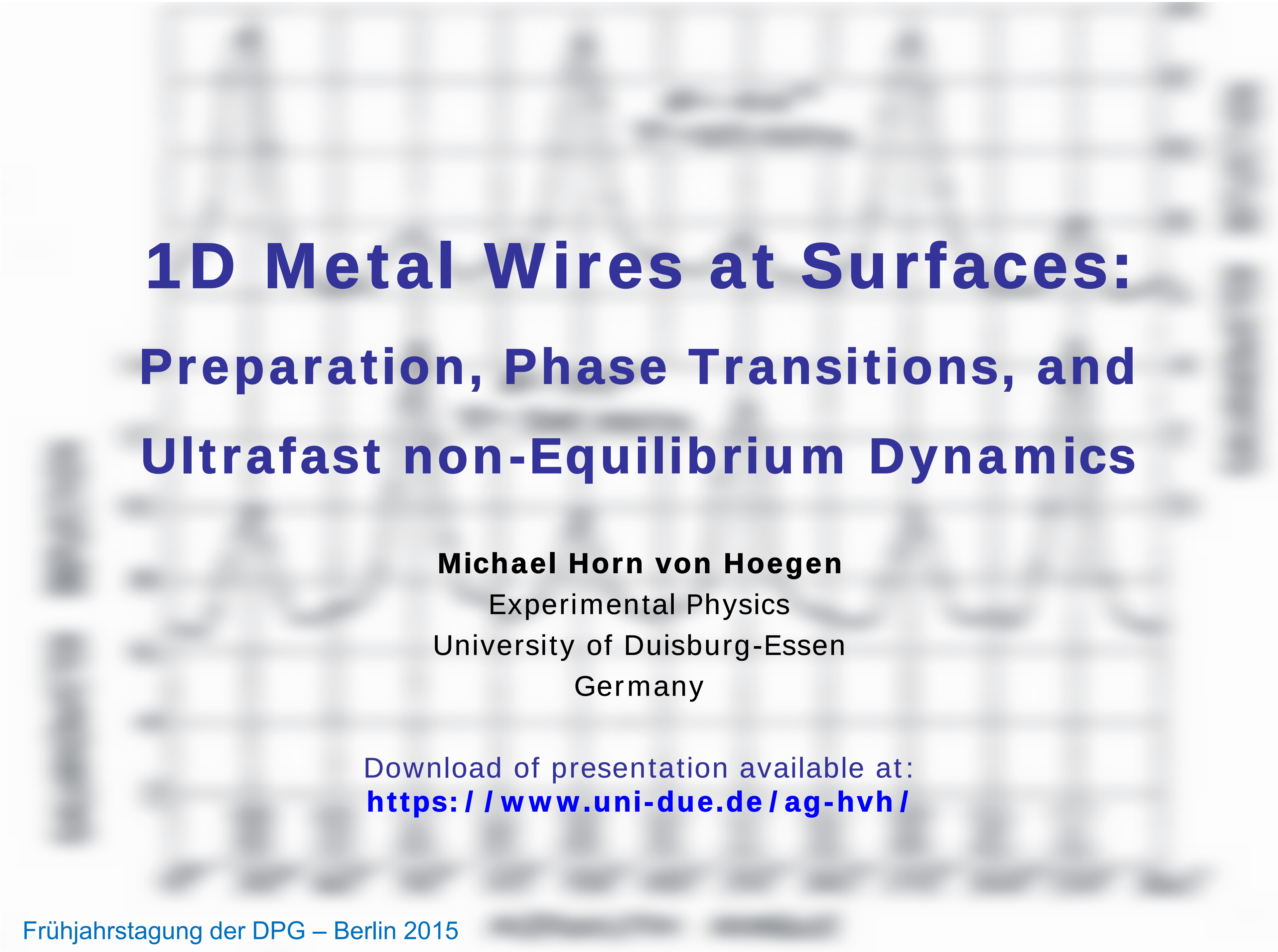


1D Metal Wires at Surfaces:

Preparation, Phase Transitions, and Ultrafast non-Equilibrium Dynamics

Michael Horn von Hoegen
Experimental Physics
University of Duisburg-Essen
Germany

1-dim Atom Wires on Si – why?

Dimensionality drastically changes properties of matter

3D Simple bulk (Pauli: „God made the bulk …“)

2D Surfaces are complicated – we struggle since centuries
(Pauli: „ …the surface was invented by the devil”)

0D Quantum dots are simple again (used in applications)

1D ?

We expect new and fascinating properties:

- Anisotropic conductivity
- 1-dim transport: Tomanaga Luttinger liquid, decouple charge and spin
- Peierls instability of atom chain

