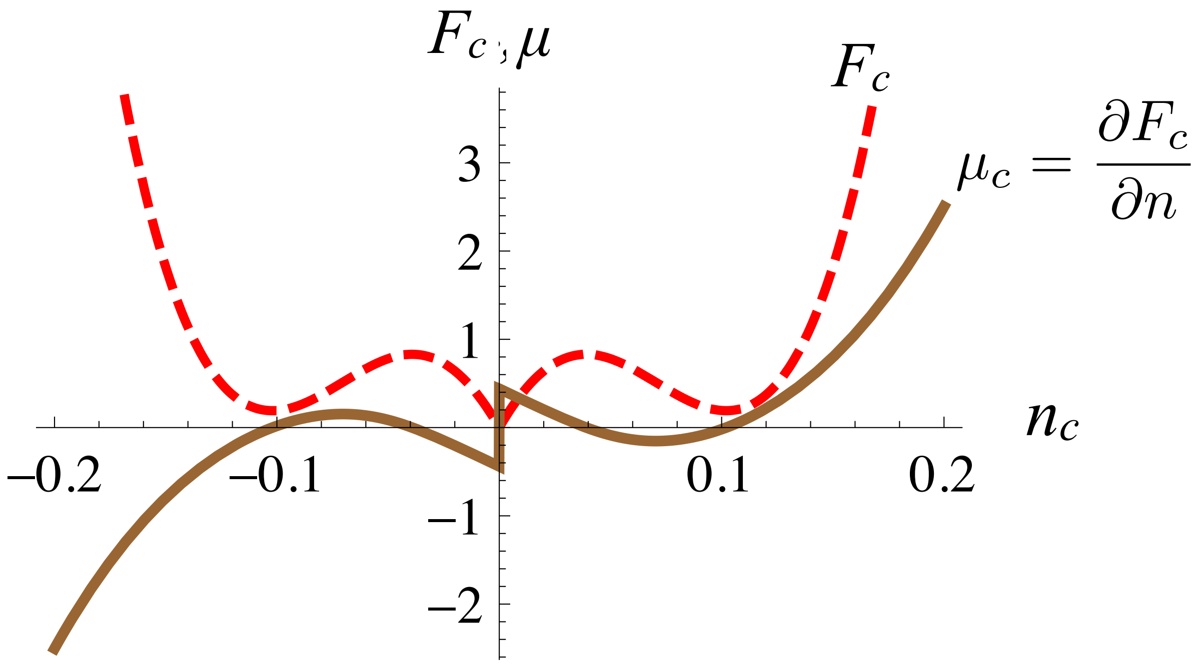


Free energy:

$$F_c(n_c) = E_{DW}(\underbrace{C_0|n_c| + C_1|n_c|e^{-1/(\xi|n_c|)}}_{\text{C - IC transition (MacMillan, 1975)}} \underbrace{- C_2\xi n_c^2}_{\text{Intersection of DW}} + \underbrace{C_4\xi^3 n_c^4}_{\text{Repulsion between DW crossings}})$$

Where $n_c = n_h - n_e$

Free energy and chemical potential:

