Structural dynamics in atomic wire systems at surfaces studied by ultrafast-electron diffraction: Excitation, metastable states and relaxation

T. Frigge, B. Hafke, T. Witte, B. Krenzer, C. Brand, J. Fortmann, T. Groven, M. Tajik, D. Janoschka, P. Dreher, F.J. Meyer zu Heringdorf, C. Streubühr, A. Samad Syed, V. Mikšić Trontl, I. Avigo, P. Zhou, M. Ligges, D. von der Linde, U. Bovensiepen, S. Wippermann[1)], A. Lücke[2)], S. Sanna[2)], U. Gerstmann[2)], W. G. Schmidt[2)],
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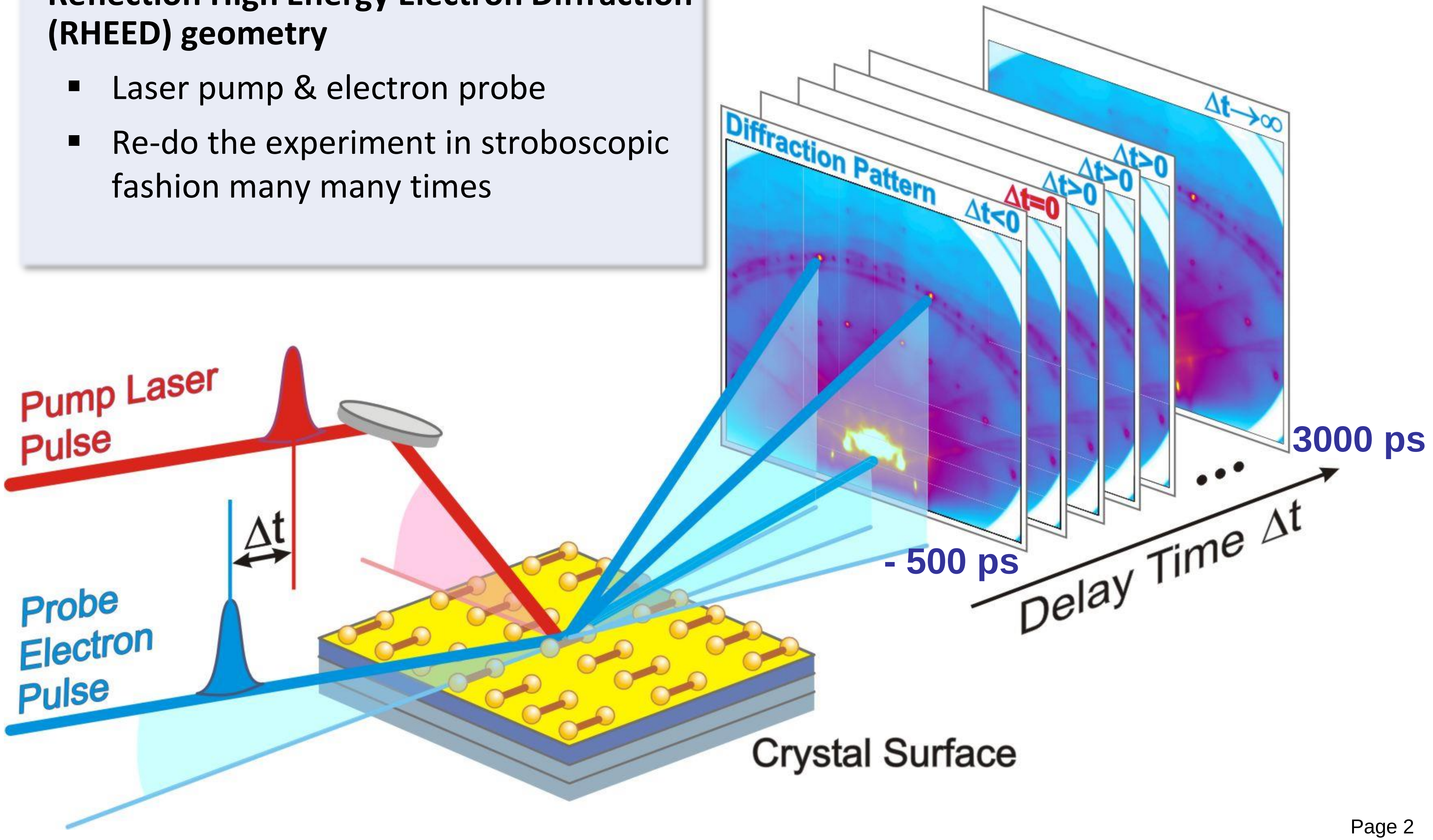
[1)] MPI Eisenforschung, Düsseldorf, Germany
[2)] University of Paderborn, Germany

TR-RHEED in pump-probe setup

Time resolved diffraction at surfaces in Reflection High Energy Electron Diffraction (RHEED) geometry

- Laser pump & electron probe
- Re-do the experiment in stroboscopic fashion many many times



Surface sensitivity with electrons

Electron scattering cross section $10^4 \ldots 10^6$ larger than x-ray

- dominant multiple scattering

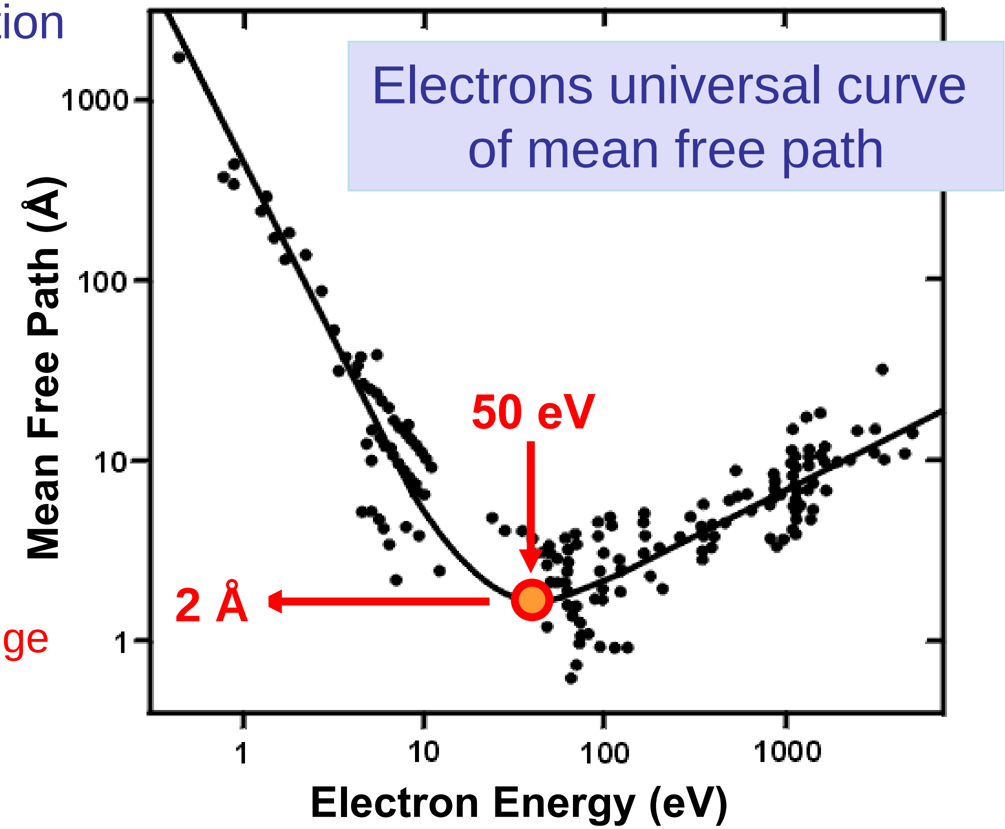
=> no simple IV-analysis

LEED

- extrem surface sensitivity
- normal incidence
- no distortion of pattern
- miniaturize setup to avoid huge temporal broadening of ns

Science **345**, 200 (2014)
M.Gulde, S. Schäfer, C. Ropers

Nature Physics **14**, 184 (2018)
S. Vogelgesang, G. Storeck, J.G. Horstmann, T. Diekmann, M. Sivis, S. Schramm, K. Rossnagel, S. Schäfer, C. Ropers



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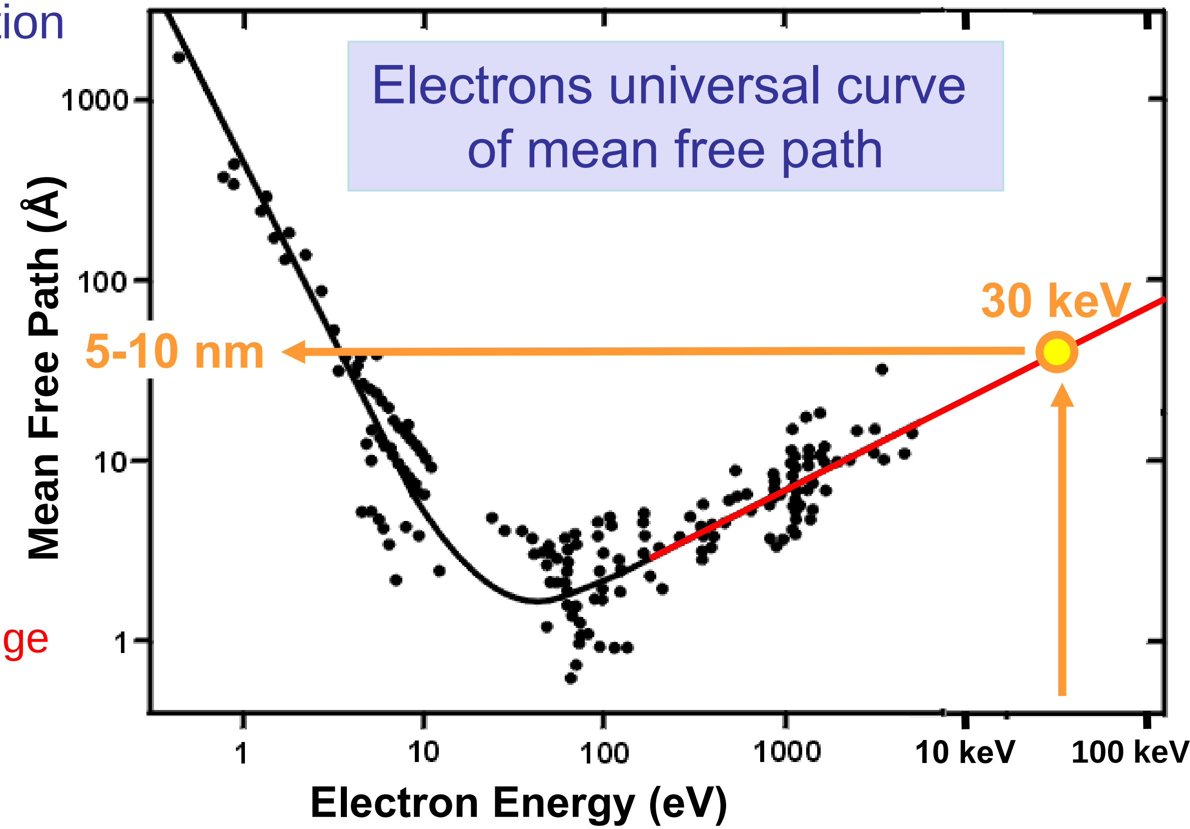
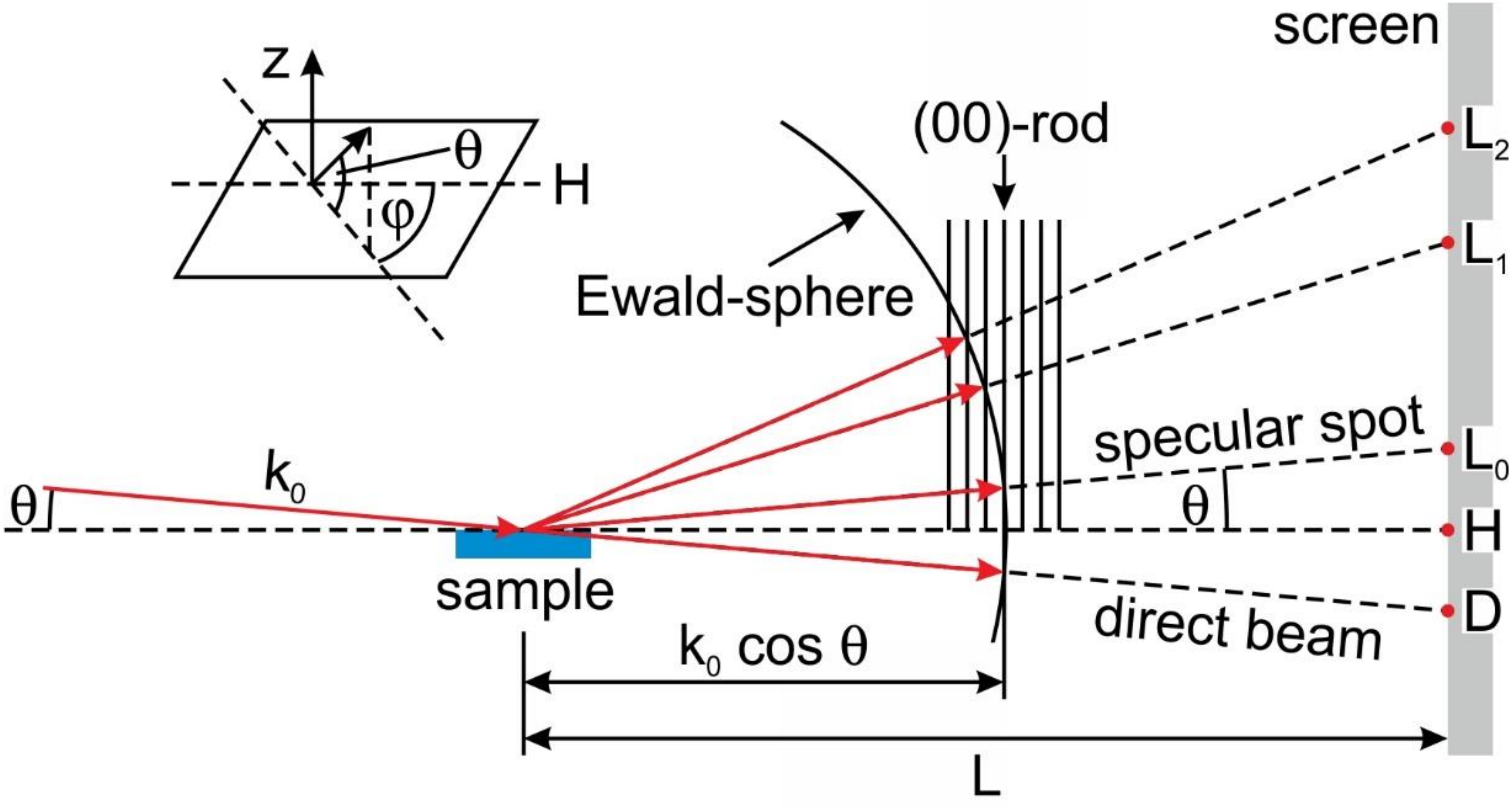


=> RHEED @ 30 keV

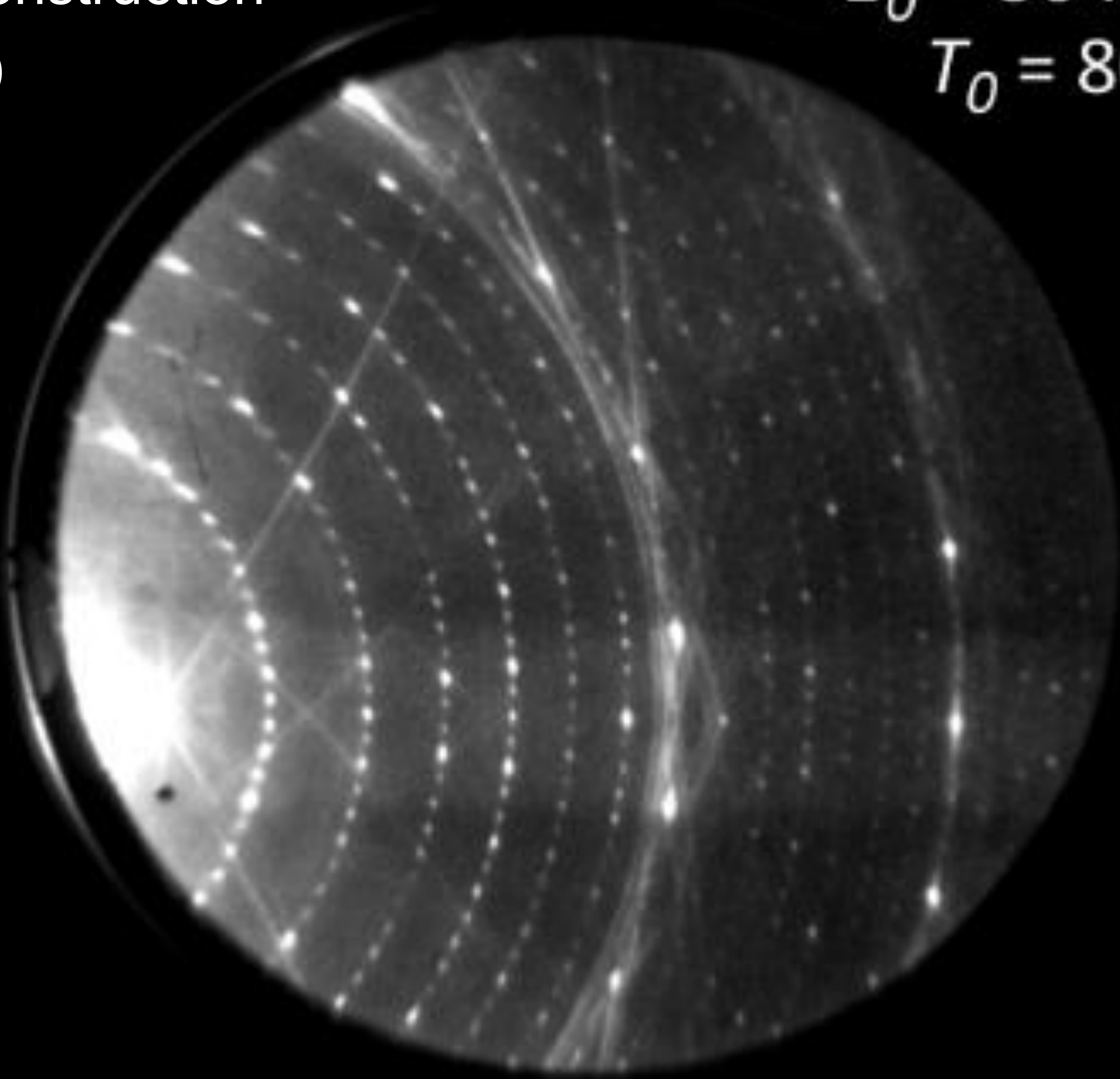
- minimum temporal broadening < ps
- grazing incidence 2° – 6° for surface sensitivity
- distortion of pattern

Curved Ewald sphere !