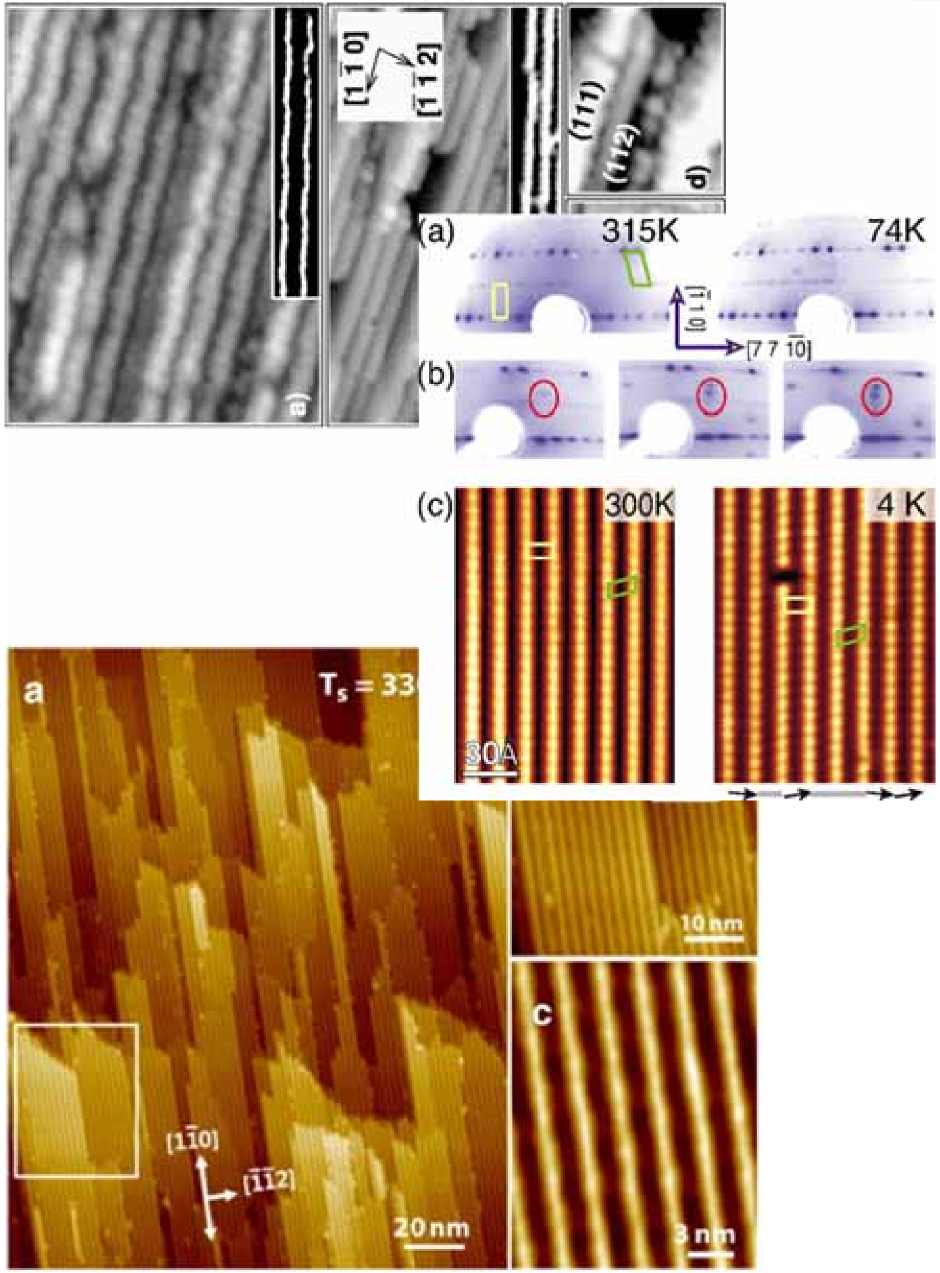
=> Playground for physicists

1-dim Atom Wires on Si

- **Si(557) – Pb:**
  - **Switching Between One and Two Dimensions: Conductivity of Pb-Induced Chain Structures onSi(557)**
    C. Tegenkamp, Z. Kallassy, H. Pfnür, H.-L. Günter, V. Zielasek, and M. Henzler, Phys. Rev. Lett. **95**, 176804 (2005)
    Coupled Pb Chains on Si(557): Origin of One-Dimensional Conductance
    C. Tegenkamp, T. Ohta, J. McChesney, H. Dil, E. Rotenberg, H. Pfnür, and K. Horn, Phys. Rev. Lett. **100** 076802 (2008)
  - **Conductance transition and interwire ordering of Pb nanowires on Si(557)**
    H. Morikawa, K.S. Kim, Y. Kitaoka, T. Hirahara, S. Hasegawa, and H.W. Yeom, Phys. Rev. B **82**, 045423 (2010)
  - **Plasmons in Pb nanowire arrays on Si(557): Between one and two dimensions**
    T. Block, C. Tegenkamp, J. Baringhaus, H. Pfnür, and T. Inaoka, Phys. Rev. B **84** 205402 (2011)
  - **Fermi nesting between atomic wires with strong spin-orbit coupling**
    C. Tegenkamp, D. Lükermann, H. Pfnür, B. Slomski, G. Landolt, J. H. Dil, Phys. Rev. Lett. **109**, 266401 (2012)

- **Si(557) – Ag:**
  - **One-dimensional collective excitations in Ag atomic wires grown on Si(557)**
    U Krieg, C Brand, C Tegenkamp and H Pfnür
    J. Phys.: Condens. Matter **25**, 014013 (2012)

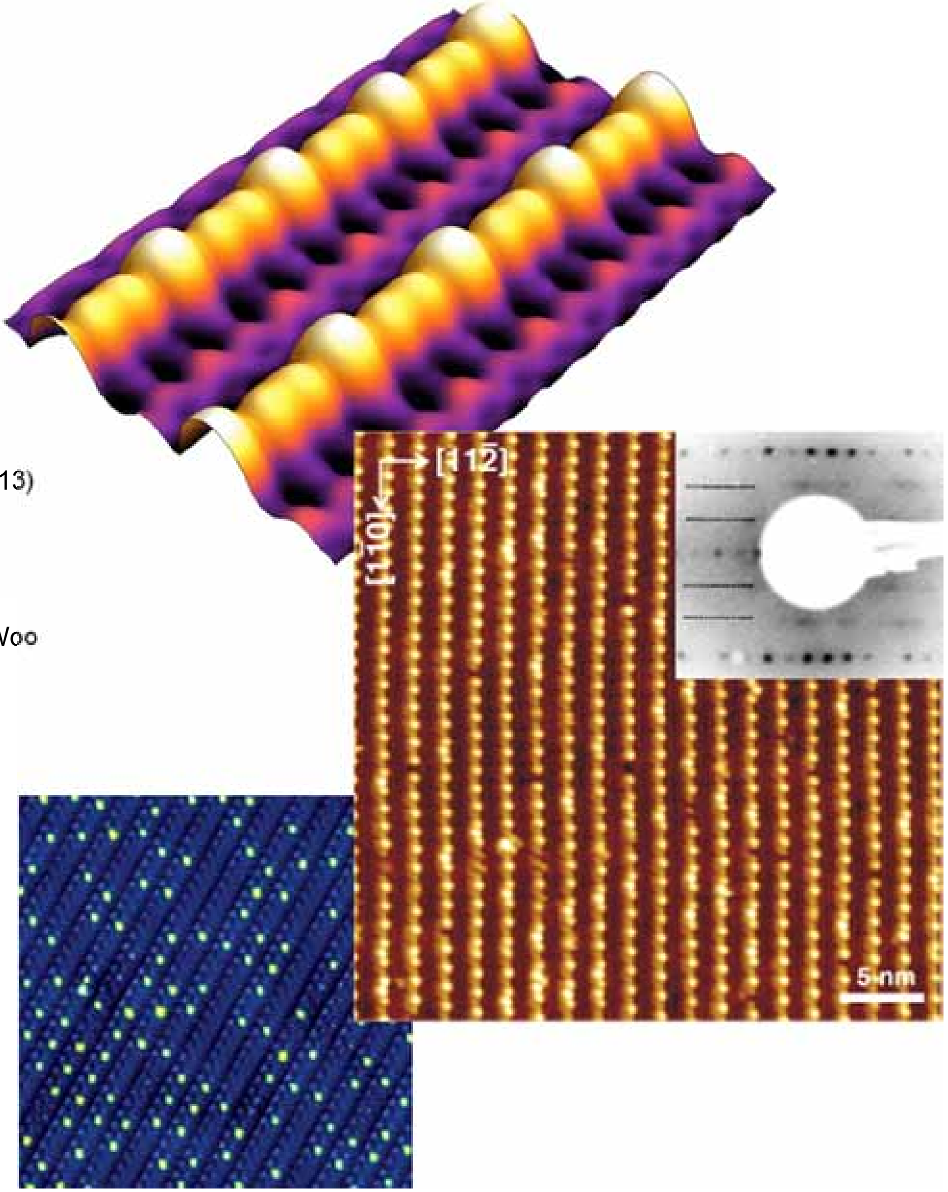
- **Si(557) – Mg:**
  - **Quintuple-period Si atomic wires with alternative double and triple modulations by metal: Mg/Si(557)**
    B.G. Shin, M.K. Kim, J.H. Lee, D.-H. Oh, I. Song, S.H. Woob, C.-Y. Park, J.R. Ahn, Surf. Sci. **606**, 57 (2012)