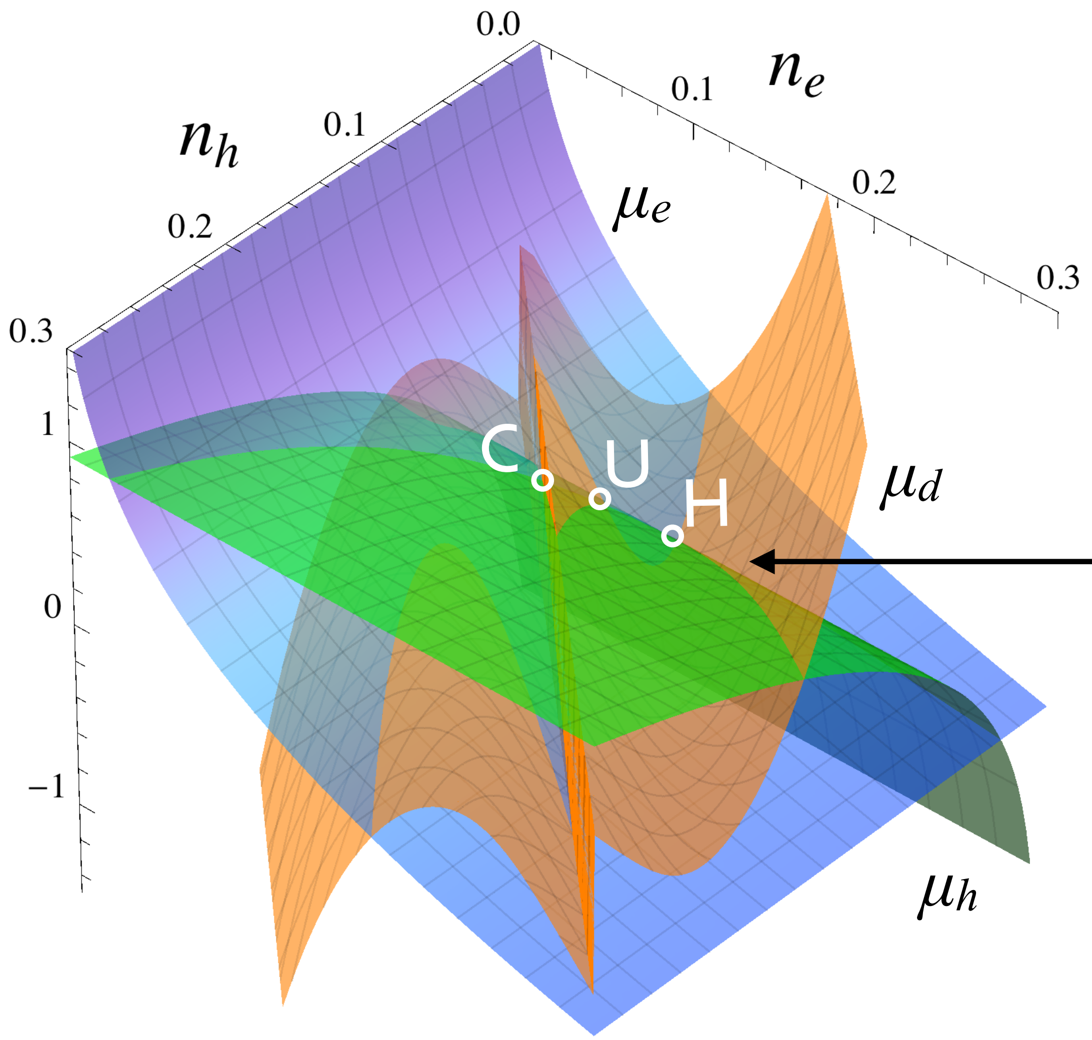


Chemical potential surfaces

The chemical potentials for electrons, holes and the condensate, $\mu_i = \dfrac{\partial F_i(n_i)}{\partial n_i}$

are given by: $\mu_{e,h}(n) = \Delta_{e,h} + k_B T \ln(e^{n_{e,h}/(k_B T N_{e,h})} - 1)$

and $\mu_c(n_c) = E_{DW}(C_1(1 + \dfrac{1}{\xi|n_c|})e^{-1/(\xi|n_c|)} + C_0 - 2C_2\xi|n_c| + 4C_4(\xi|n_c|)^3)sign(n_c)$



The system is stable (in equilibrium) when:

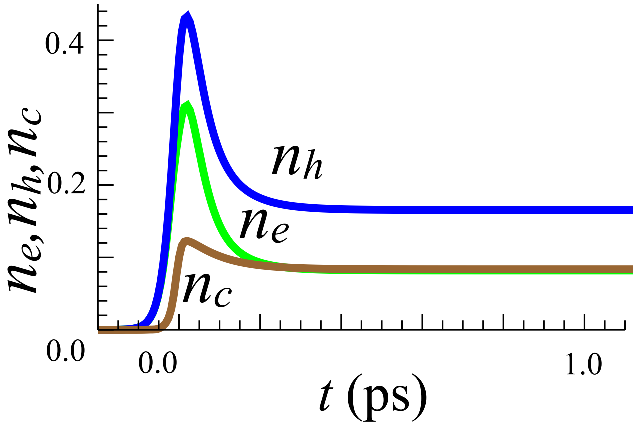
$$\mu_e = \mu_h = \mu_c$$

L Stojchevska et al. Science 2014;344:177-180

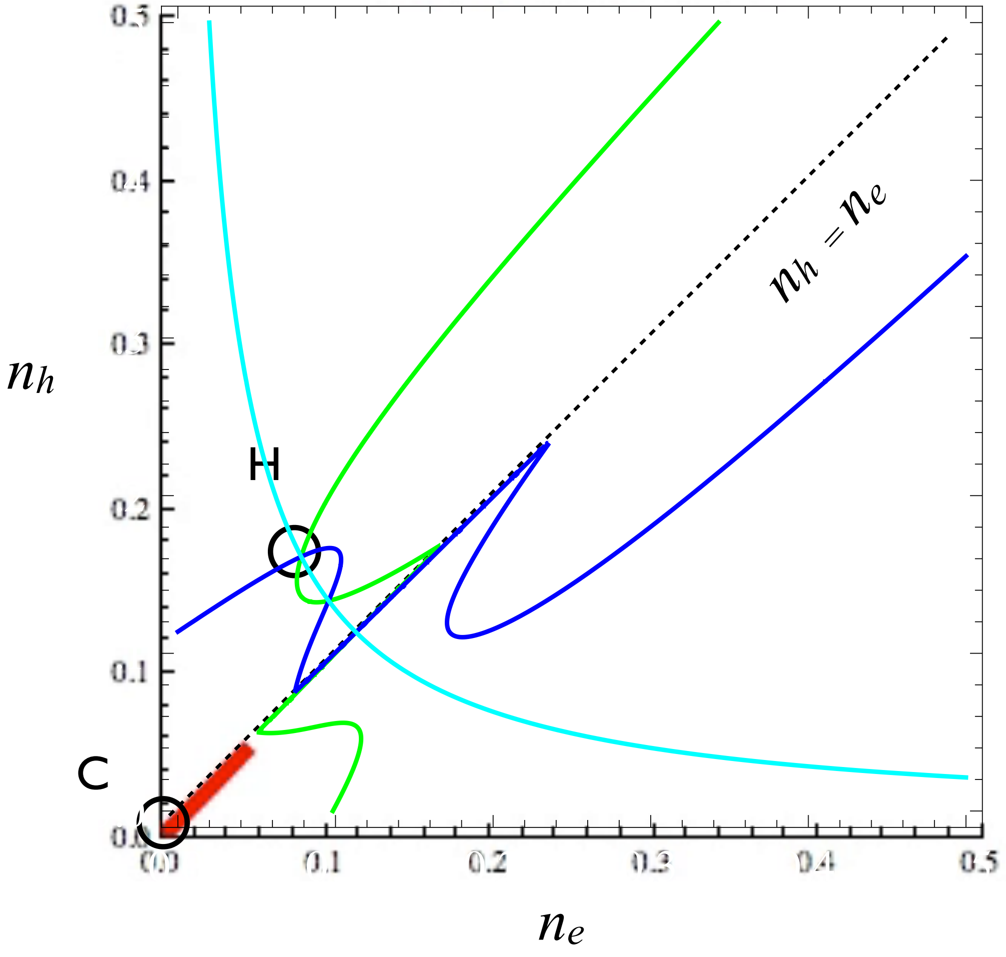
Calculated trajectory

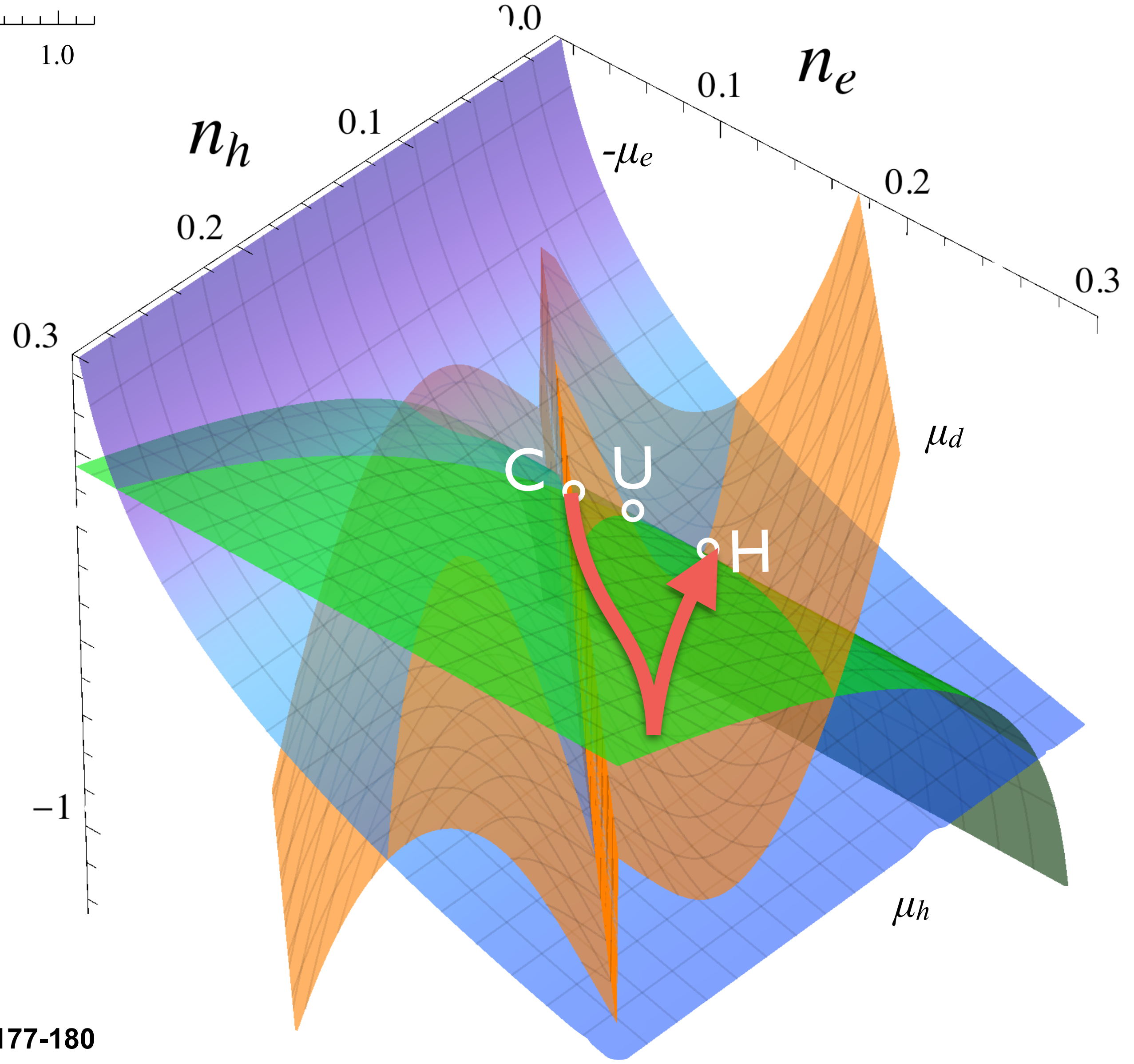
Laser pulse energy **above** threshold ($U_W > U_T$):