Curved Ewlad sphere !

(7x7) reconstruction of Si(111)



Experimental setup: 1st generation

fs Laser Pulses

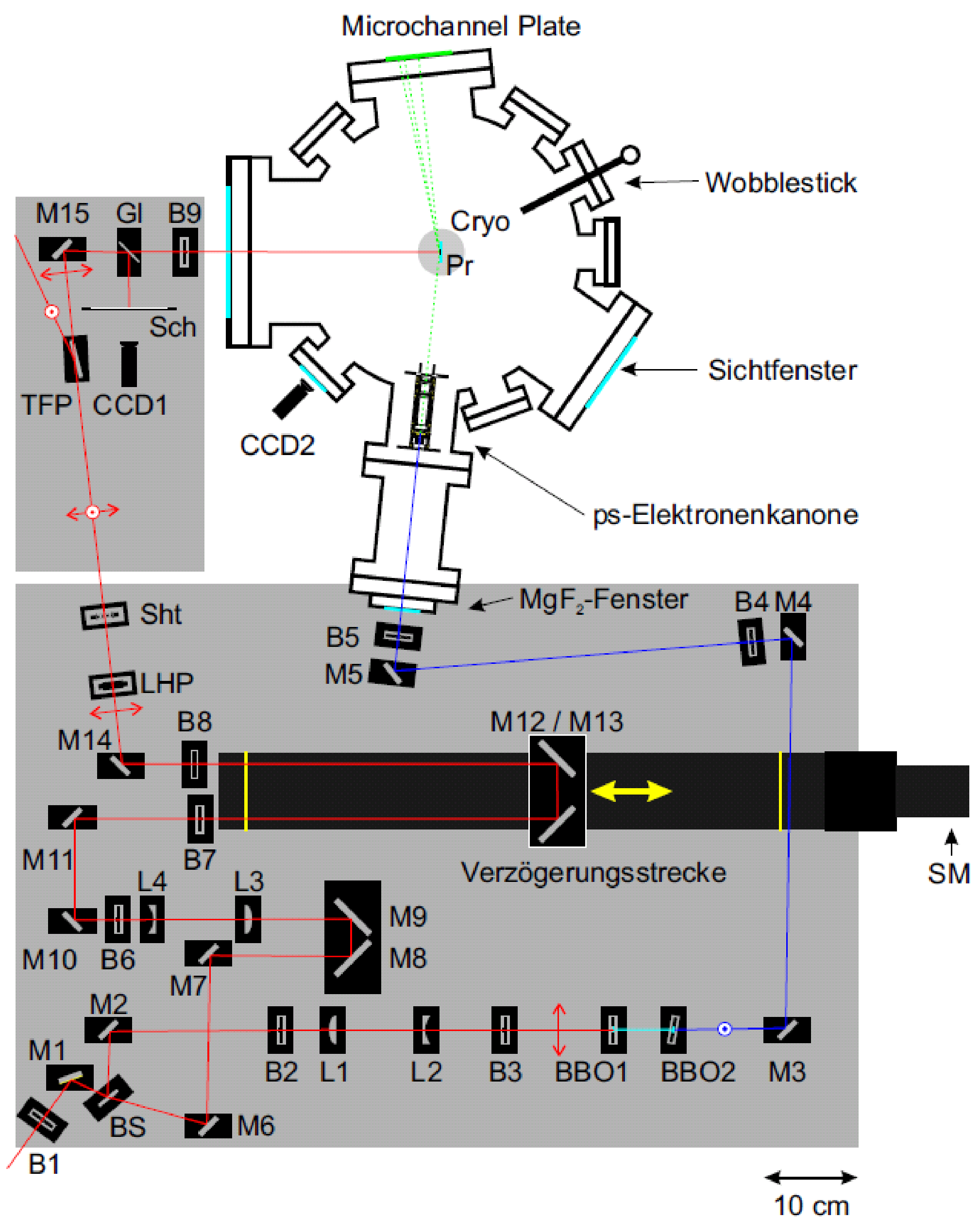
- Ti-Saphire amplifier system
- λ = 800 nm, $\hbar\omega$ = 1.55 eV
- 80 fs, 1 mJ per pulse @ 5 kHz
- fluence of up to 15 mJ/cm^2

UHV-System

- pressure p = 1 x 10^{-10} mbar
- sample 30 K – 1200 °C
- in-situ deposition of In, Bi, Pb …

e-Diffraction

- RHEED 7 – 30 keV
- grazing incidence 2°- 6°
- vertical momentum transfer $\Delta k_\perp$ = 4 - 20 Å^{-1} => significant Debye-Waller effect
- reversible surface / film system => robust systems without radiation damage! More than 10^7 laserpulses per experiment



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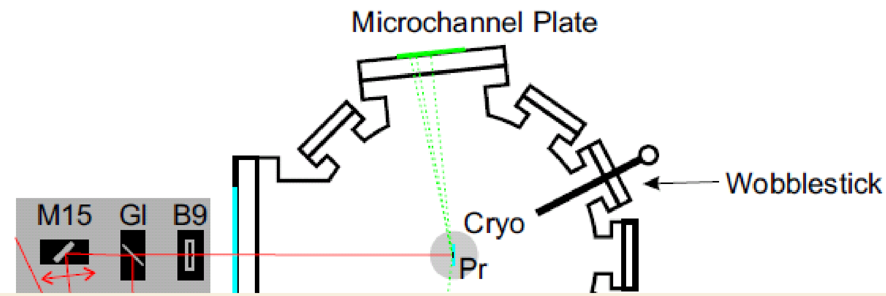
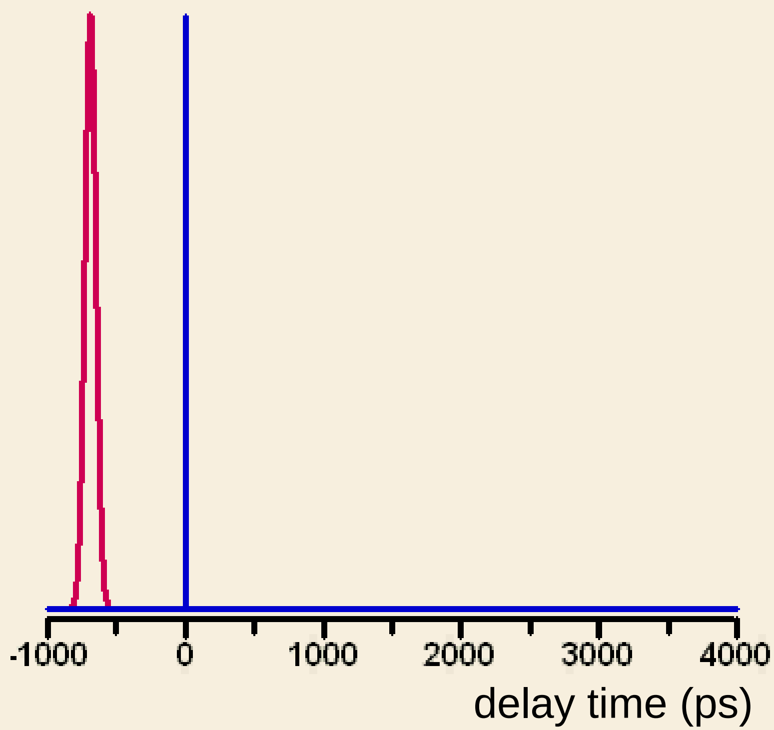
Transient Changes of Pattern

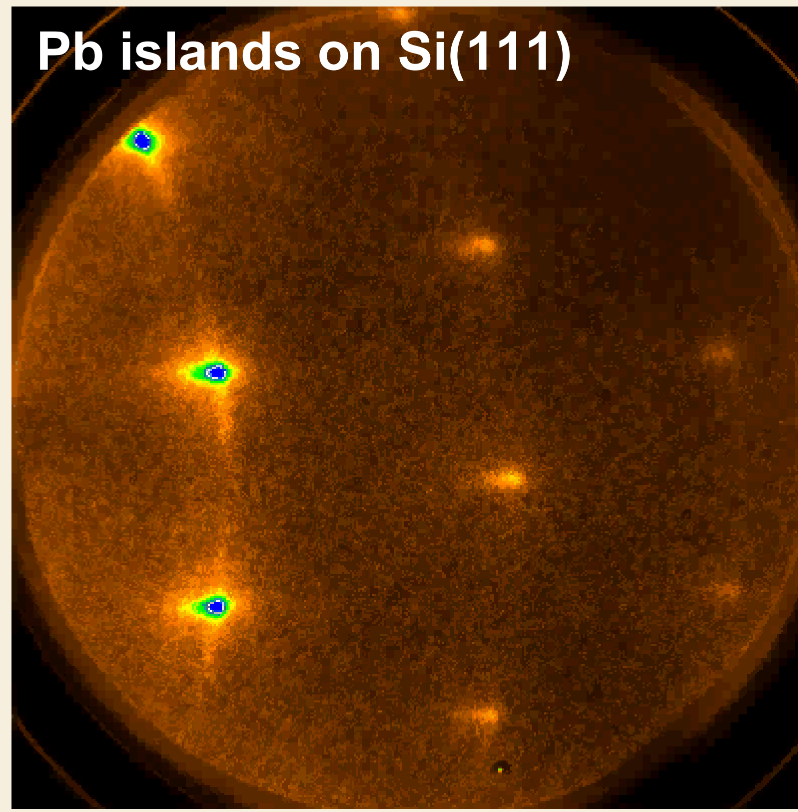
fs Laser Pulses

- Ti-Saphire amplifier system
- λ = 800 nm, ħω = 1.55 eV
- 80 fs, 1 mJ per pulse @ 5 kHz
- Fluence of up to 15 mJ/cm²

per experiment







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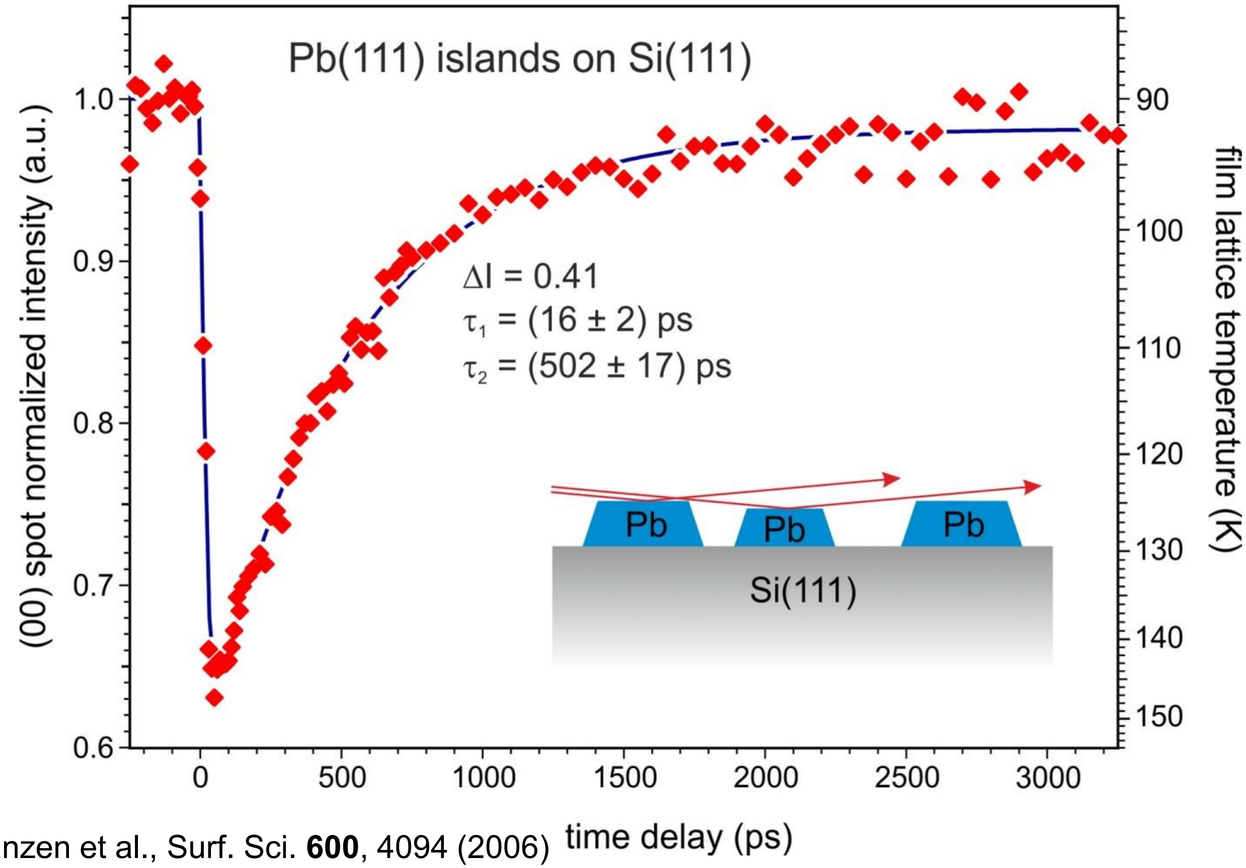
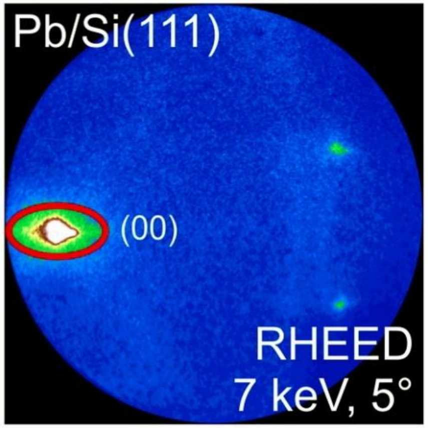
Debye Waller effect $I/I_0 = \exp -{}^1/_3\langle u^2k^2\rangle$

Cooling on the Nanoscale: 6 nm thick Pb(111) islands on Si(111)

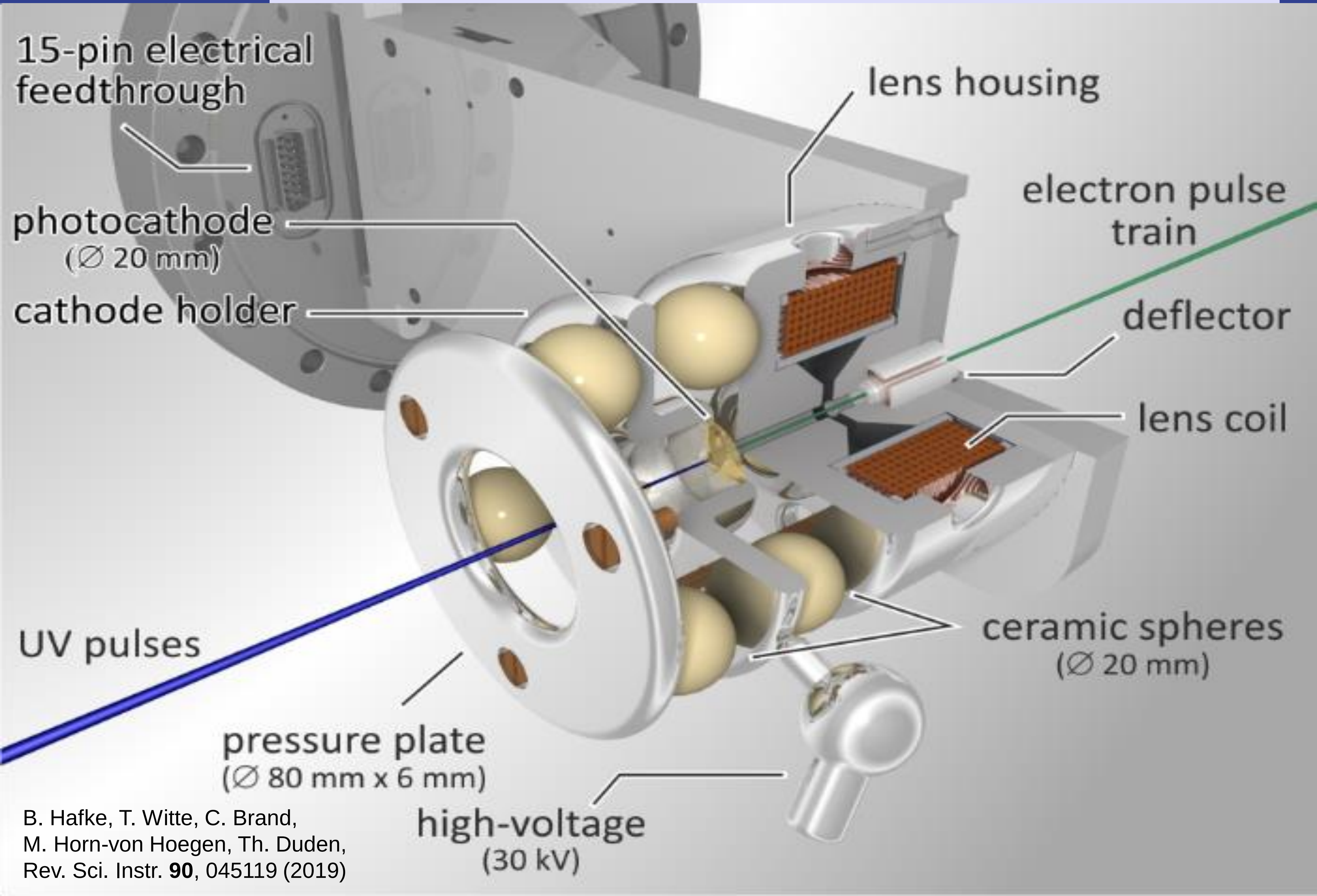
Dominated by total internal reflection of phonons at Pb/Si interface: **„heat is trapped in film“**