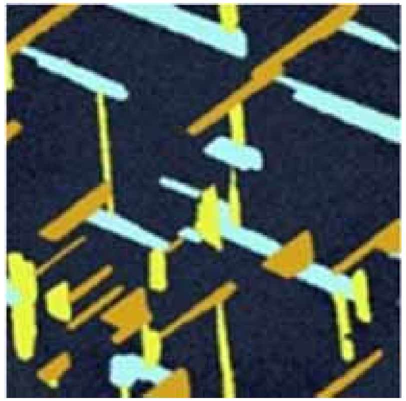


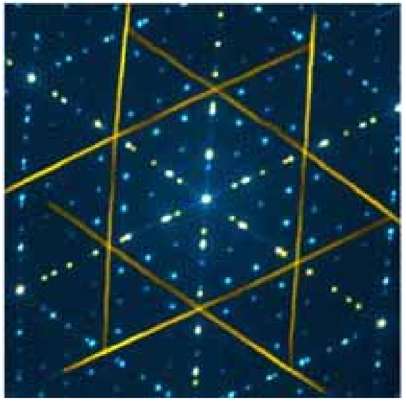
UNIVERSITÄT DUISBURG ESSEN

1-dim Atom Wires on Si

- ## Si(553) – Au:
    - **Intrinsic magnetism at silicon surfaces**
      Steven C. Erwin & F.J. Himpsel
      Nature Communications **1**, 58 (2010)
    - **Spin-split silicon states at step edges of Si(553)-Au**.
      K. Biedermann et al. , Phys. Rev. B **85**, 245413 (2012).
    - **Spectroscopic evidence for spin-polarized edge states in graphitic Si nanowires**.
      P.C. Snijders et al. New J. Phys. **14**, 103004 (2012).
    - **Evidence for long-range spin order instead of a Peierls transition in Si(553)-Au chains**
      J. Aulbach, J. Schäfer, S.C. Erwin, S. Meyer, C. Loho, J. Settelein, and R. Claessen, Phys. Rev. Lett. **111**, 137203 (2013)
- ## Si(553) – In:
    - **Indium-induced triple-period atomic wires on a vicinal Si(111) surface: In/Si(557)**
      I Song, D-H Oh, J H Nam, M K Kim, C Jeon, C-Y Park, S H Woo and J R Ahn, New J. Phys. **11** (2009) 063034,
- ## Si(111)-Au (5x2)