The time evolution of n_e and n_h:



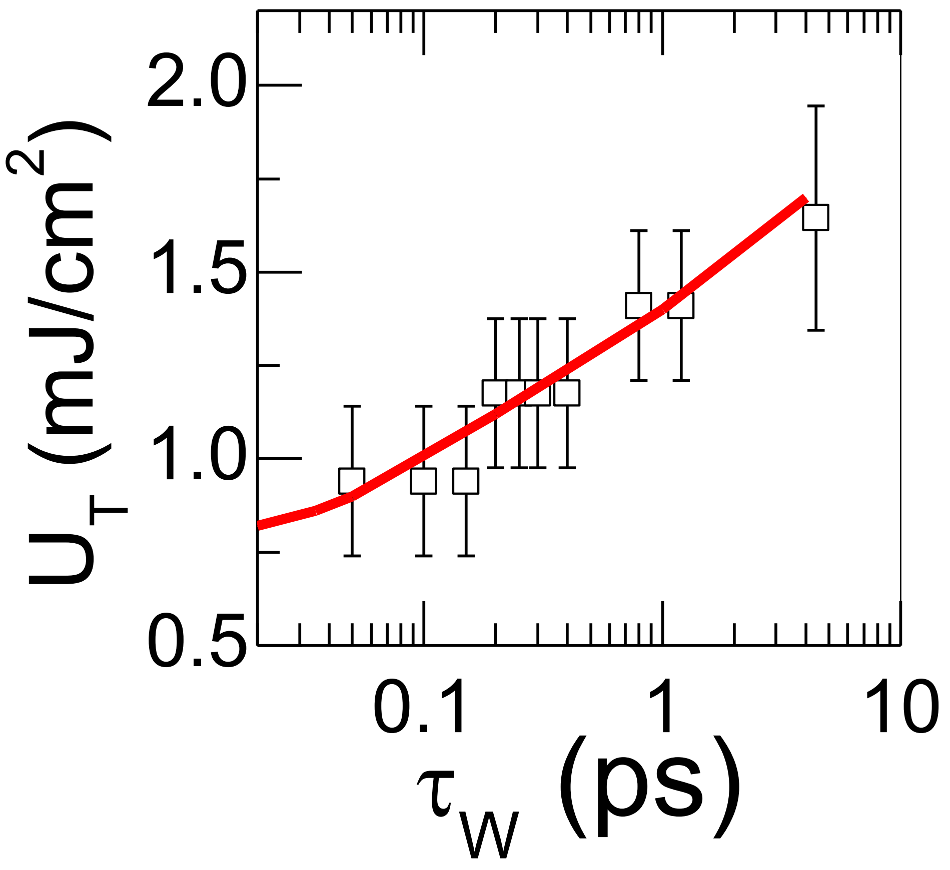
System trajectory (parametric plot)





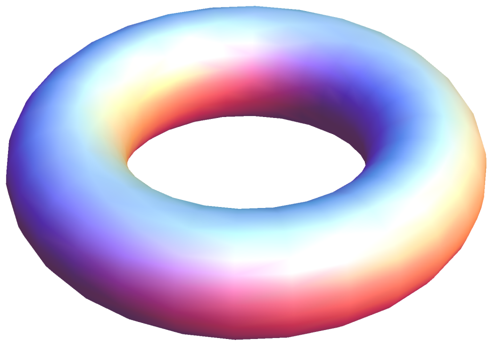
L Stojchevska et al. Science 2014;344:177-180