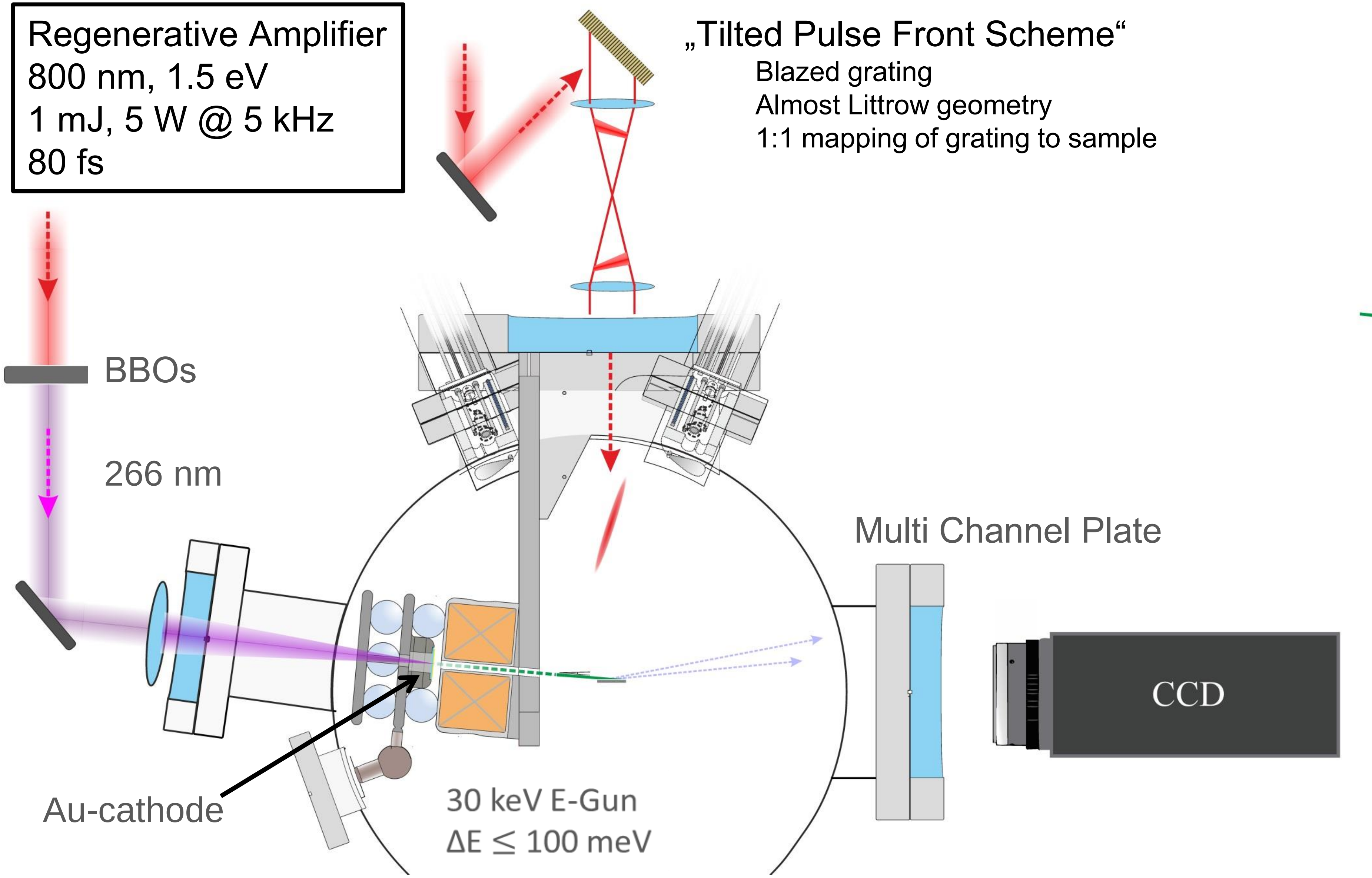
A. Janzen et al., Surf. Sci. **600**, 4094 (2006)
B. Krenzer, A. Janzen, M. Horn-von Hoegen et al., New J. Phys. **8**, 190 (2006)
A. Hanisch, B. Krenzer, T. Pelka, S. Möllenbeck and M. Horn-von Hoegen, Phys. Rev. B **77**, 125410 (2008)
B. Krenzer, A. Hanisch-Blicharski, …, R. Meyer, M. Horn-von Hoegen, Phys. Rev. B **80**, 024307 (2009)
T. Witte, T. Frigge, B. Hafke, B. Krenzer, and M. Horn-von Hoegen, Appl. Phys. Lett. **110** (2017) 243103
A. Hanisch-Blicharski et al., Nano Letters **21**, 7145 (2021)

Ultrafast fs-RHEED: 3rd generation



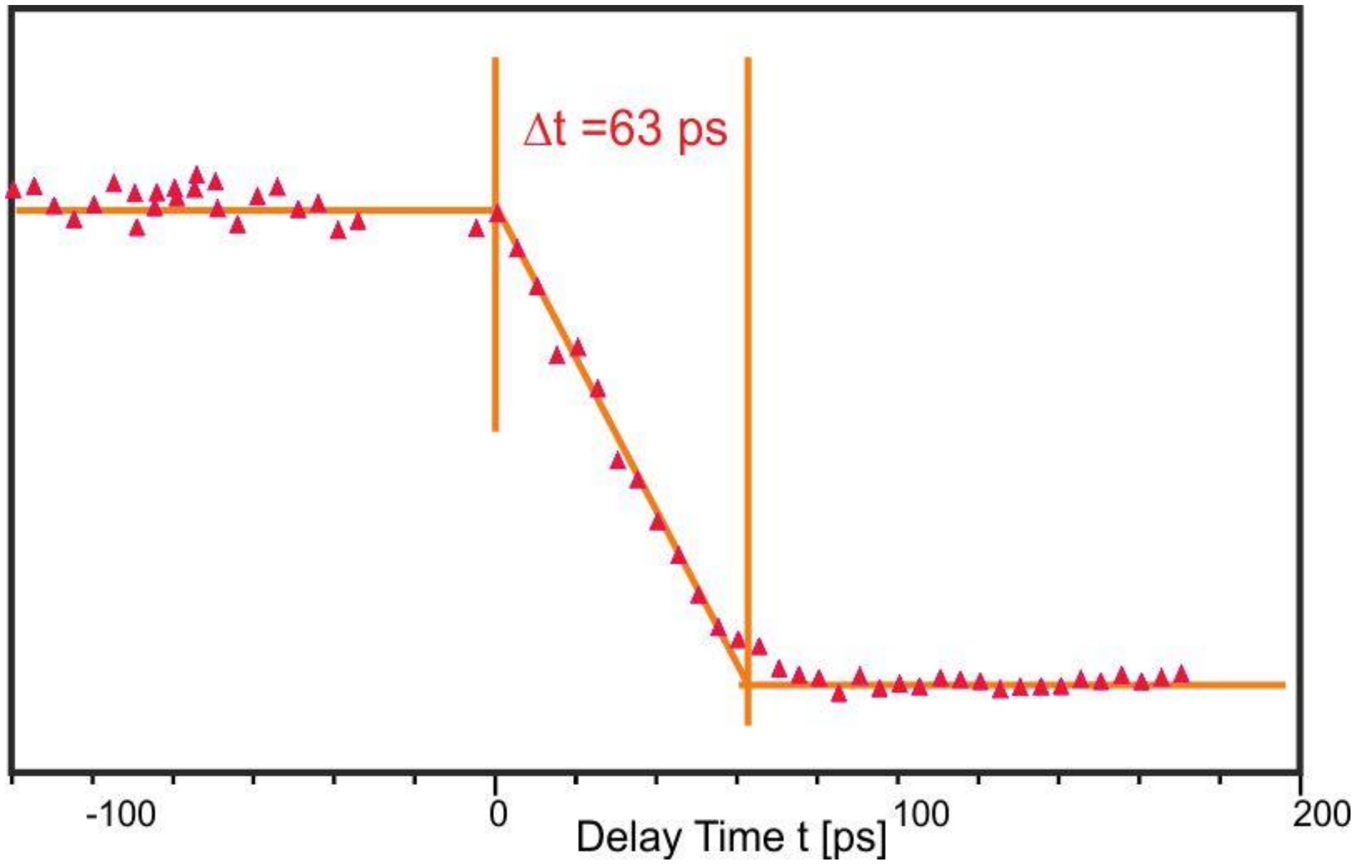
B. Hafke, T. Witte, C. Brand,
M. Horn-von Hoegen, Th. Duden,
Rev. Sci. Instr. **90**, 045119 (2019)

Ultrafast fs-RHEED: 3rd generation



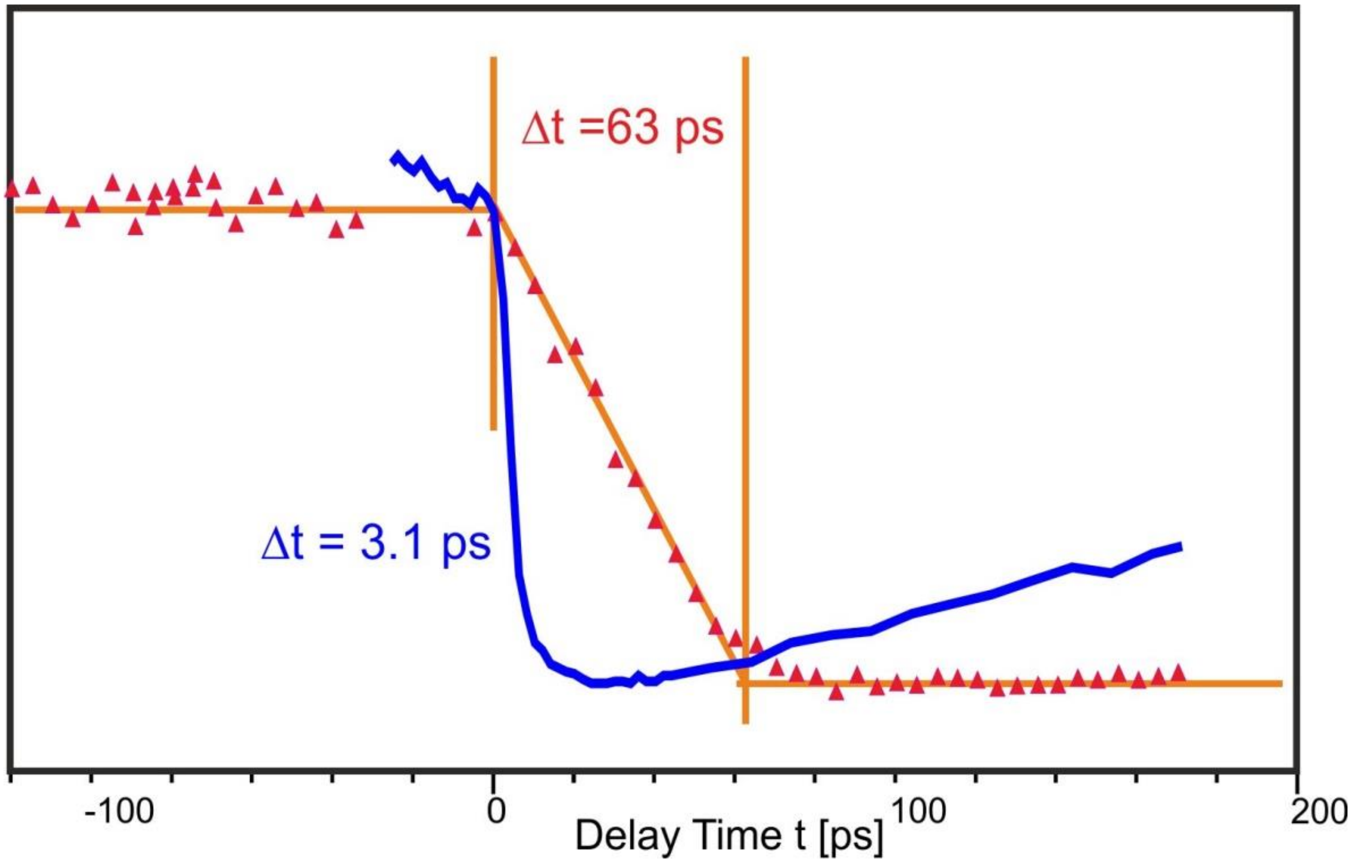
2005: ... fast at 60 ps!

Heating of Bi(111) Film on Si(111) @ 80 K



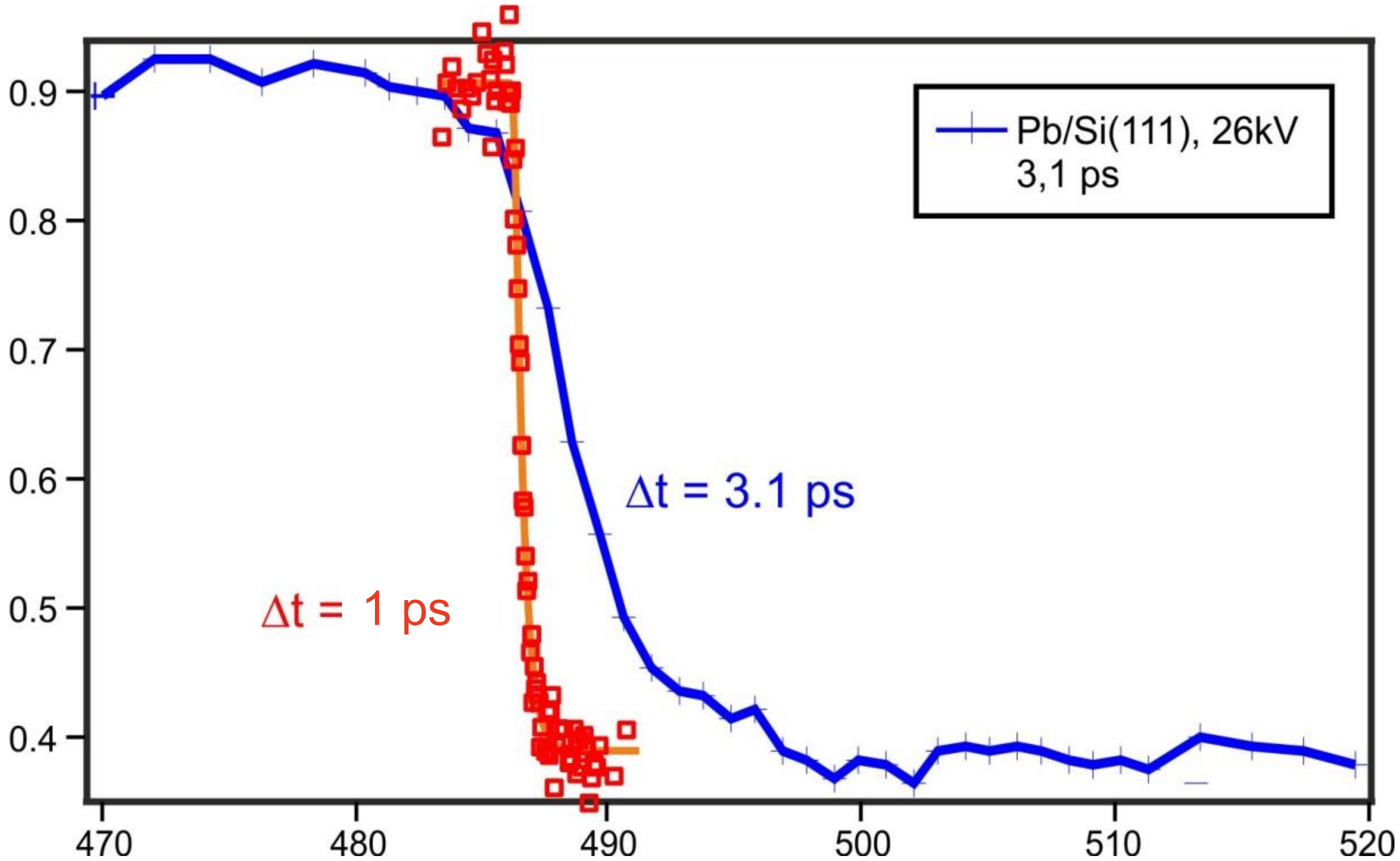
2011: … 20 x faster: 3 ps!