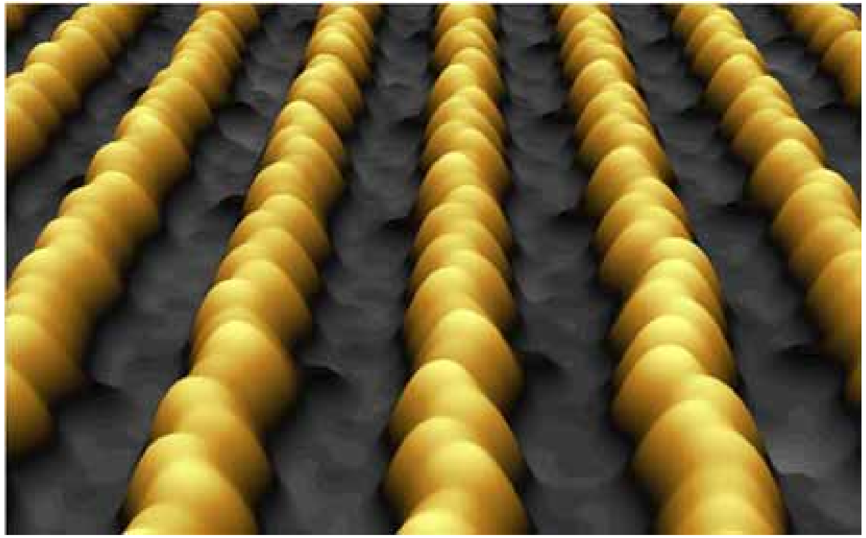




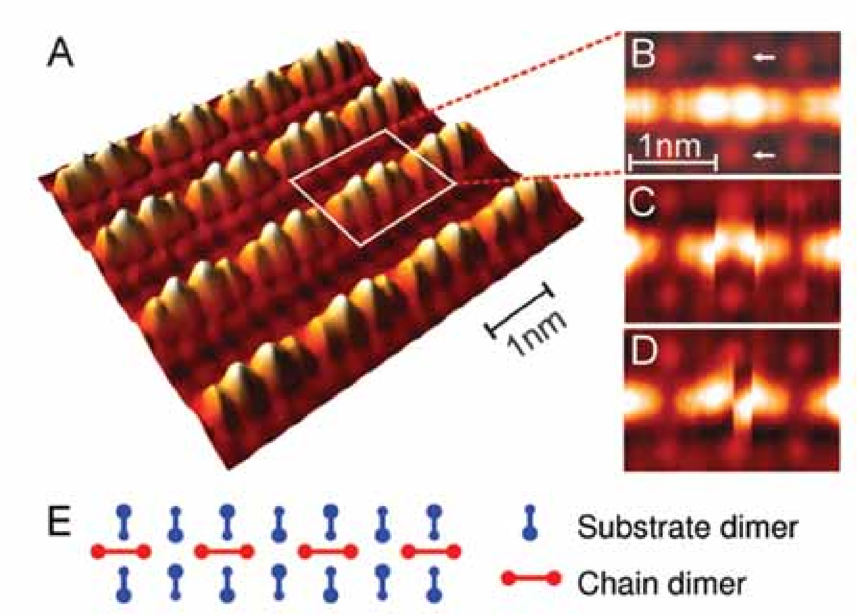


1-dim Atom Wires on Ge

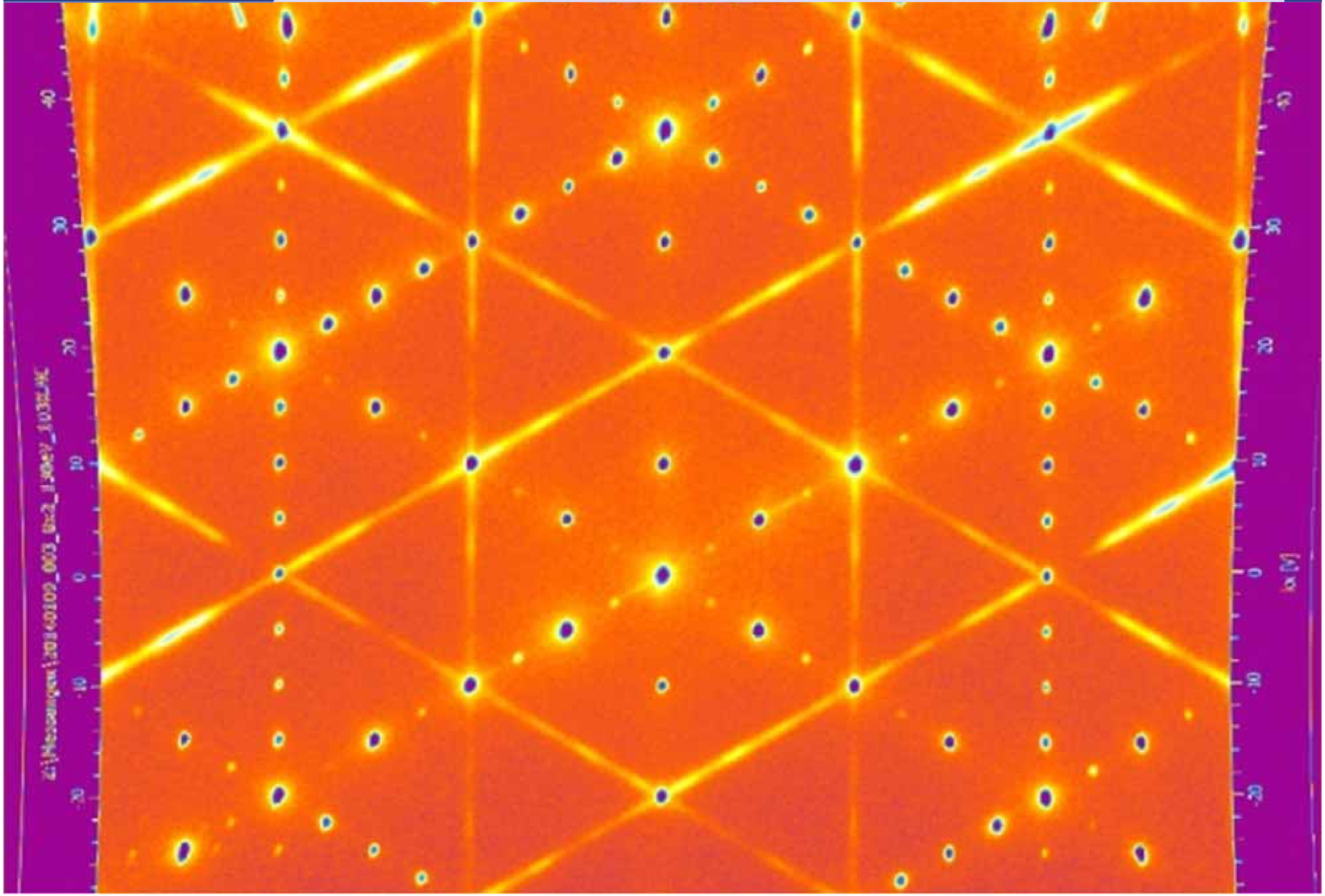
- ## Ge(001) – Au:
  - **Scanning tunneling microscopy study of self-organized Au atomic chain growth on Ge(001)**
    J. Wang, M. Li, E. I. Altman, Phys. Rev. B 70, 233312 (2004)
  - **New Model System for a One-Dimensional Electron Liquid: Self-Organized Atomic Gold Chains on Ge(001)**
    J. Schäfer, C. Blumenstein, S. Meyer, M. Wisniewski, and R. Claessen, Phys. Rev. Lett. **101**, 236802 (2008)
  - **First-principles studies of Au-induced nanowires on Ge(001)**
    S. Sauer, F. Fuchs, F. Bechstedt, C. Blumenstein, J. Schäfer, Phys. Rev. B **81**, 075412 (2010)
  - **Atomically controlled quantum chains hosting a Tomonaga–Luttinger liquid**
    C. Blumenstein, J. Schäfer, S. Mietke, S. Meyer, A. Dollinger, M. Lochner, X. Y. Cui, L. Patthey, R. Matzdorf, R. Claessen, Nature Physics **7**, 776 (2011)