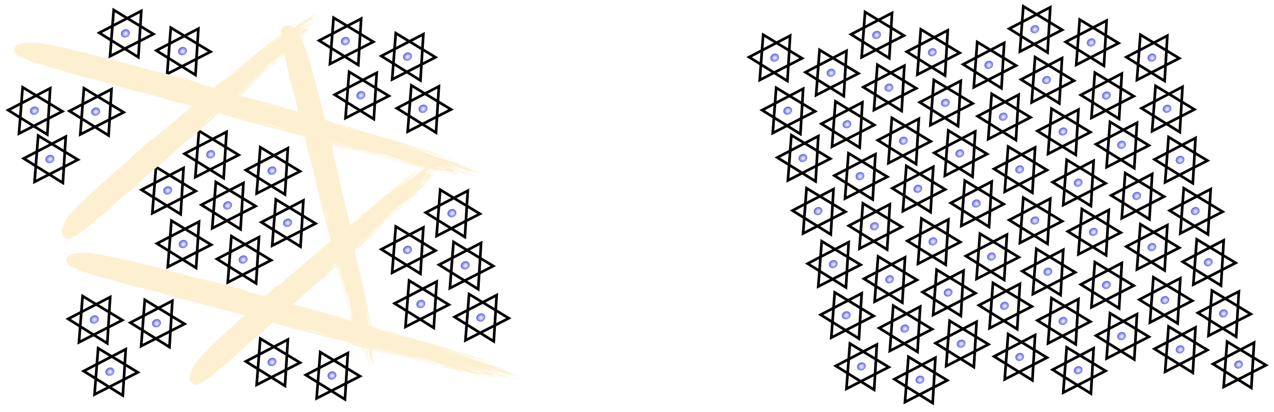
The predicted short pulse switching threshold:

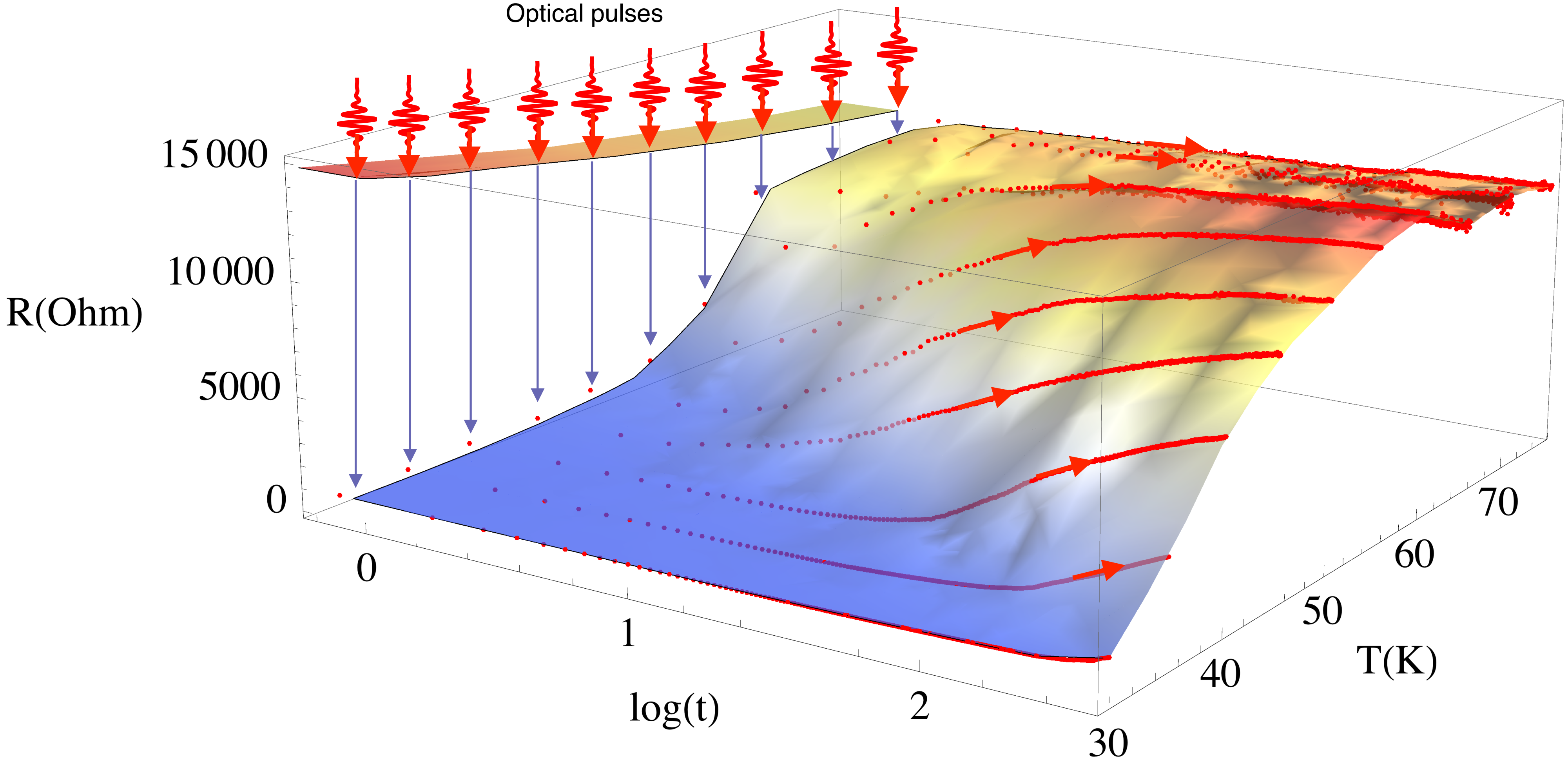


H state relaxation in *1T*-TaS$_2$

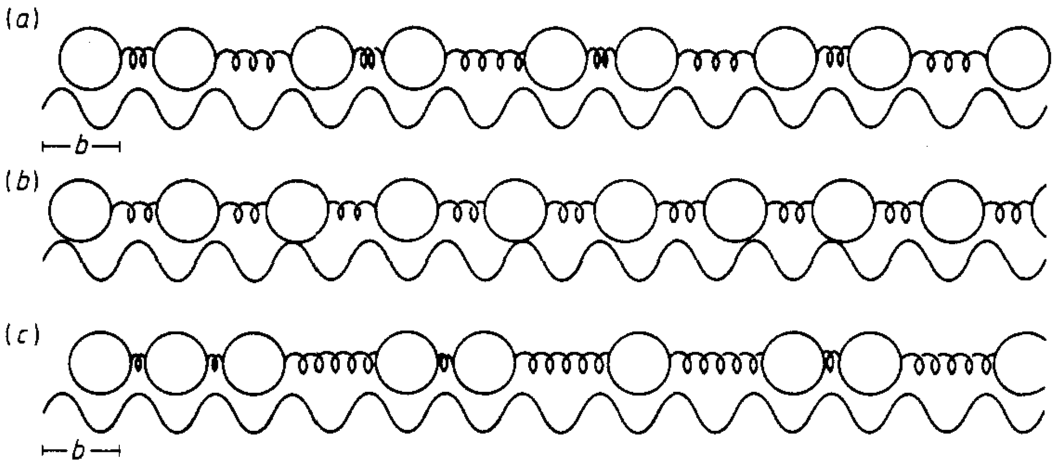
Incommensurate → commensurate Relaxation







Incommensurate → commensurate Relaxation



Commensurate

Incommensurate

Chaotic

Frank and Van der Merwe model (1949):

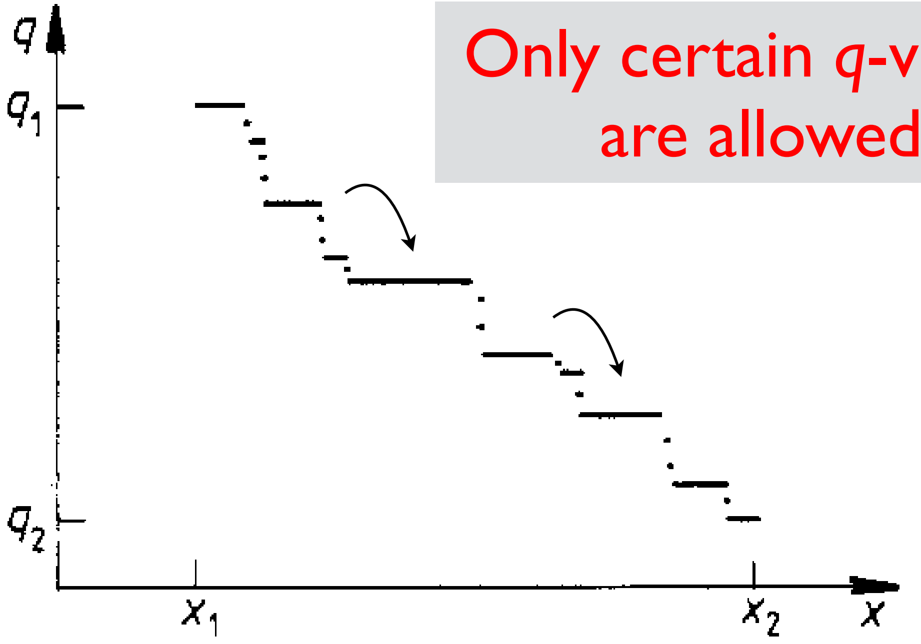
$$H = \int \left[\frac{1}{2} \left(\frac{\mathrm{d}\varphi}{\mathrm{d}n} - \delta \right)^2 + V(1 - \cos p\varphi) \right] \mathrm{d}n$$

x_n is the position of the nth atom:

$$x_n = nb + \frac{b}{2\pi} \varphi_n$$

In the continuum limit: $\varphi_n - \varphi_{n-1} = \mathrm{d}\varphi / \mathrm{d}n$