Pb islands on Si(111) @ 80 K …

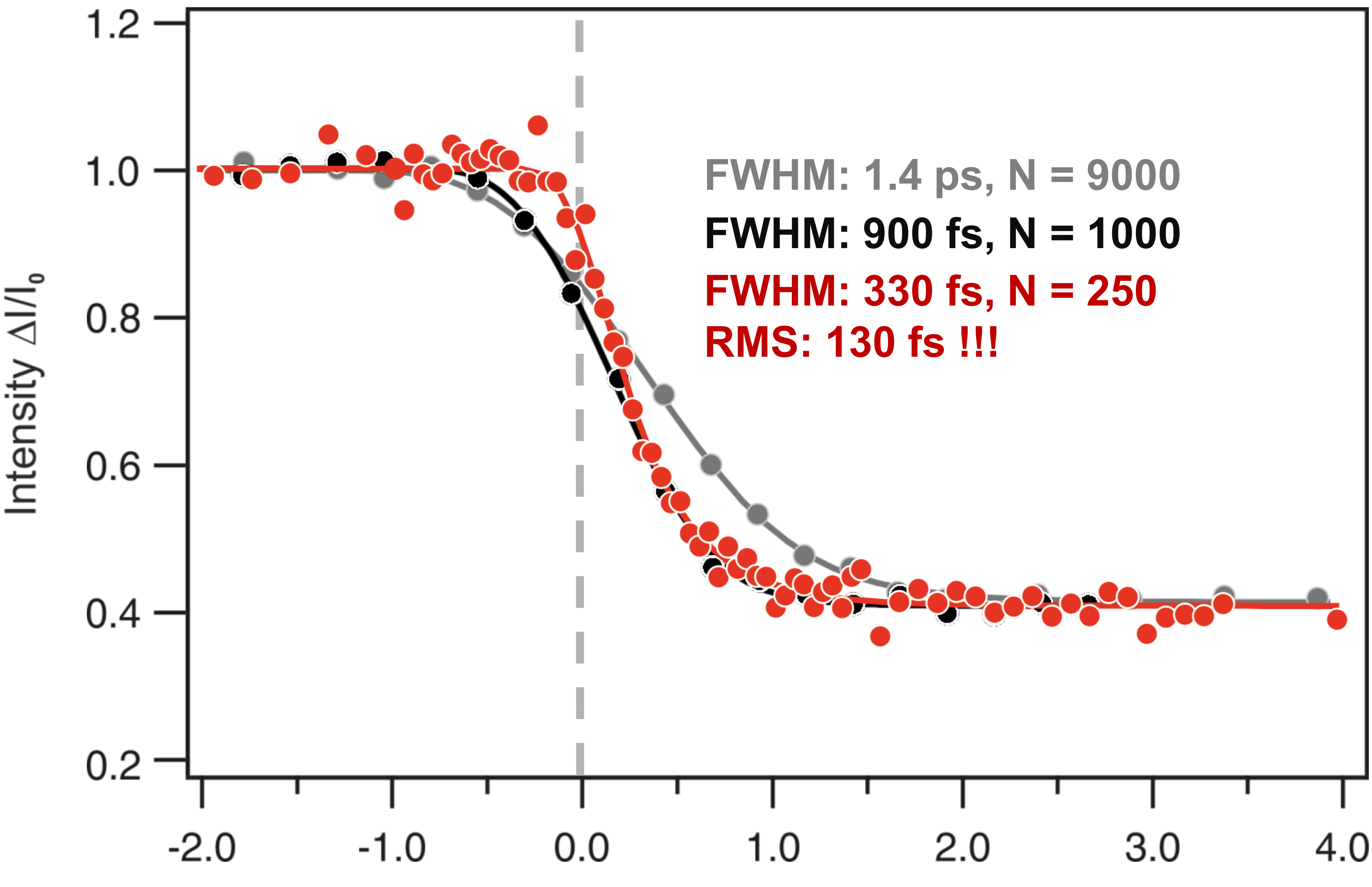


2014: … 50 x faster: ~ 1ps

In on Si(111) @ 30 K …

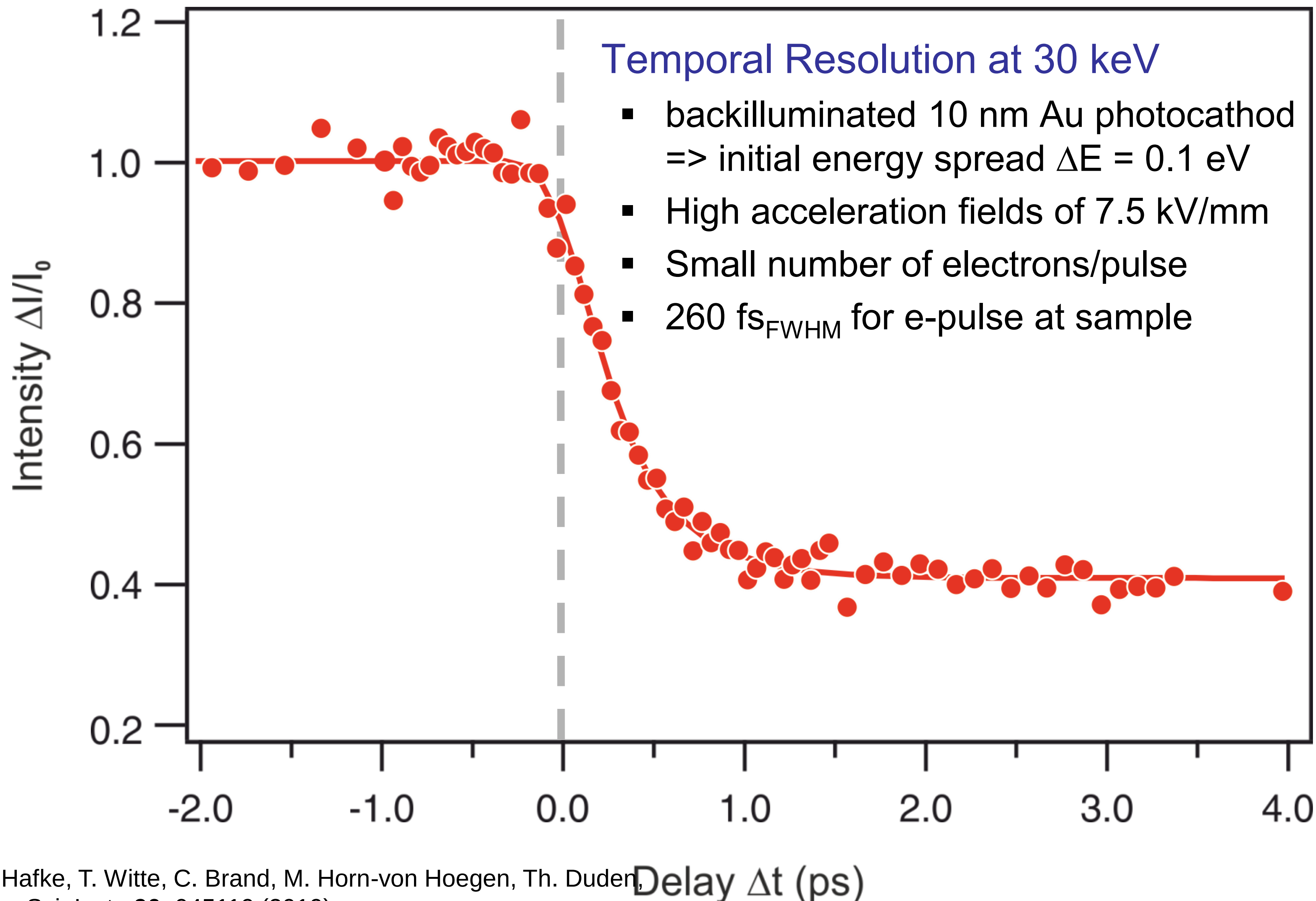


Ultimate Temporal Resolution !



B. Hafke, T. Witte, C. Brand, M. Horn-von Hoegen, Th. Duden,
Rev. Sci. Instr. **90**, 045119 (2019)

Ultimate Temporal Resolution



B. Hafke, T. Witte, C. Brand, M. Horn-von Hoegen, Th. Duden,
Rev. Sci. Instr. **90**, 045119 (2019)

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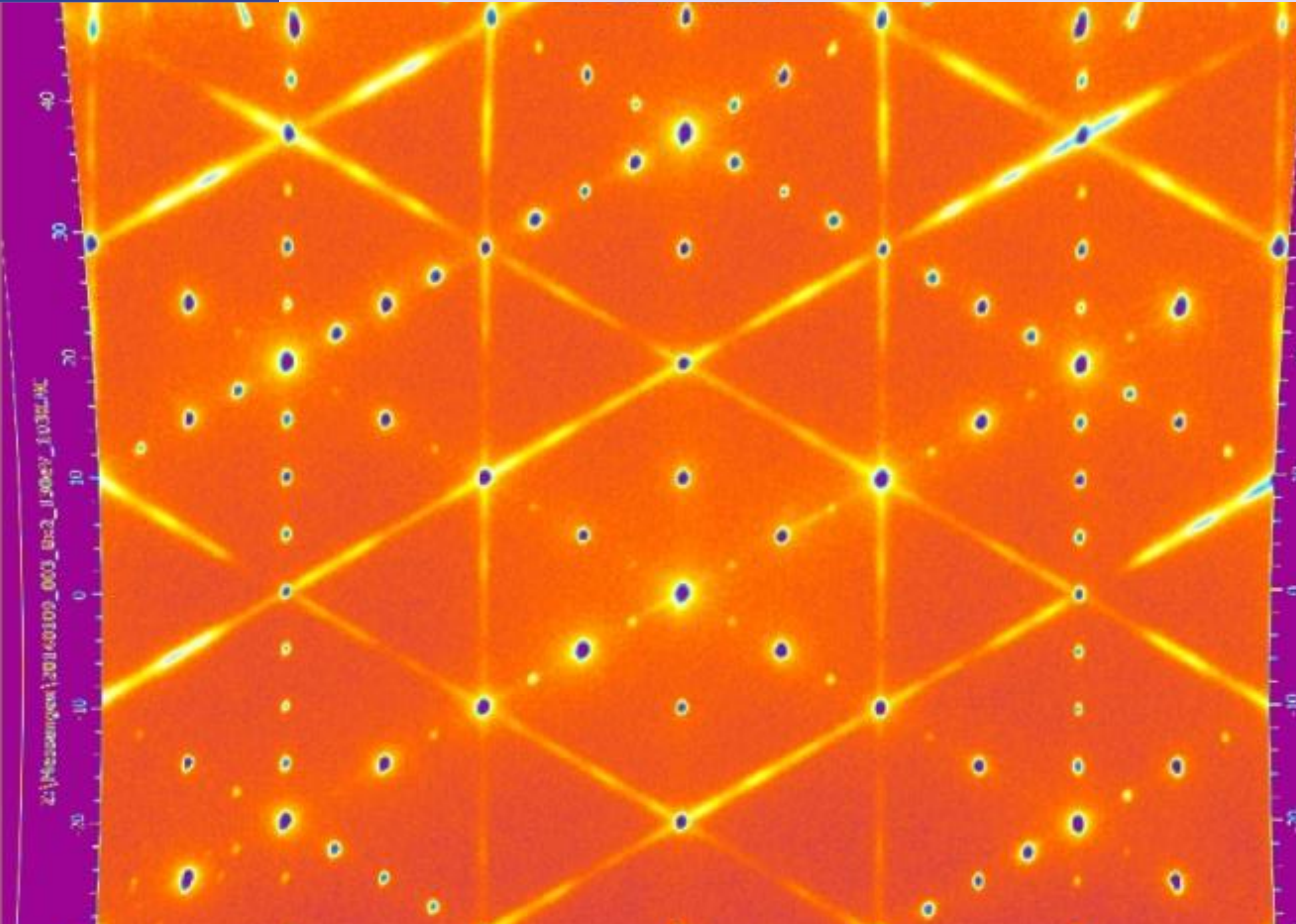
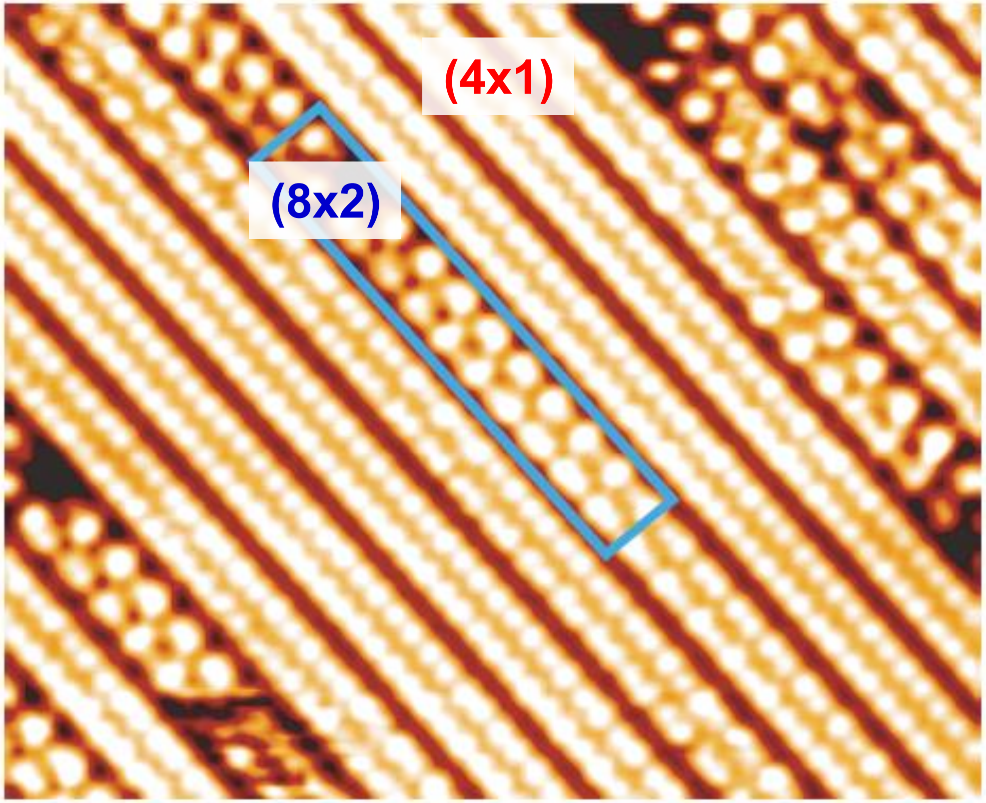
Si(111)-In(8x2) – ground state

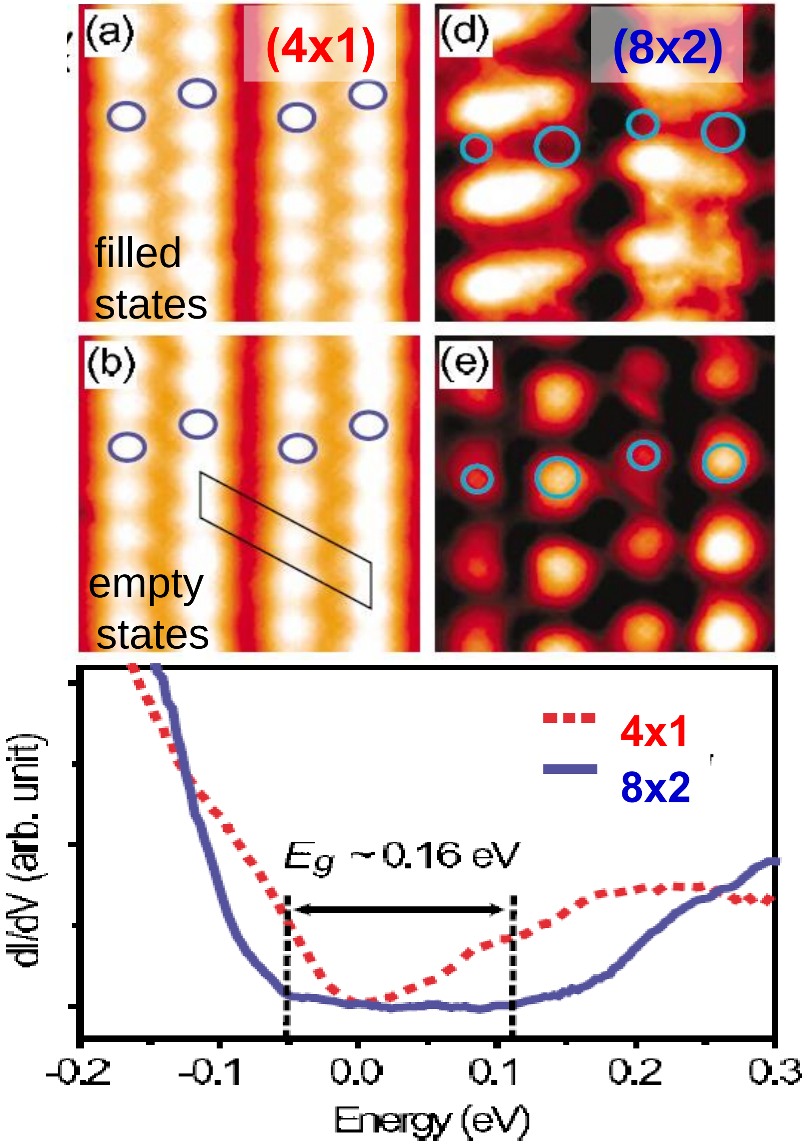


Bernd Hafke – SPA-LEED pattern@150.4 eV

Si(111)-In(8x2)↔(4x1)



S. J. Park, **H.W. Yeom**, S. H. Min, D.H. Park, and I.-W. Lyo, Phys. Rev. Lett. **93**, 106402 (2004)



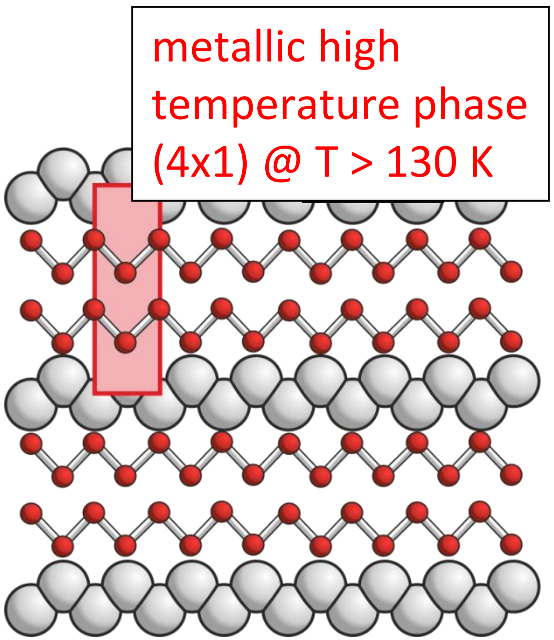
Prototypical atomic wire system:

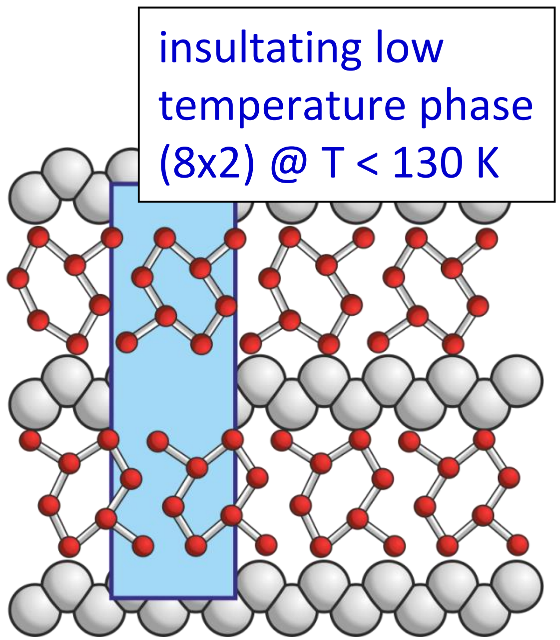
- metal-insulator transition
- opening of 0.16 eV bandgap
- symmetry breaking

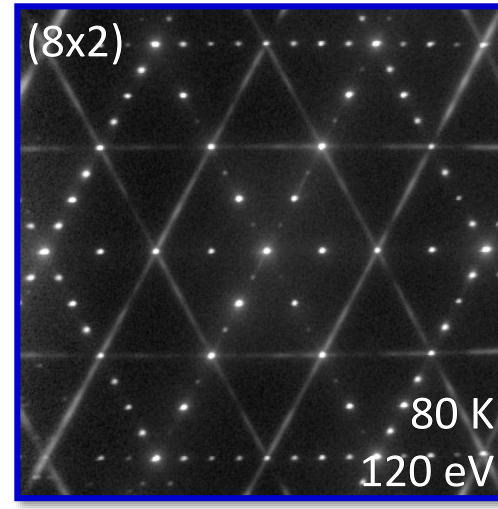
Phase transition of In/Si(111)

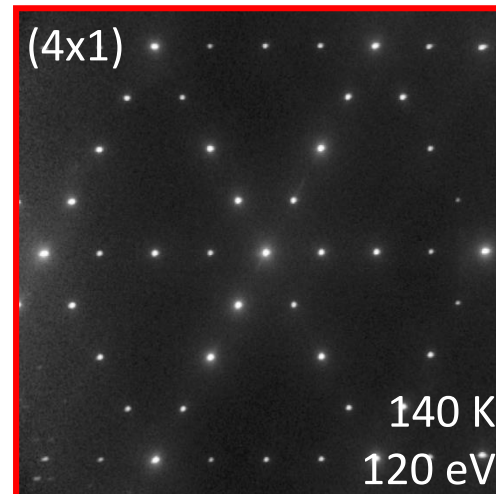
In(4x1)/Si(111) – a quasi 1D atomic wire system

Below T_c ~ 130 K phase transition into (8x2):
insulating phase, periodicity doubling,
formation of charge density wave