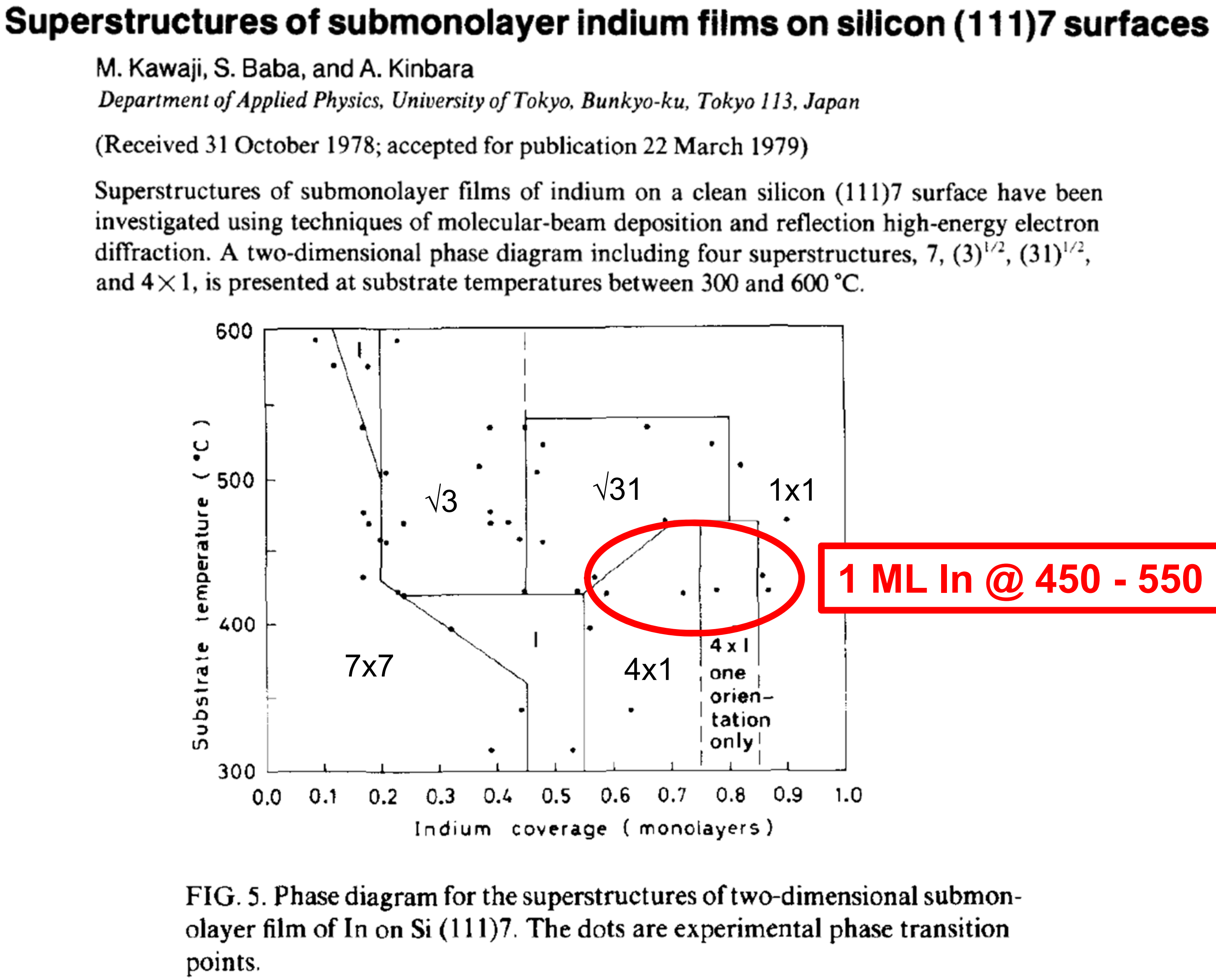
- ## Ge(001) – Pt:
  - **Quantum Confinement between Self-Organized Pt Nanowires on Ge(001)**
    N. Oncel, A. van Houselt, J. Huijben, A.-S. Hallbäck, Phys. Rev. Lett. **95**, 116801 (2005)
  - **Spatial Mapping of the Electronic States of a One-Dimensional System**
    A. van Houselt, N. Oncel, B. Poelsema, H.J.W. Zandvliet, Nano Lett. **6**, 1439 (2006)
  - **Playing Pinball with Atoms**
    A. Saedi, A. van Houselt, R. van Gastel, B. Poelsema, H.J.W. Zandvliet, Nano Lett. **9**, 1733 (2009)



Si(111)-In(8x2)



Adsorbat System: Si(111)-In



Superstructures of submonolayer indium films on silicon (111)7 surfaces

M. Kawaji, S. Baba, and A. Kinbara
Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

(Received 31 October 1978; accepted for publication 22 March 1979)

Superstructures of submonolayer films of indium on a clean silicon (111)7 surface have been investigated using techniques of molecular-beam deposition and reflection high-energy electron diffraction. A two-dimensional phase diagram including four superstructures, 7, $(3)^{1/2}$, $(31)^{1/2}$, and 4×1, is presented at substrate temperatures between 300 and 600 °C.

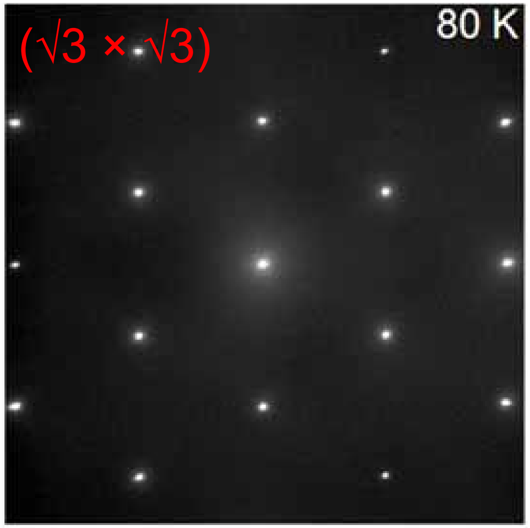
FIG. 5. Phase diagram for the superstructures of two-dimensional submonolayer film of In on Si (111)7. The dots are experimental phase transition points.

1 ML In @ 450 - 550 °C

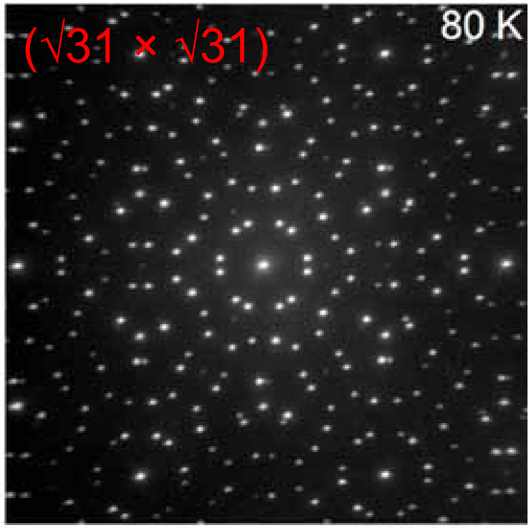
M. Kawaji, S. Baba, and A. Kinbara, Appl. Phys. Lett. **34**, 748 (1979)

Adsorbatsystem: Si(111)-In

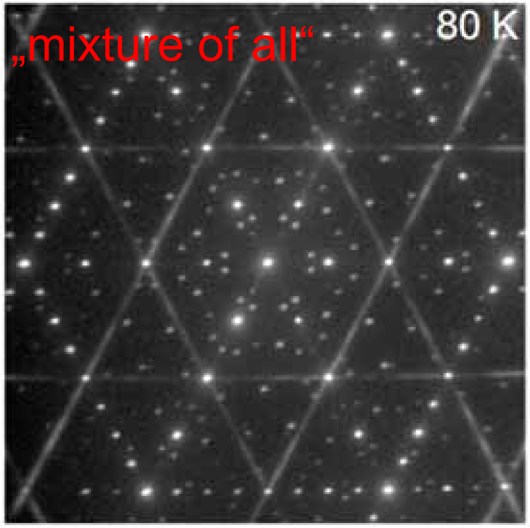
- precision-oriented (±0.1°) Si(111) sample (phosphorus doped, 0.8 Ωcm)
- Si-substrate cleaned by flash-anneal cycles up to 1200°C
- clean Si(111) surface repeatedly checked by (7x7) superstructure spots in LEED
- Indium-deposition at elevated Si substrate temperatures
- constant deposition rate controlled by quarz microbalance
- SPA-LEED pattern taken at 130 eV directly after rapid cooling down to ~ 80 K