A devil's staircase

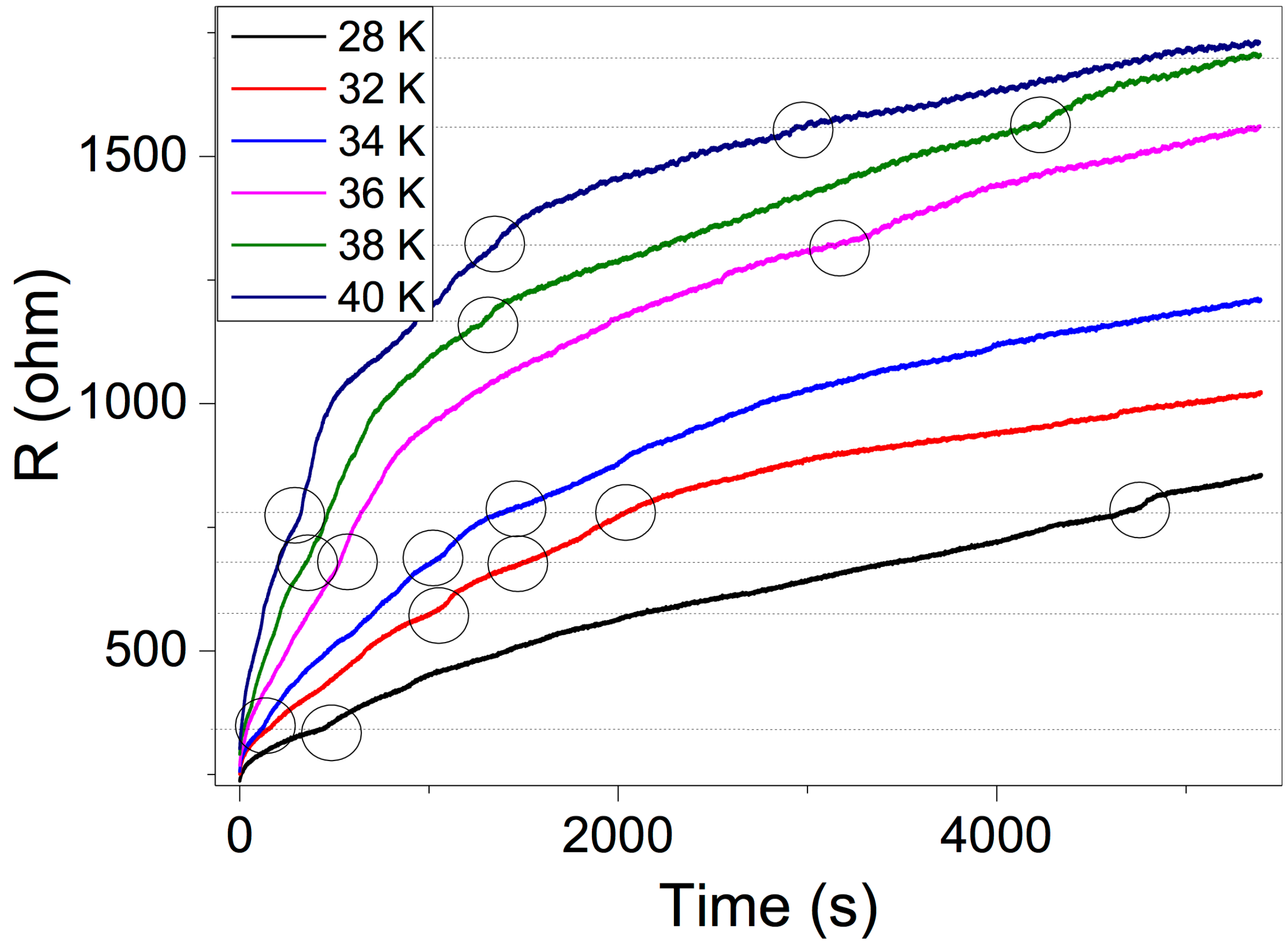


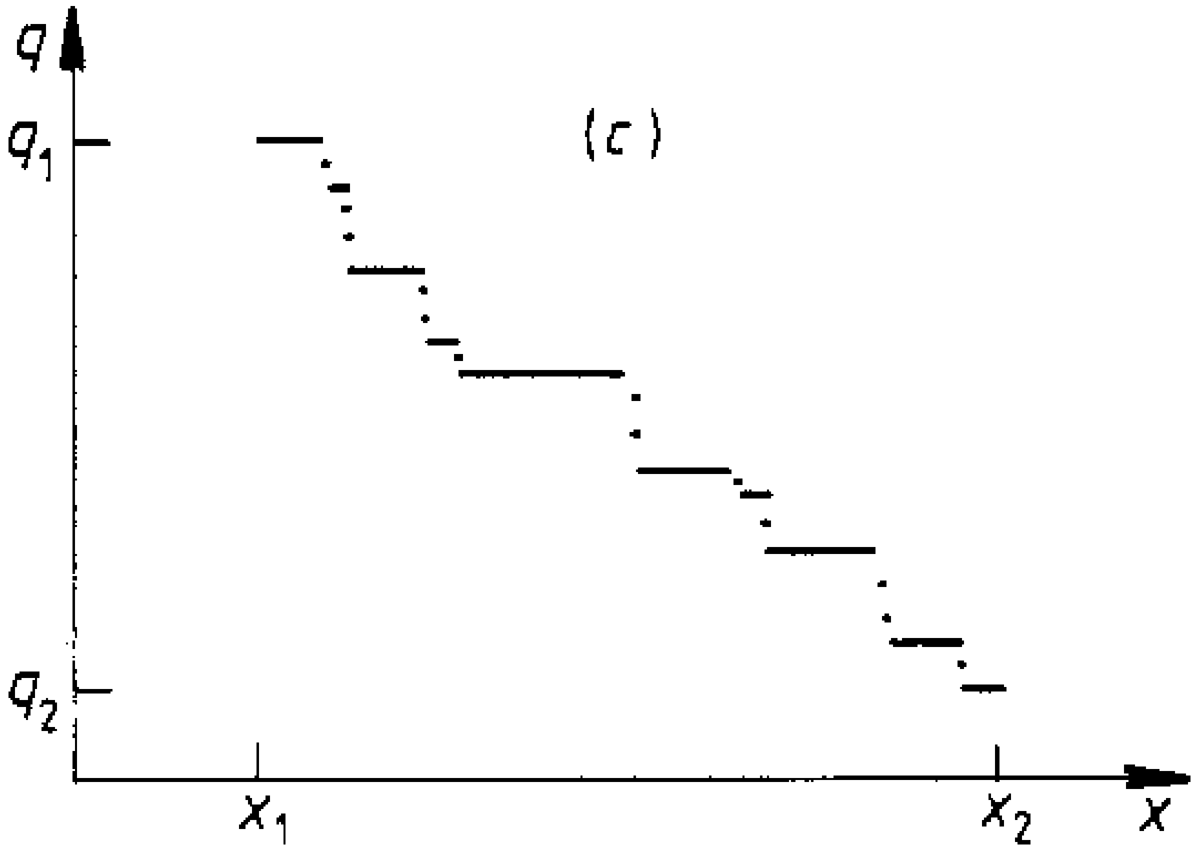
Only certain *q*-values are allowed

time

Per Bak, Rep Prog Phys **45**, 587–629 (1982).

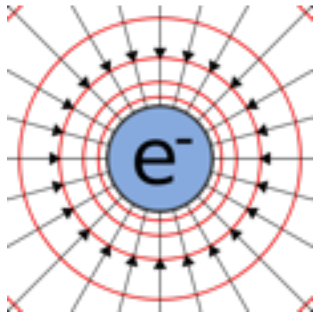
Evidence for a Devil's staircase relaxation processs





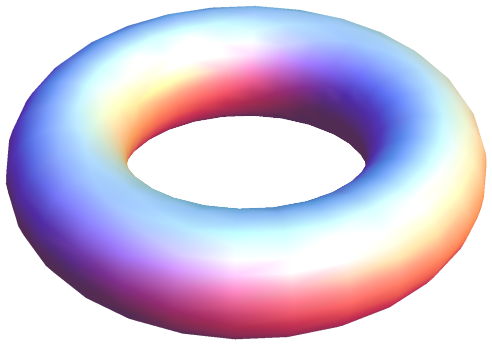
time

Memory: Spin or charge?



- Spins are <u>weakly coupled</u> to the environment, whence they hold information
- But, for the same reason, it is both **hard** and (usually) **slow** to write information.
- It is relatively easy to write information into charge ordered systems (charge is coupled strongly to light)
- Charge is also strongly coupled to the lattice, whence any information is rapidly dissipated (ps)

If charge order could be topologically stabilised, we have a winning combination!




Pat. appl. 022-P329/12, PCT 2013, UK patent 2014