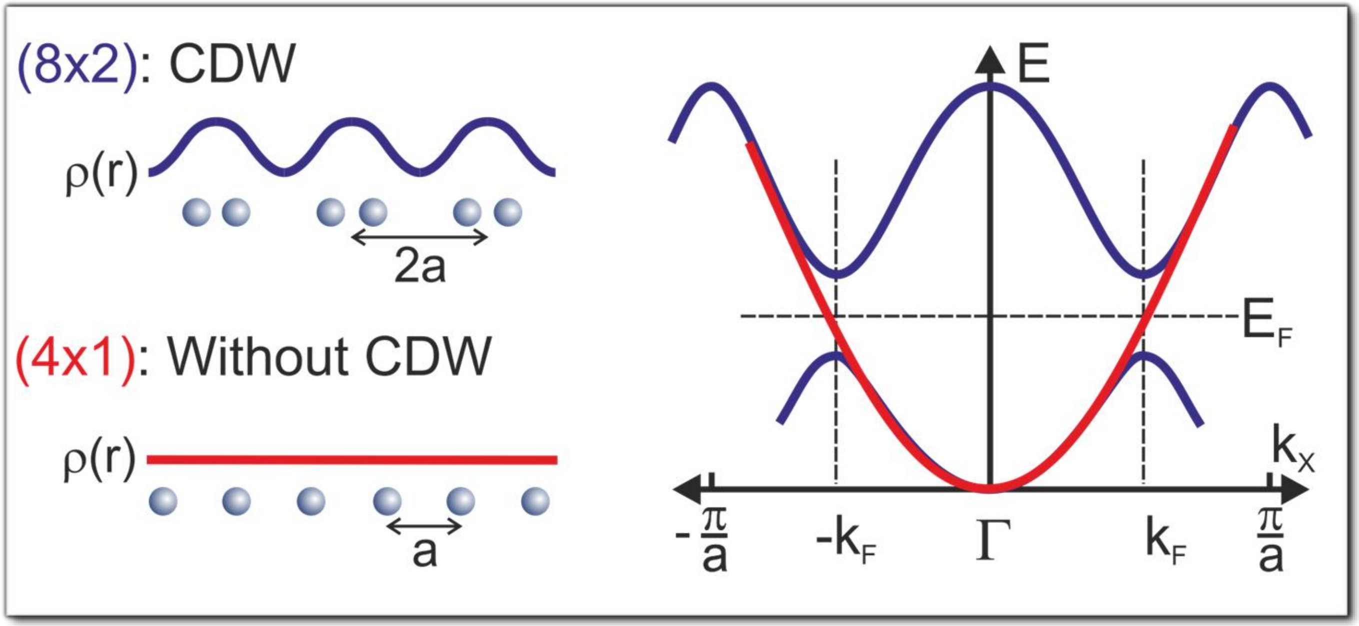


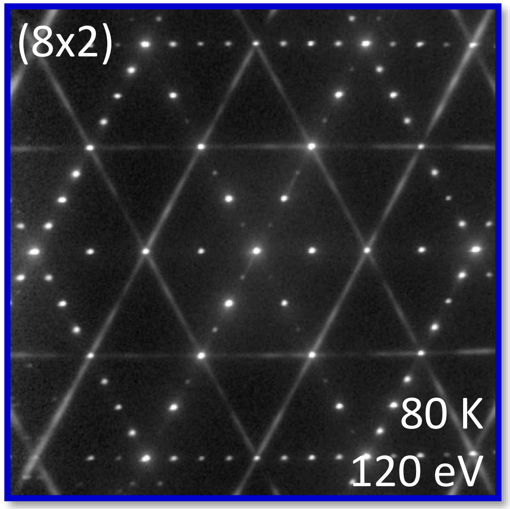
H. W. Yeom, S. Takeda, E. Rotenberg, I. Matsuda, K. Horikoshi, J. Schaefer, C. M. Lee, S. D. Kevan, T. Ohta, T. Nagao, S. Hasegawa, Phys. Rev. Lett. **82**, 4898 (1999),
S.V. Ryjkov, et al., Surf. Sci. **488**, 15 (2001).

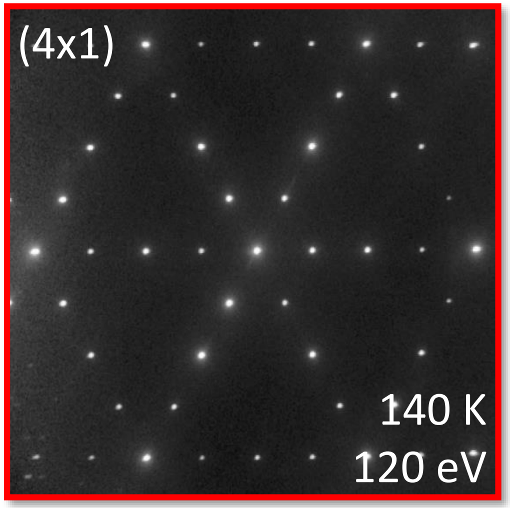
G. Falkenberg, R.L. Johnson, R. Feidenhans'l et al., Phys. Rev. B **59** 12228 (1999)

C. Kumpf, O. Bunk, J.H. Zeysing, Y. Su, M. Nielsen, R.L. Johnson, R. Feidenhans'l, K. Bechgaard, Phys. Rev. Lett. **85**, 4916 (2000)

Peierls like structural instability

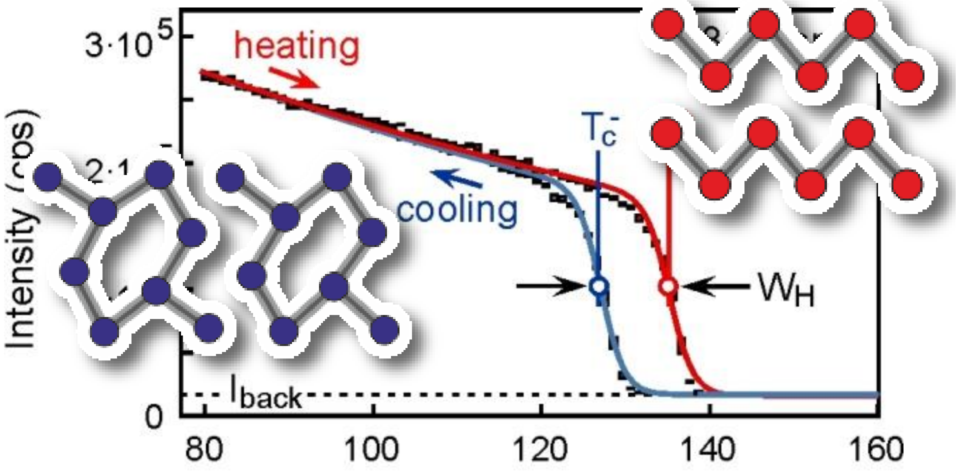


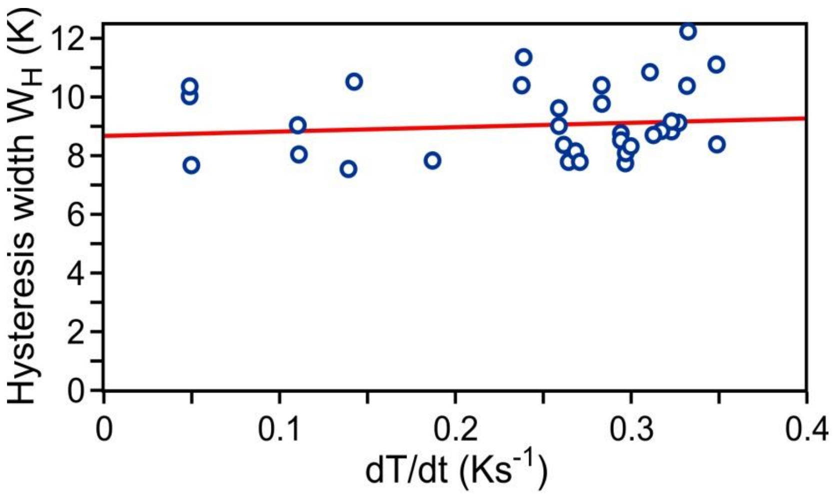


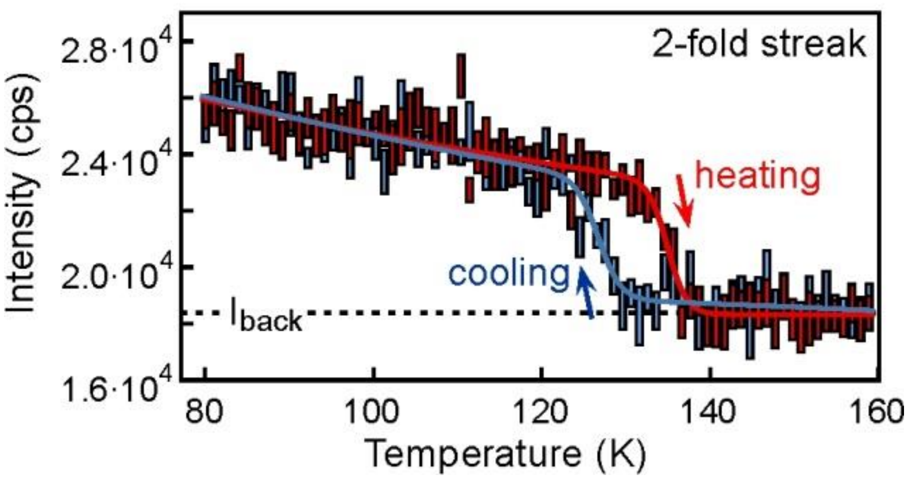


1st order transition

- Phase transition temperature T_c = 130 K
- Robust hysteresis of width W_H = 10 K
- Proof of **1st order** transition
  => Peierls like distortion [*]
  => **not** order-disorder transition



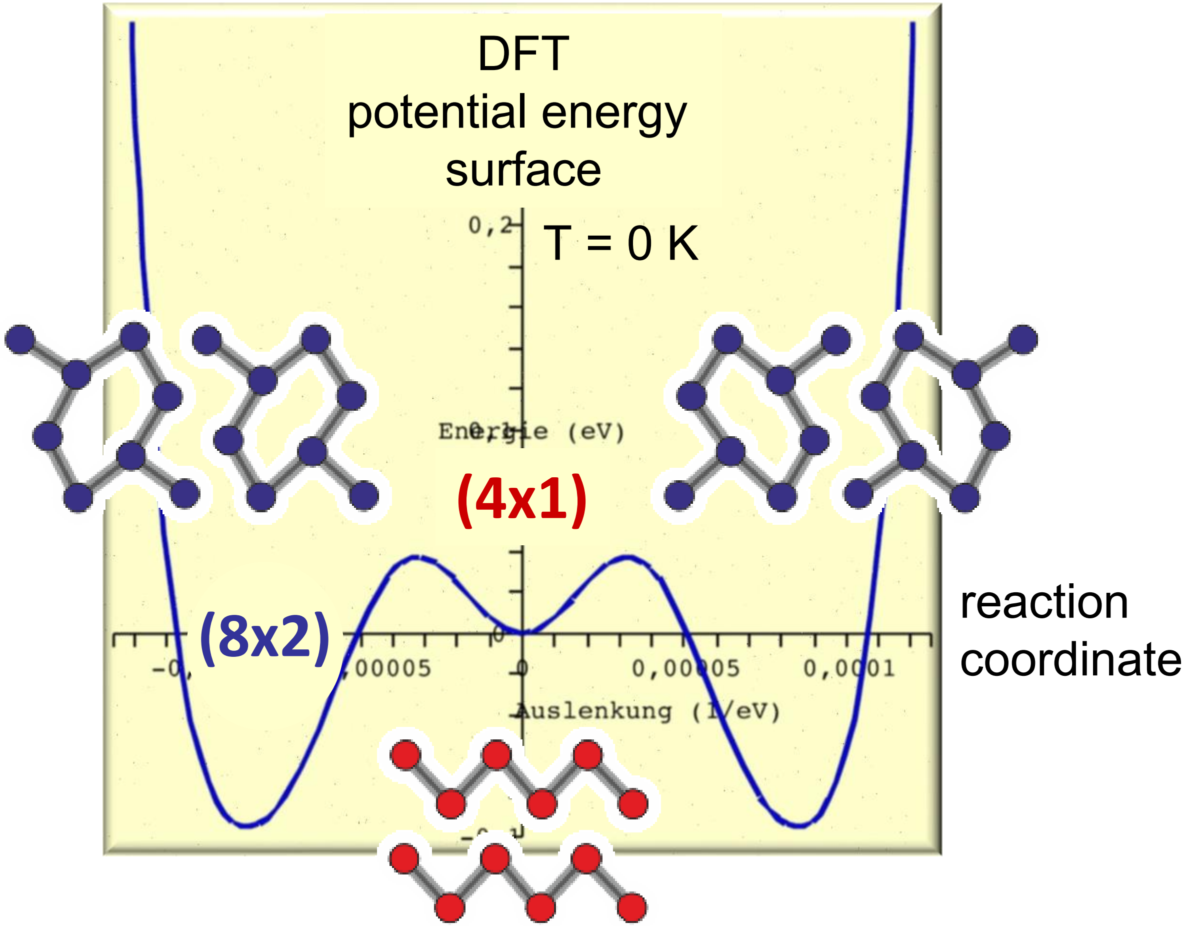




F. Klasing, T. Frigge, B. Hafke, S. Wall, B. Krenzer, A. Hanisch-Blicharski, and M. Horn-von Hoegen
Phys. Rev. B **89**, 121107(R) (2014)

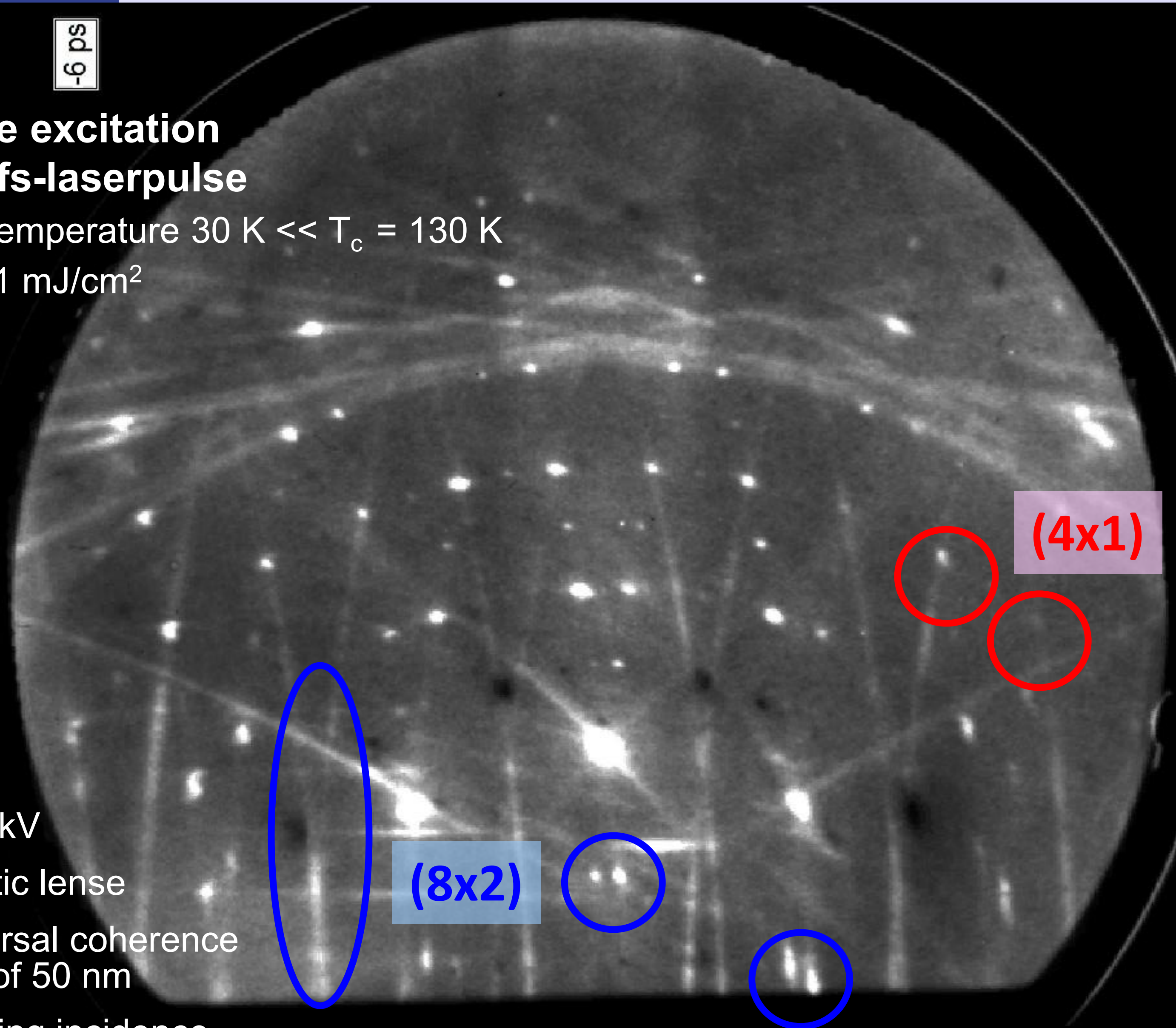
[*] S. Wippermann, W.G. Schmidt, Phys. Rev. Lett. **105**, 126102 (2010);
W.G. Schmidt, S. Wippermann, S. Sanna, M .Babilon, N.J. Vollmers, U. Gerstmann, phys. stat. sol. (b) **249**, 343 (2012)

Energy barrier between (8x2) ↔ (4x1)



S. Wall, B. Krenzer, S. Wippermann, S. Sanna, F. Klasing, A. Hanisch-Blicharski, M. Kammler, W. Gero Schmidt, M. Horn-von Hoegen, Phys. Rev. Lett. **109**, 186101 (202)