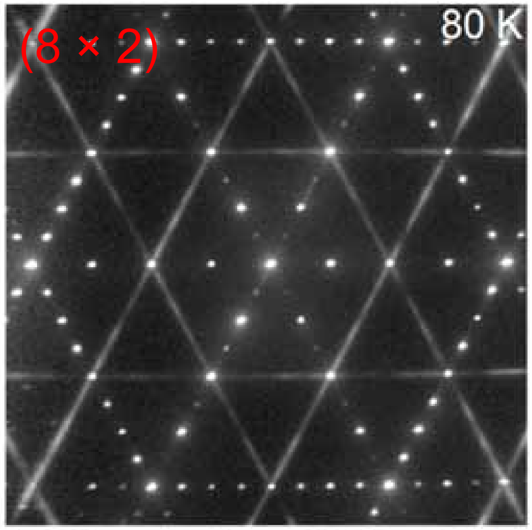
In(√3x√3) absorbed at ~ 450 °C and annealed for 180 s at ~ 600 °C



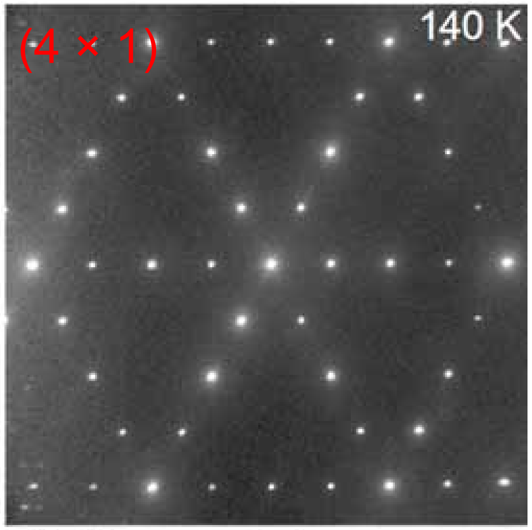
In(√31x√31) absorbed ~ at 450 °C and annealed for 60 s at ~ 600 °C



In(√3x√3)/(√31x√31)/(8x2) absorbed at ~ 450 °C, annealed for 180 s at ~ 450 °C



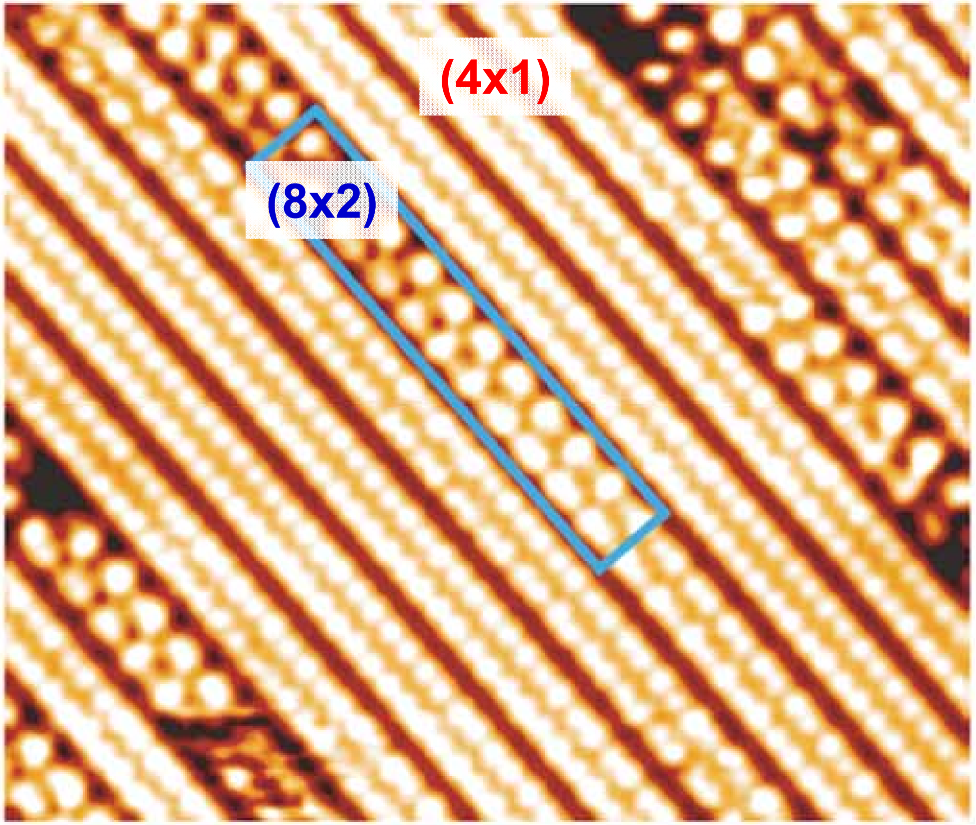
In(8x2) absorbed at ~ 500 °C and annealed for 60 s at ~ 500 °C



In(4x1) heated up (8x2) structure

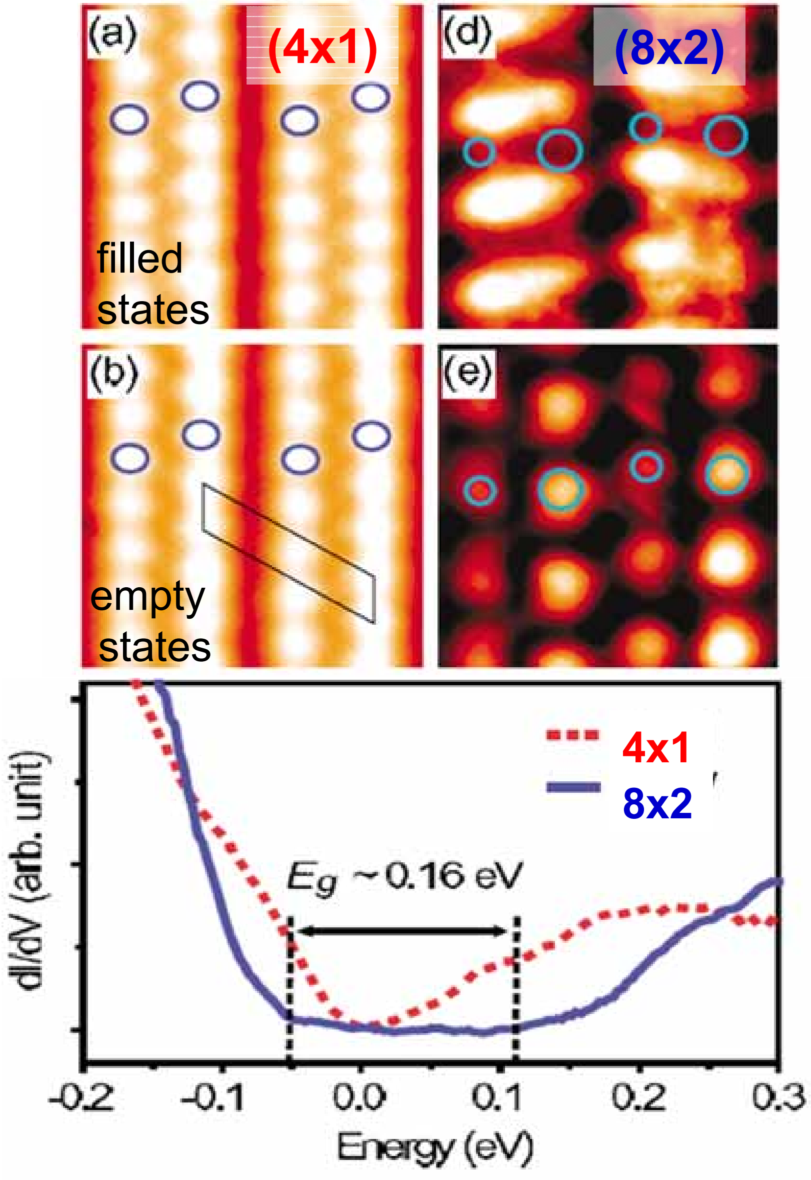
Si(111)- In(8x2)↔(4x1)