Movie of transition

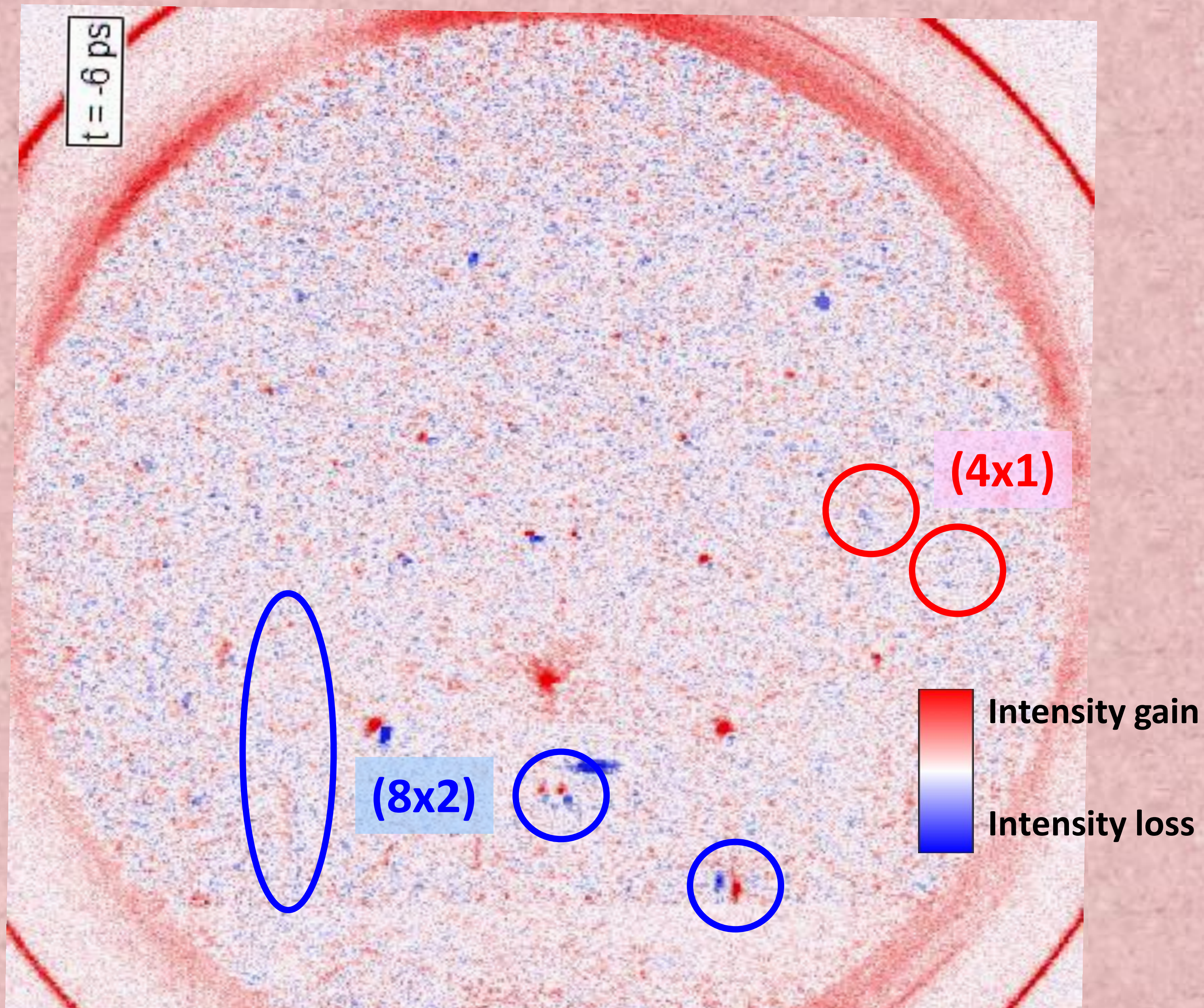


Impulsive excitation through fs-laserpulse

- Base temperature 30 K << T_c = 130 K
- Φ = 2.1 mJ/cm^2

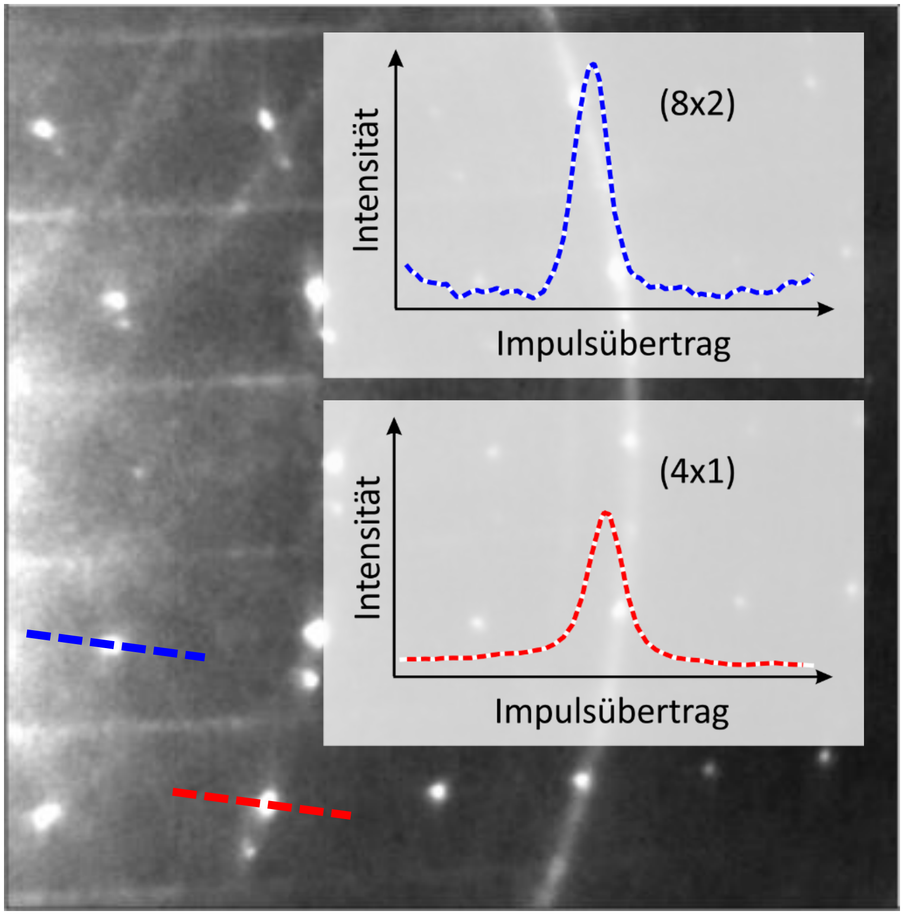
- E = 30 kV
- magnetic lense
- transversal coherence length of 50 nm
- 2° grazing incidence

Movie of transition – gains & losses

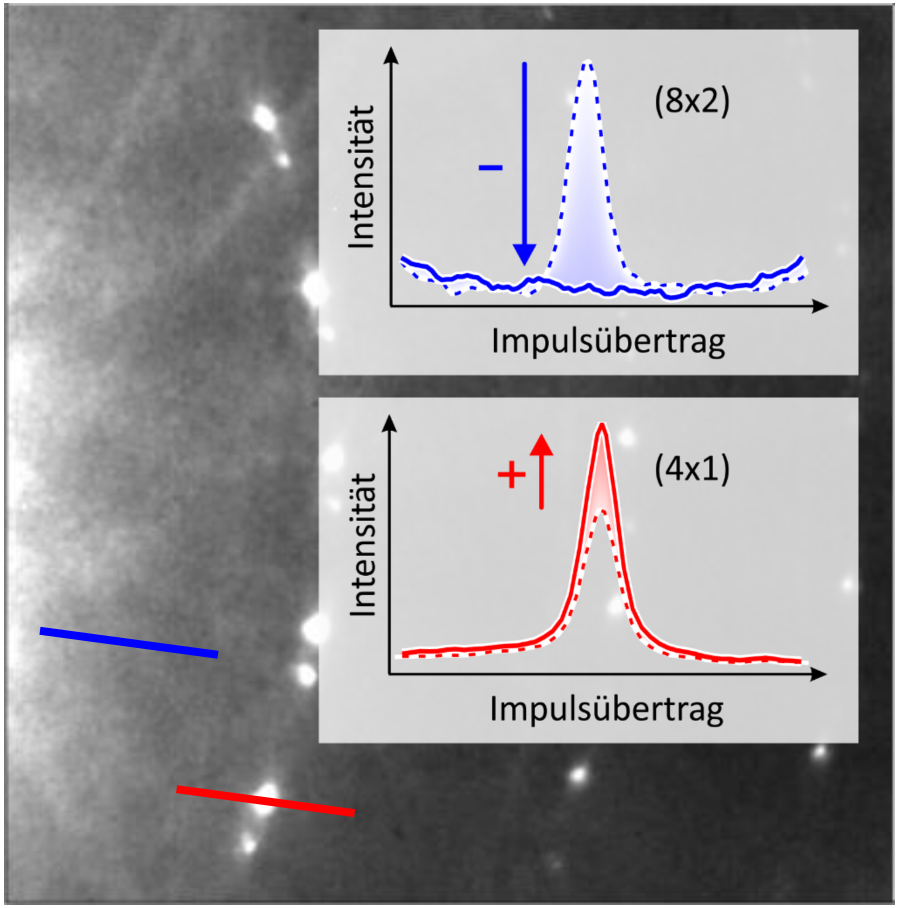


Lifting of ground state – how fast?

Si(111)(8x2)-In ground state,
prior to photo excitation $\Delta t < 0$ ps

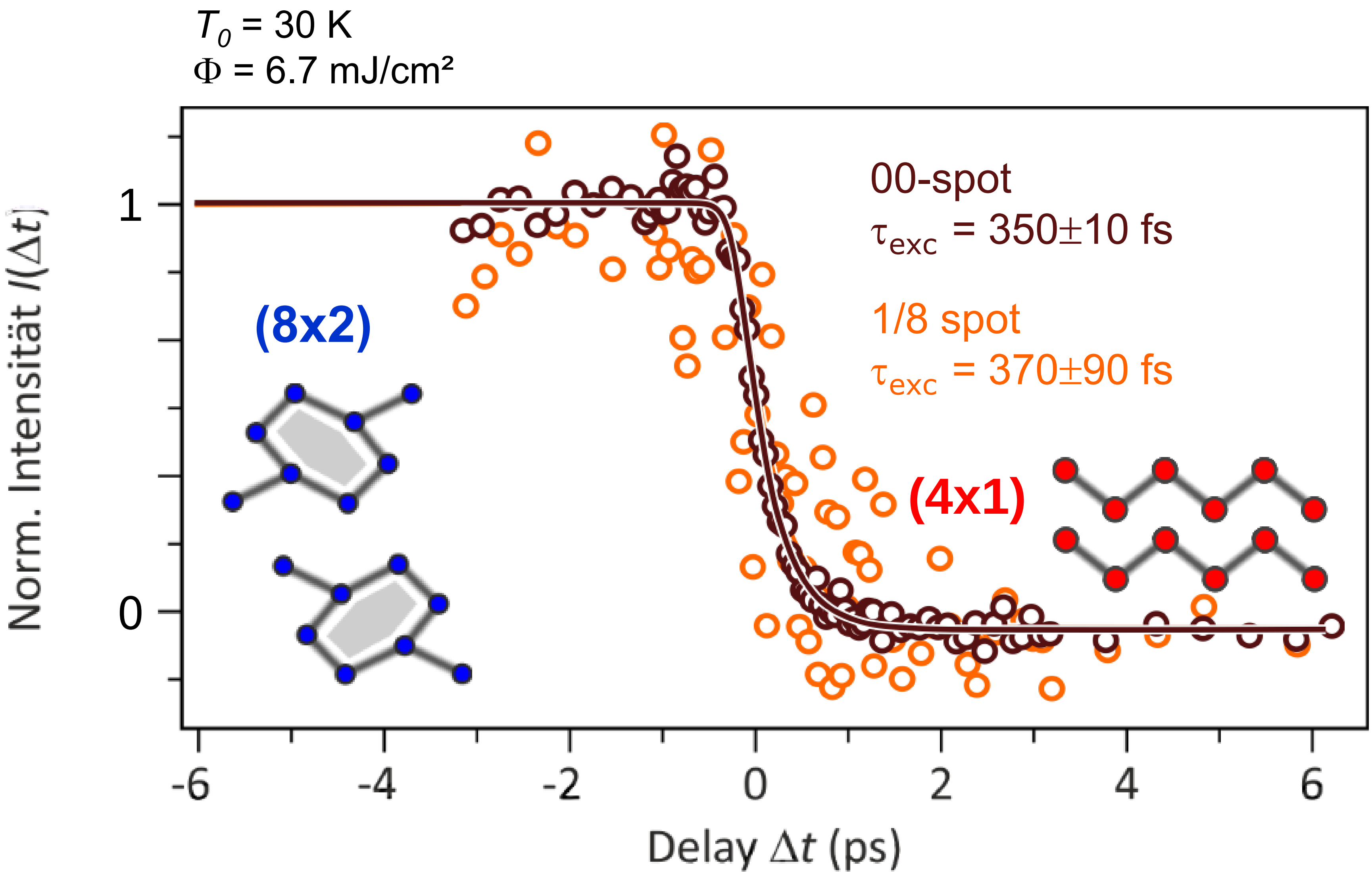


Si(111)(4x1)-In,
after photo excitation $\Delta t = 3$ ps



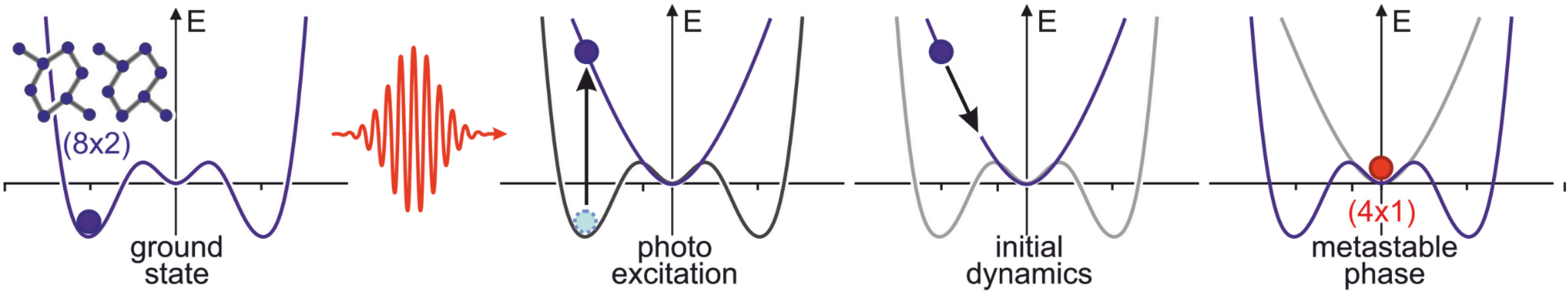
$T_0 = 30$ K, $\Phi = 6.7$ mJ/cm²

Lifting of low-T (8x2) ground state



T. Frigge et al., Nature **544**, 207 (2017)

Accelerated displacive excitation



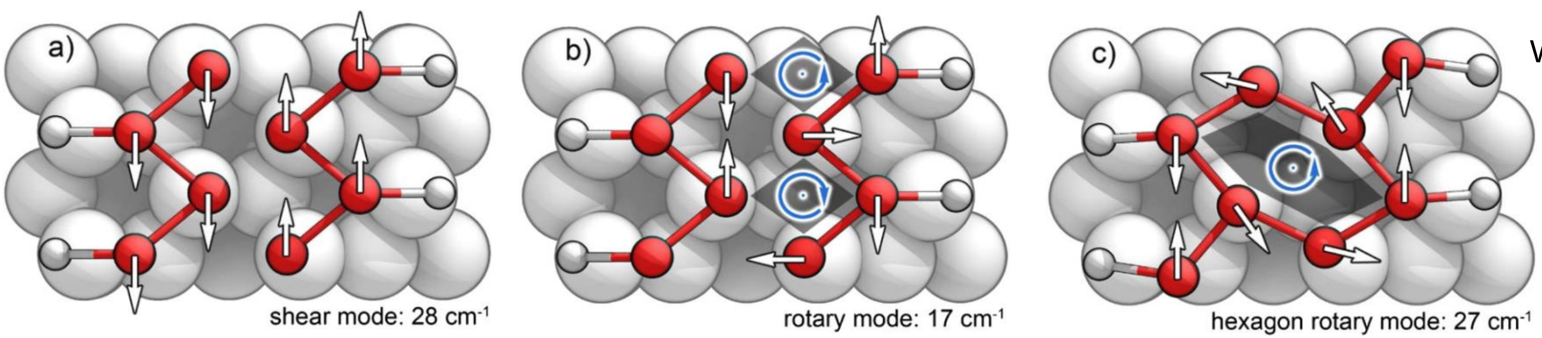
E_{gap} = -100 meV

$h\nu >> E_{gap}$

$k_bT << E_{barrier}$

Transient changes of potential energy surface upon photo excitation:

- Accelerated displacive transition from (8x2) to (4x1) in 350 fs
- Transition in ¼ period of the characteristic shear and rotational soft phonon modes nessary for the structural change



E = 3.4 meV
T = 1.2 ps

E = 2.1 meV
T = 2.0 ps

E = 3.0 meV
T = 1.4 ps

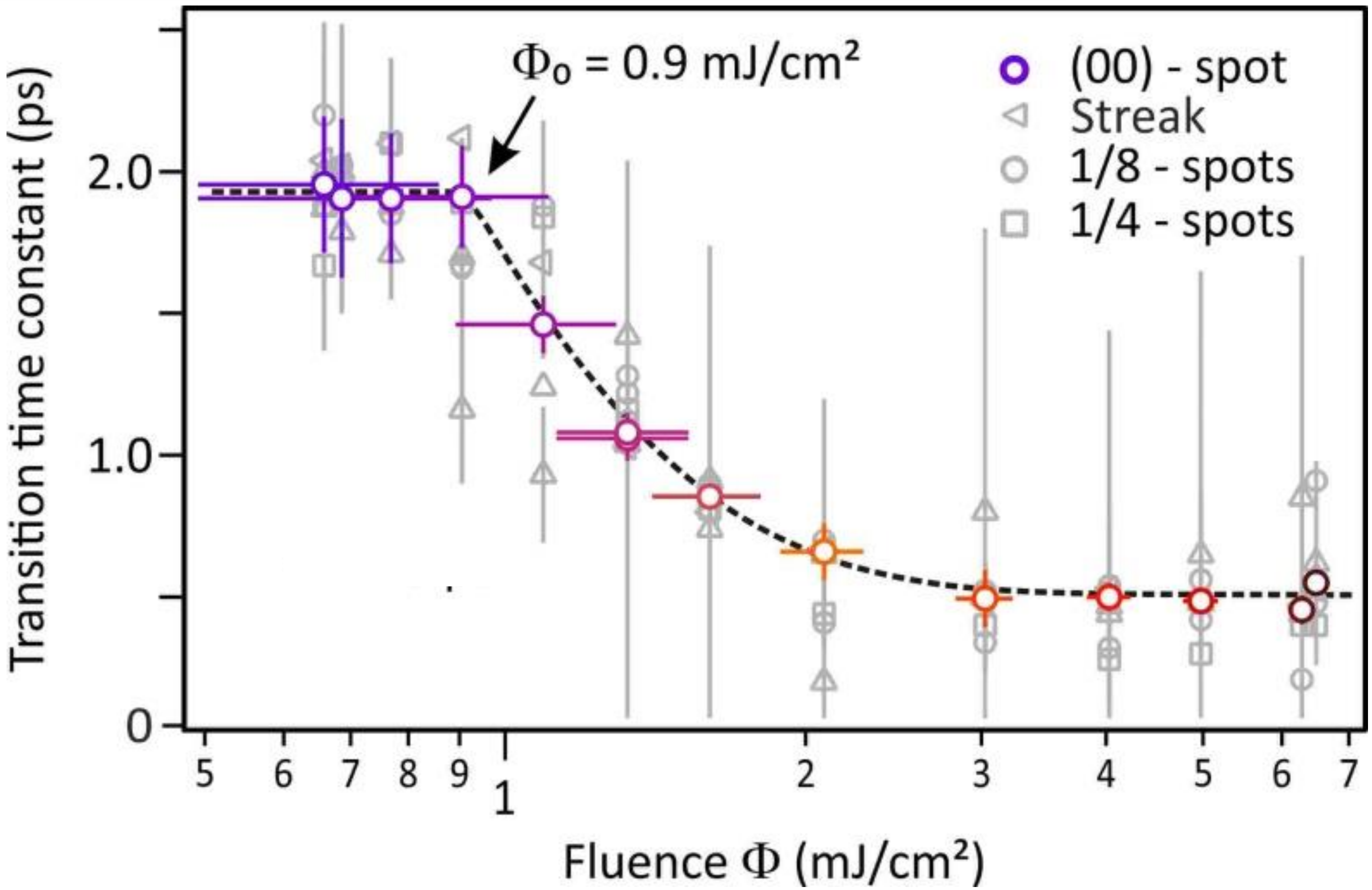
Wippermann et al., PRL **105**, 126102 (2010)

Fluence dependence of transition

Threshold fluence of 1 mJ/cm² for structural transition to (4x1)

Increase of transition speed from 1 mJ/cm² up to 3 mJ/cm²

Saturation at τ = 350 fs for the structural transition, i.e., motion of atoms, thus **fastest switching from insulator to metal**!



T. Frigge et al., Nature **544**, 207 (2017)

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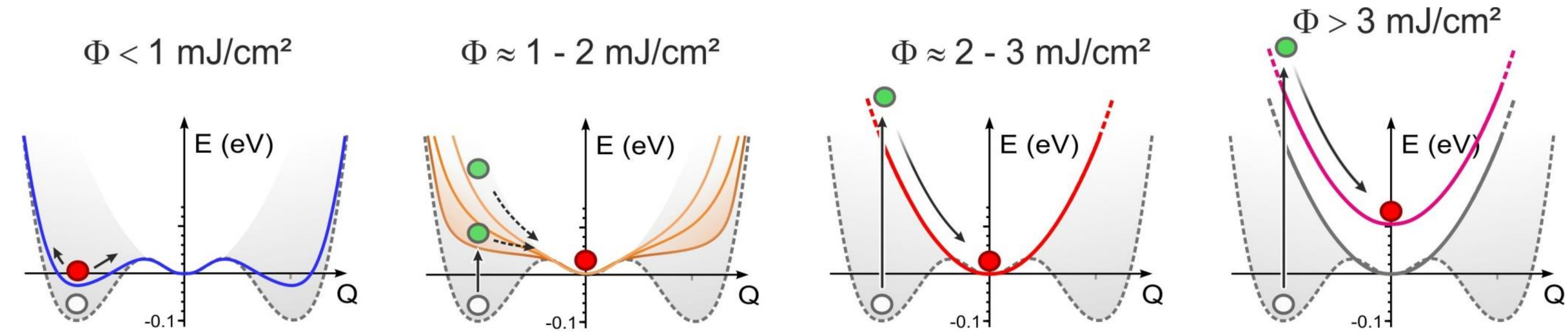
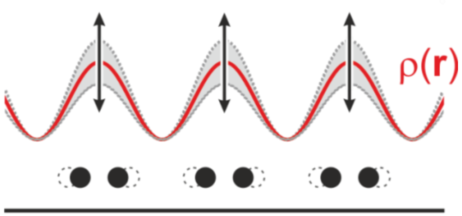
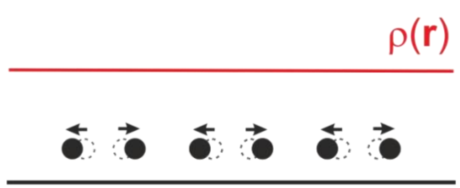


τ = 1900 fs | τ = 1900 - 350 fs | τ = 350 fs | τ = 350 fs





Bandgap still open

Observation of collective CDW amplitudon mode !

J.G.Horstmann et al., Nature **583**, 232 (2020)

Bandgap closes

Incomplete melting of CDW:

Phase transition speeds up

Complete melting of CDW and strongly accelerated displacive transition:

Highest slope of free energy

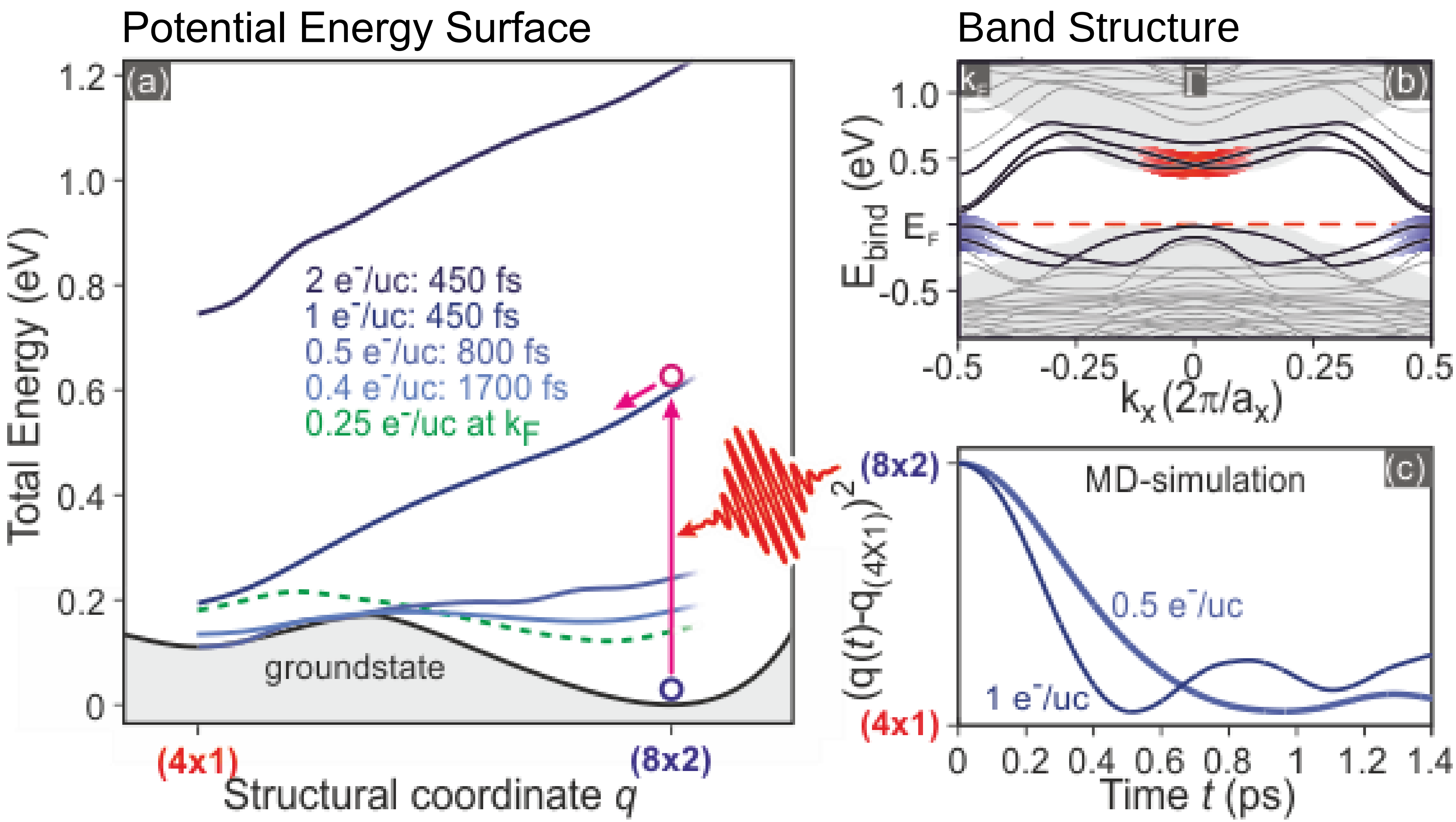
Vertical shift of free energy curve:

Saturation of acceleration

As fast as possible! => Quantum Limit

Quantum limit is the nonstatistical regime of rates in which the nuclear motion is directed and deterministic on the shortest scales of length (0.1–1 nm) and time (10^{-13} to 10^{-12} s)
C.Y. Ruan, F. Vigliotti, V.A. Lobastov, S. Chen, & A.H. Zewail, *PNAS* **101,** 1123 (2004)

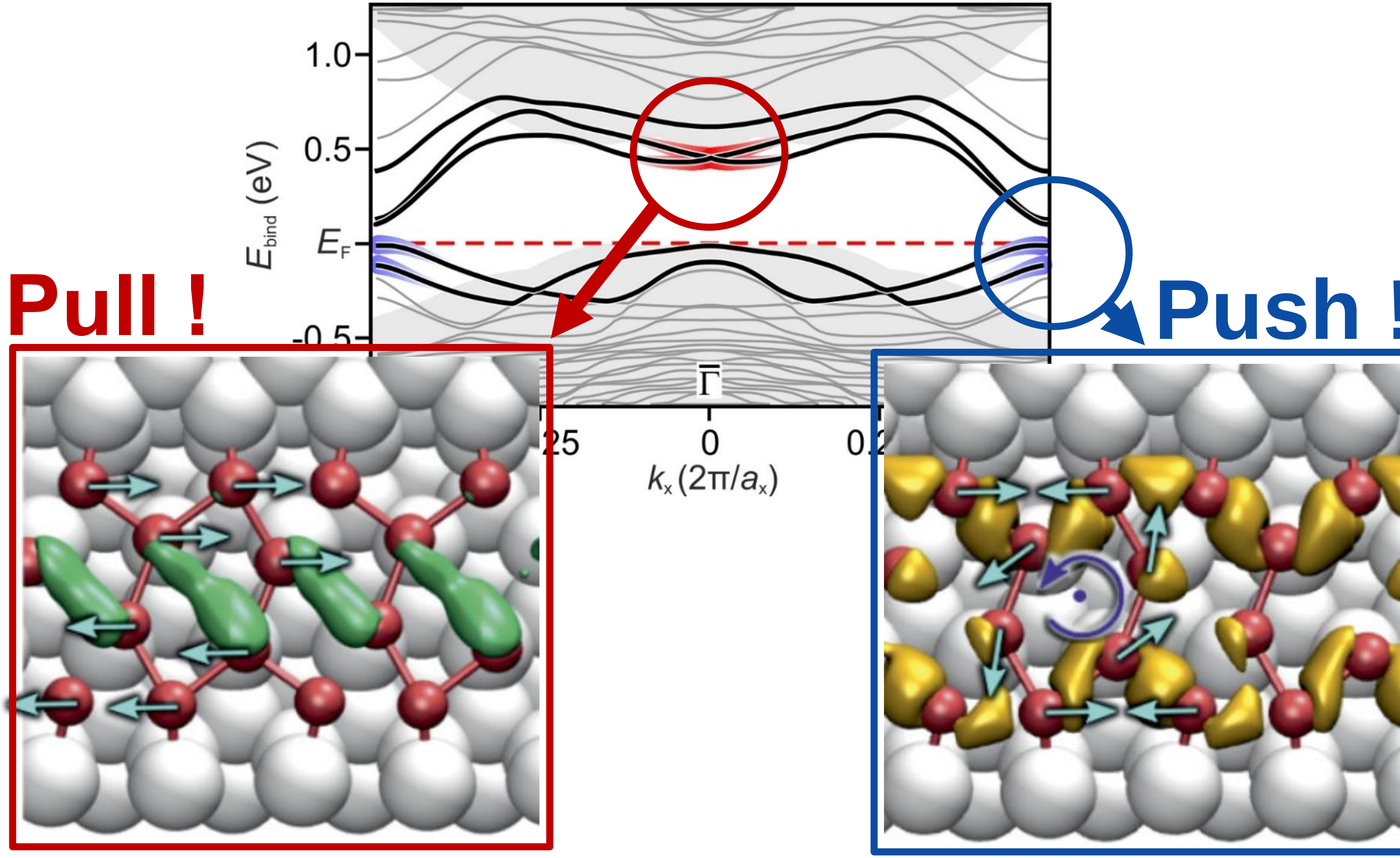
Theory: structural transition in 500 fs



T. Frigge et al., Nature **544**, 207 (2017)

Non-equilbrium constraint DFT and ab-inito molecular dynamics by Wolf Gero Schmidt, Uni-Paderborn

Specific electronic states drive PT

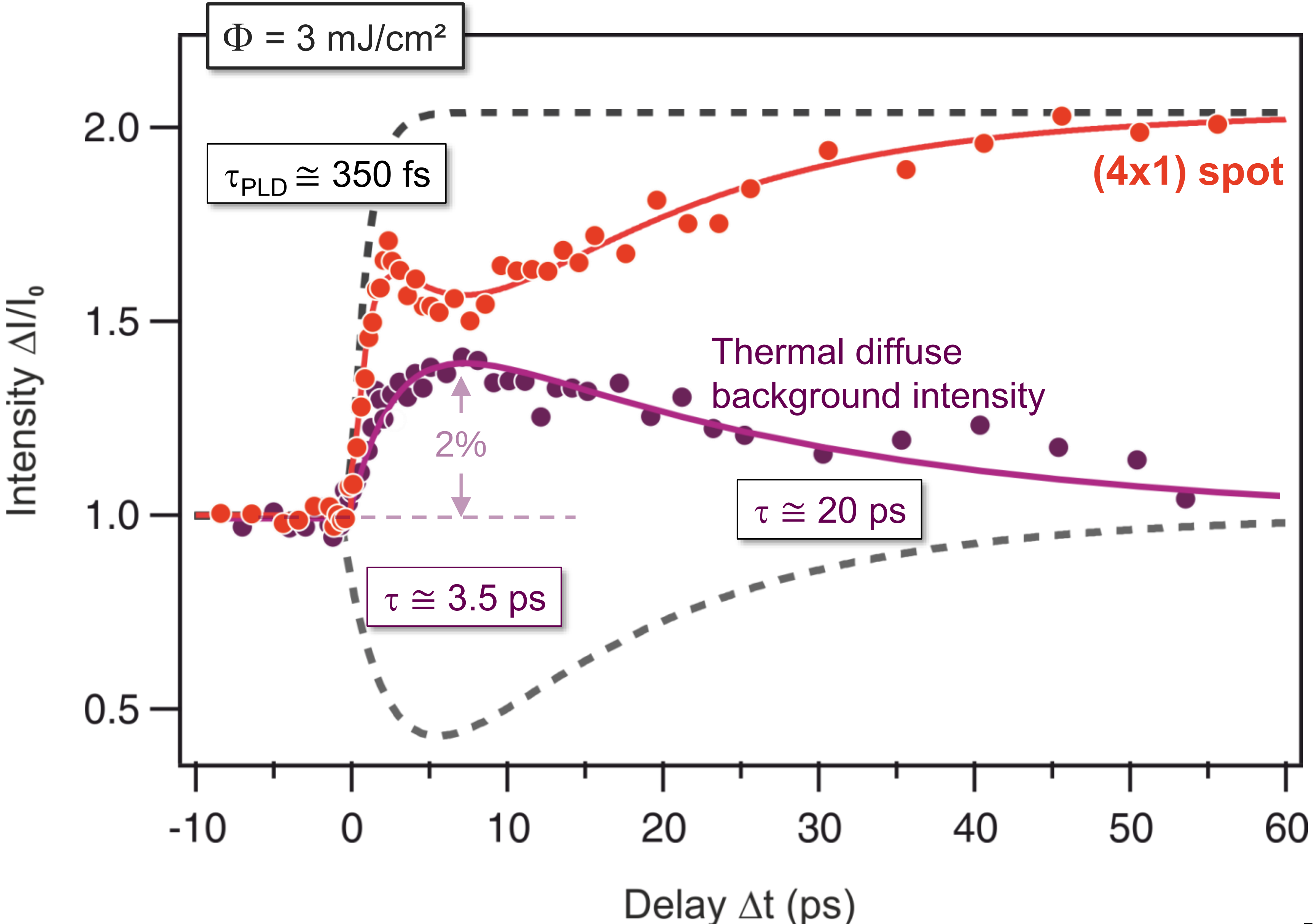


Electrons in conduction band at Γ
Population of bonding state
Excitation of **soft shear mode**

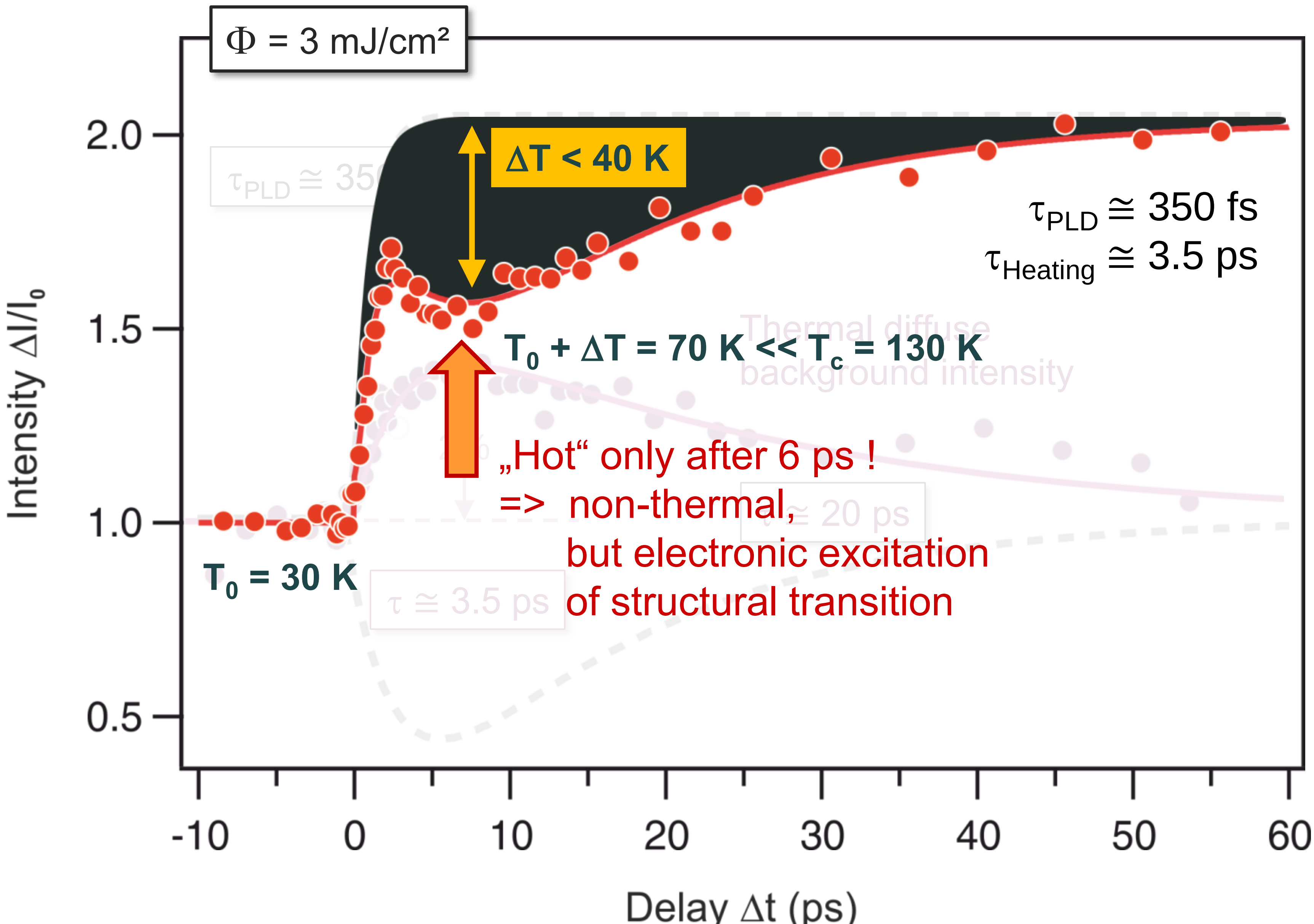
Holes in valence band at zone boundary
De-population of bonding states
Excitation of **soft rotational mode**

“Beyond the molecular movie: ultrafast dynamics of bands and bonds during a photo-induced phase transition”,
C.W. Nicholson et al., Science **362**, 821 (2018)

Thermal or non-thermal excitation?