1-dim. Indium atom wires on Si(111)



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

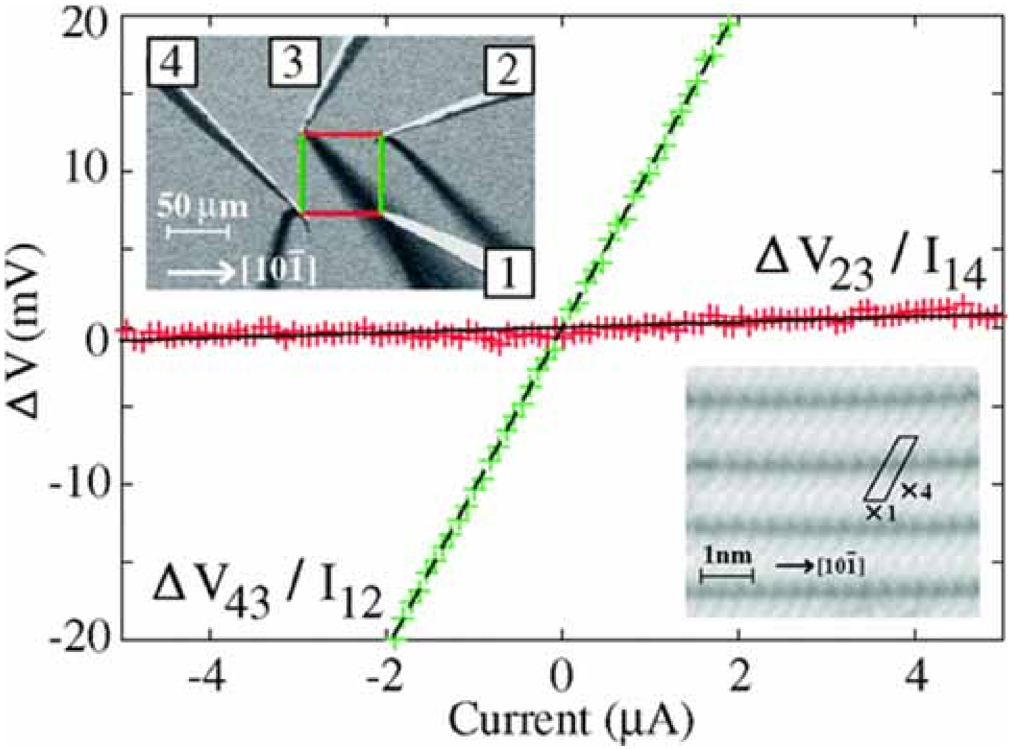
high temperature low temperature



Anisotropic Conductivity

Si(111)-In (4x1) at 300 K

- Conductivity
  parallel to the wires
  60 x larger than perpendicular



T. Kanagawa, R. Hobara, I. Matsuda, T. Tanikawa, A. Natori, and S. Hasegawa, Phys. Rev. Lett. **91**, 036805 (2003)

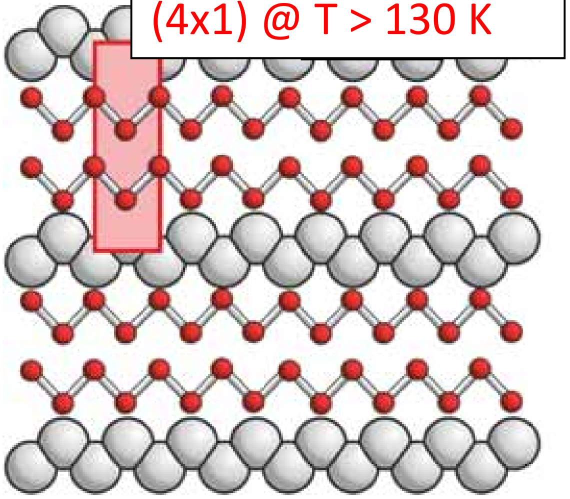
Phasetransition of In/Si(111)

In(4x1)/Si(111) – a quasi 1-dim. metallic wire system

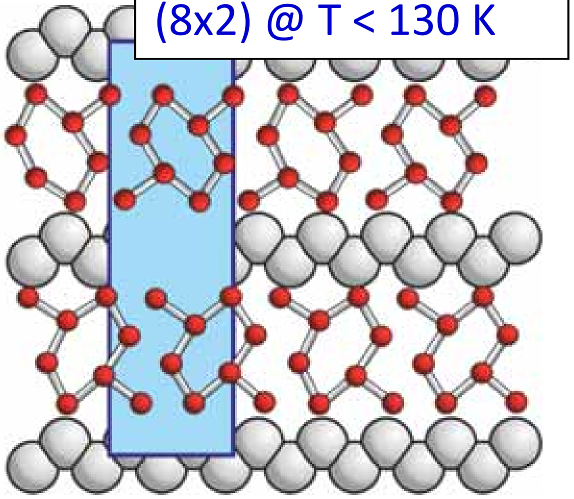
Below T_c ~ 130 K structural phase transition into (8x2):
insulating phase
periodicity doubling