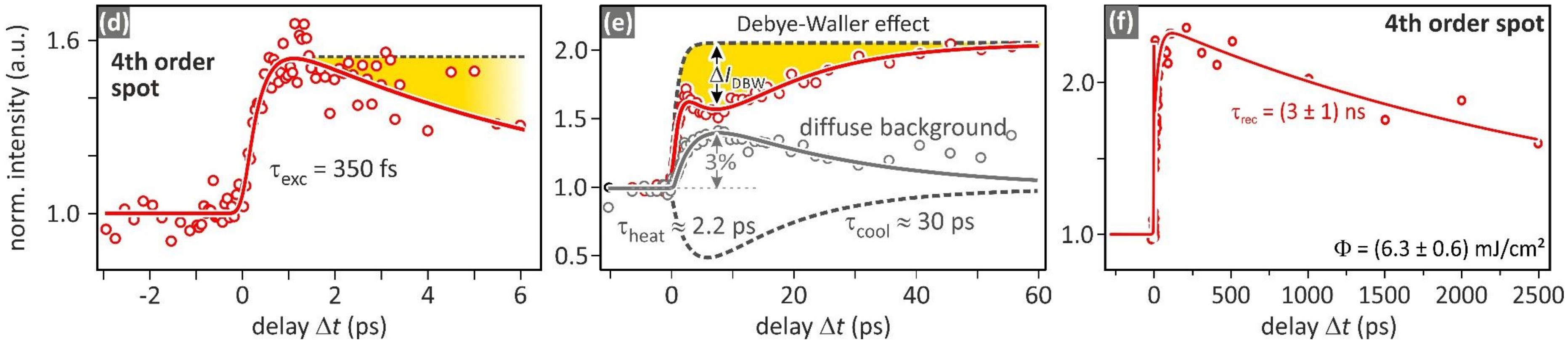


Delayed thermal excitation



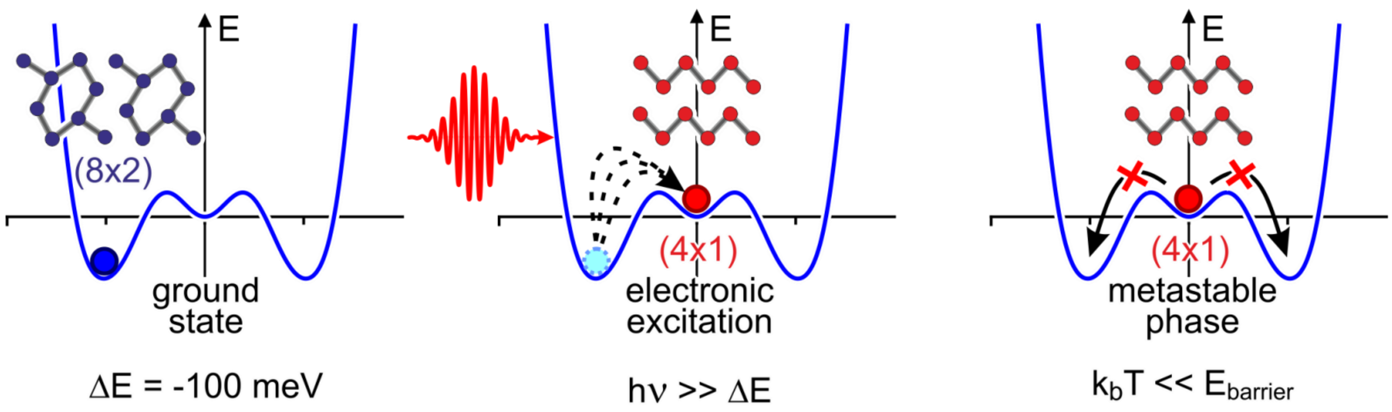
T. Frigge et al., Structural Dynamics **5**, 025101 (2018)

Slow recovery to groundstate



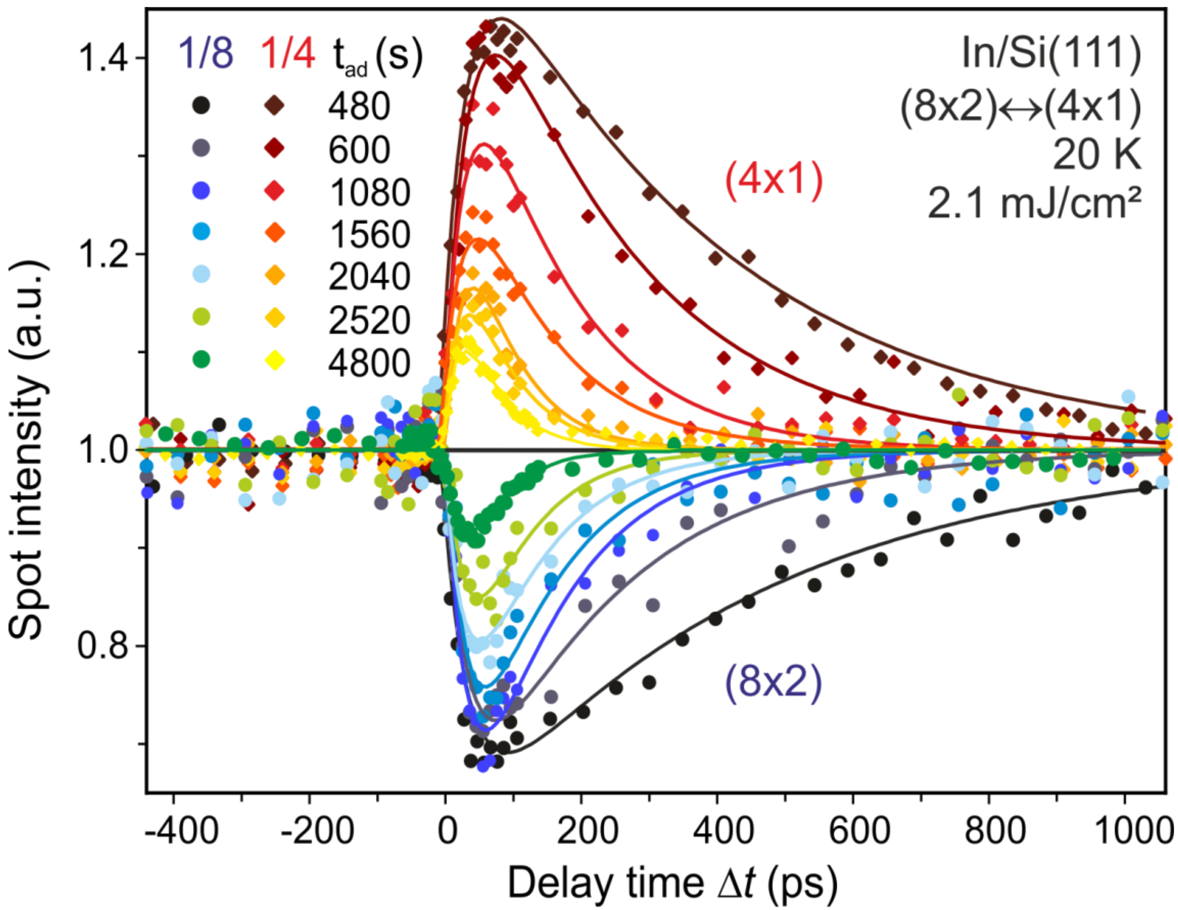
Supercooled metastable surface phase:

- 40 meV barrier hinders immediate recovery of (8x2) groundstate
- System is trapped in high temperature state - unaccessible under equilibrium



S. Wall, B. Krenzer, S. Wippermann, S. Sanna, F. Klasing, A. Hanisch-Blicharski, M. Kammler, W. Gero Schmidt, M. Horn-von Hoegen, Phys. Rev. Lett. **109**, 186101 (2012) + Phys. Rev. Lett. **111**, 149602 (2013)

Adsorbates acting as seeds



Recovery of groundstate sensitive to

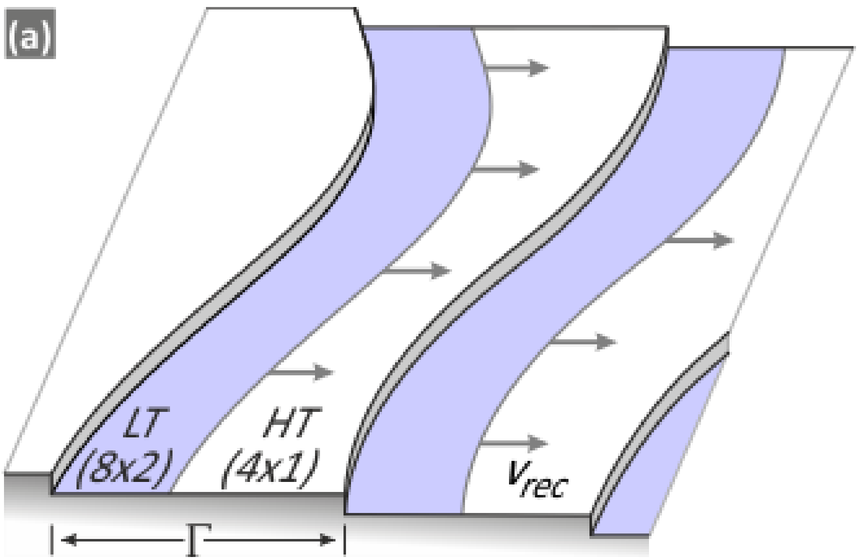
- Adsorption from residual gas in UHV, most likely H_20
- 1D-recovery front at 100 m/s

S. Wall, B. Krenzer, S. Wippermann, S. Sanna, F. Klasing, A. Hanisch-Blicharski, M. Kammler, W. Gero Schmidt, M. Horn-von Hoegen, Phys. Rev. Lett. **109**, 186101 (2012) & Phys. Rev. Lett. **111**, 149602 (2013)

Steps acting as seeds

Extreme slow recovery of ground state

- Improved vaccuum conditions - adsorbates acting as seed are not present
- Step edges trigger recovery of (8x2) ground state
- Use step morphology => determine velocity of 1-dim. recovery front through $v_{8x2} = s / t$

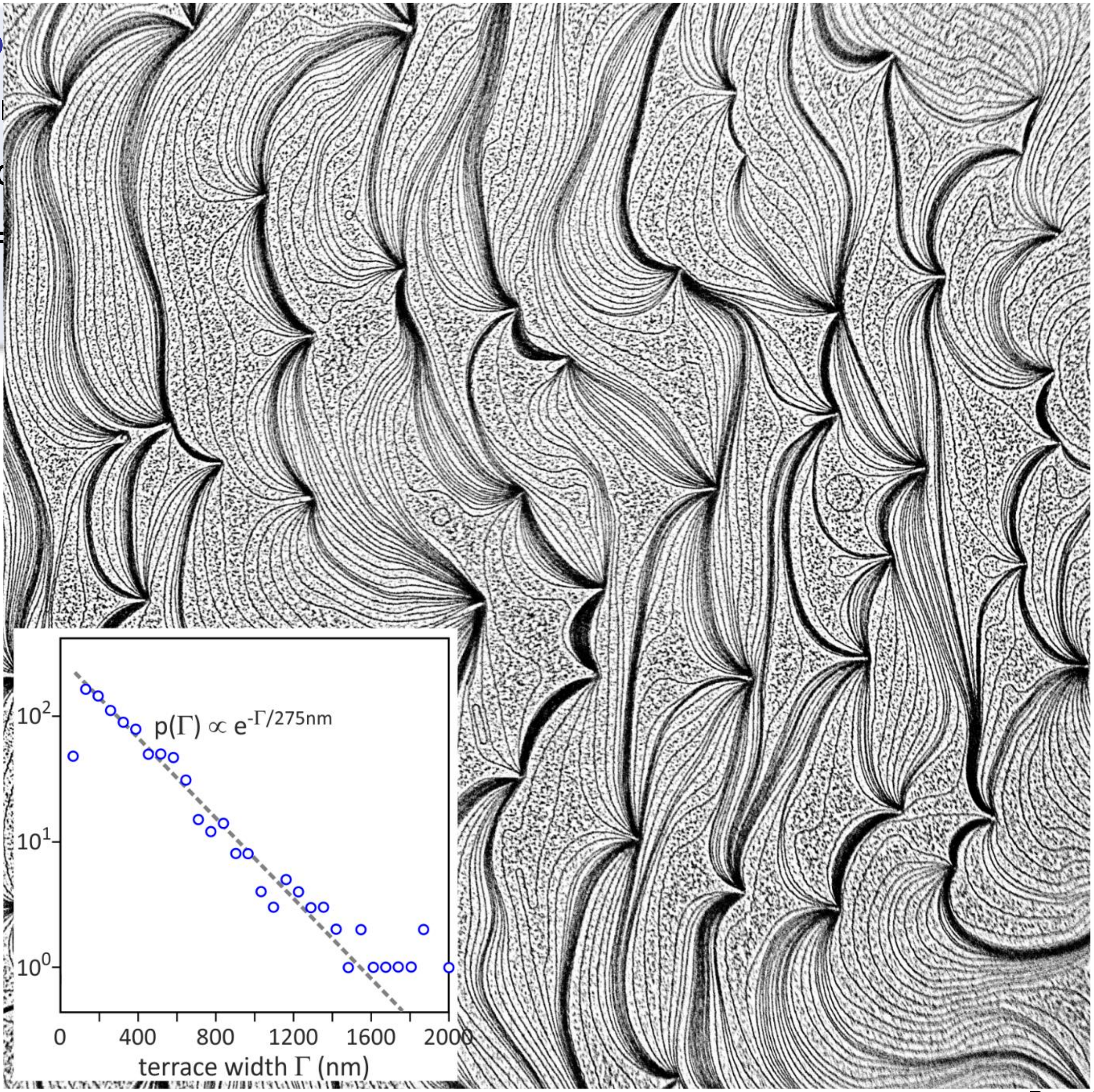


Steps acting as seeds

Extreme slow recovery of gro

- Improved vaccuum co
- Step edges trigger rec
- Use step morphology
  1-dim. recovery front

PEEM - micrograph
Si(111) - 0.08°
FoV = 50 μm
<Γ> = 340 nm



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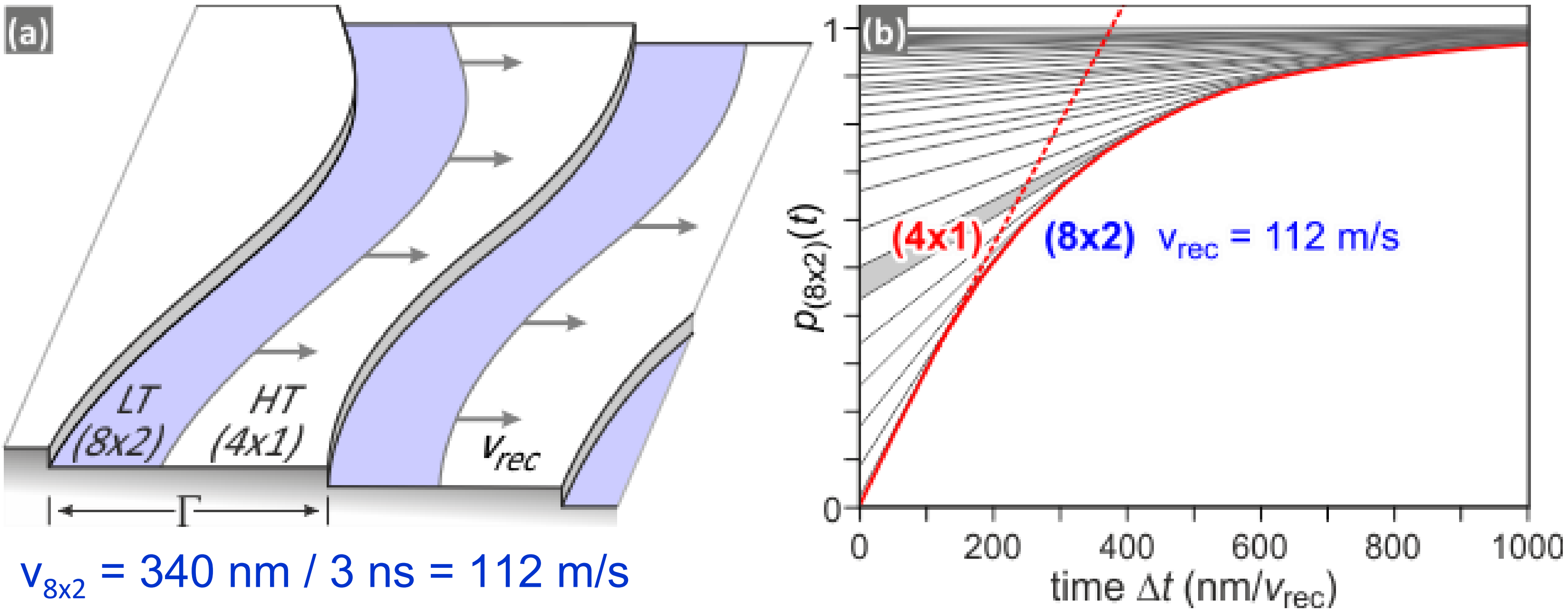

v_{8x2} = 340 nm / 3 ns = 112 m/s

B. Hafke, T. Witte, t. Frigge, D. Janoschka, P. Dreher, F.-J. Meyer zu Heringdorf, M. Horn von Hoegen Struct. Dyn. **6**, 045101 (2019)

Relaxation dynamics

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DFG

SFB616

SFB 1242

Summary

Si(111)-In(8x2)↔(4x1)

System with Peierls instabililty

1st order phase transition at 130 K

Non-equilibrium dynamics of structural transition

- ultrafast photo excitation of phase transition in 350 fs
- accelerated displacive transition
- critical damping
- delayed thermal excitation of surface atoms at 7 ps
- formation of a supercooled, metastable surface phase
- speed of recovery ~100 m/s