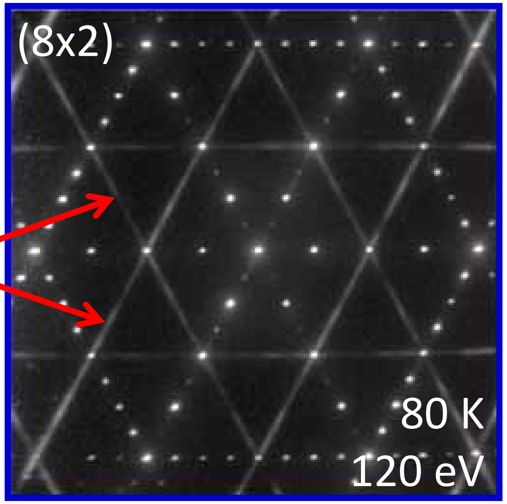
2-fold streaks reflect weak interchain coupling of 1-dim atom wires

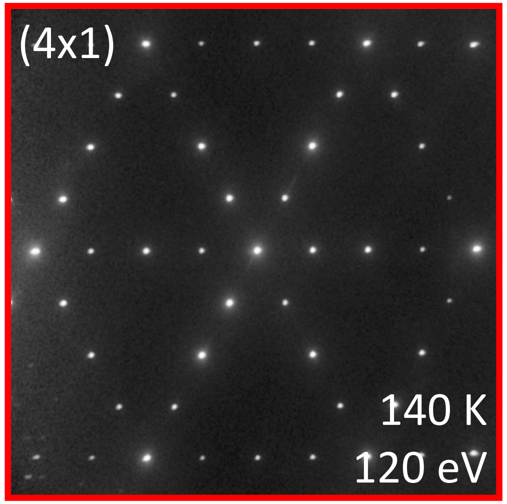
Metallic High Temperature Phase (4x1) @ T > 130 K



Insulating Low Temperature Phase (8x2) @ T < 130 K







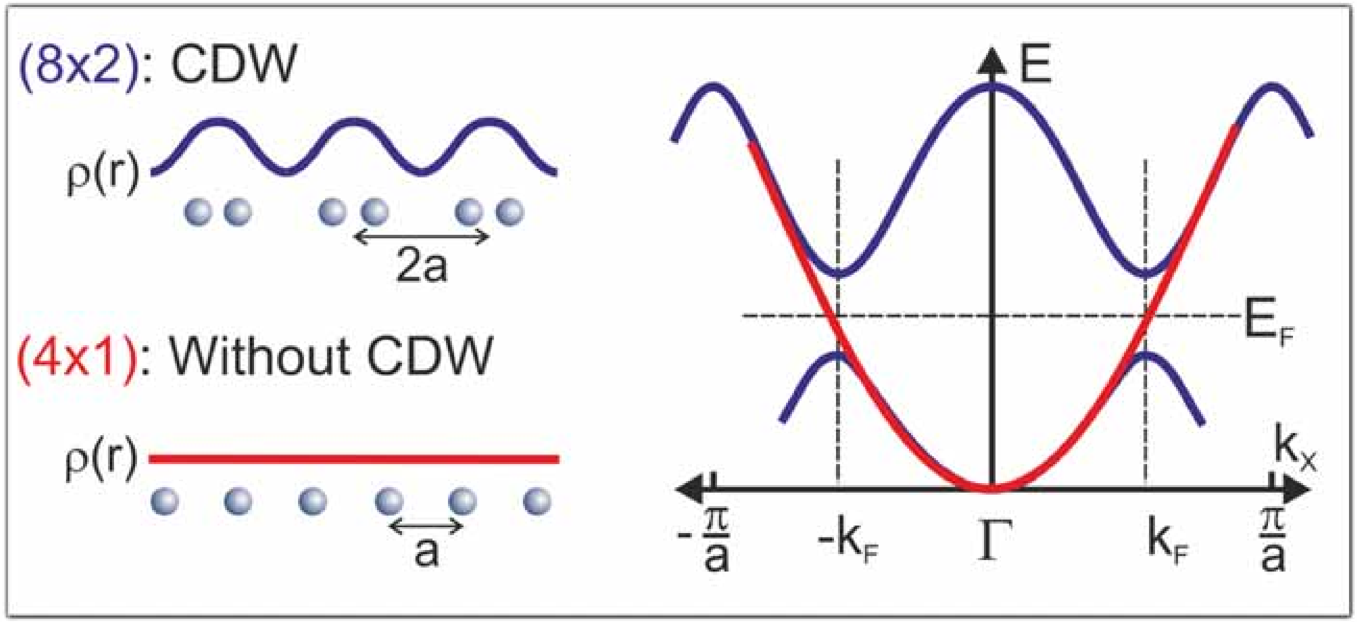
H.W. Yeom, S. Takeda, E. Rotenberg, I. Matsuda, K. Horikoshi, J. Schaefer, C.M. Lee, S. D. Kevan, T. Ohta, T. Nagao, S. Hasegawa, Phys. Rev. Lett. **82**, 4898 (1999),

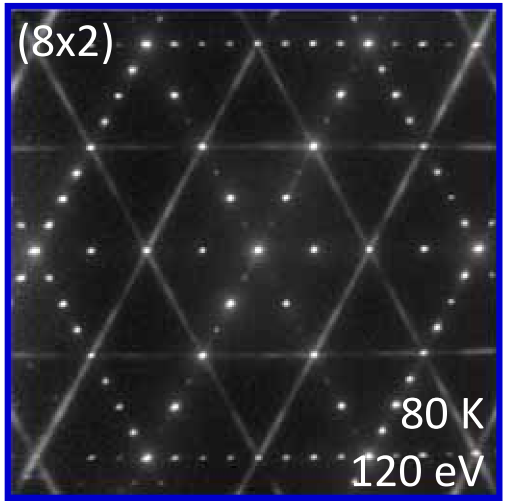
S.V. Ryjkov, et al., Surf. Sci. **488**, 15 (2001).

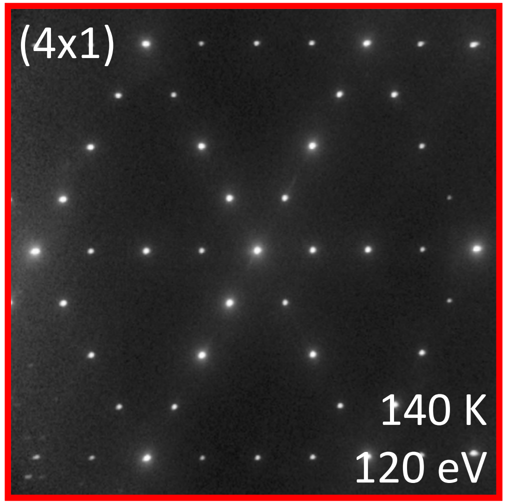
G. Falkenberg, R.L. Johnson, R. Feidenhans'l et al., Phys. Rev. B **59** 12228 (1999)

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 Mechanism

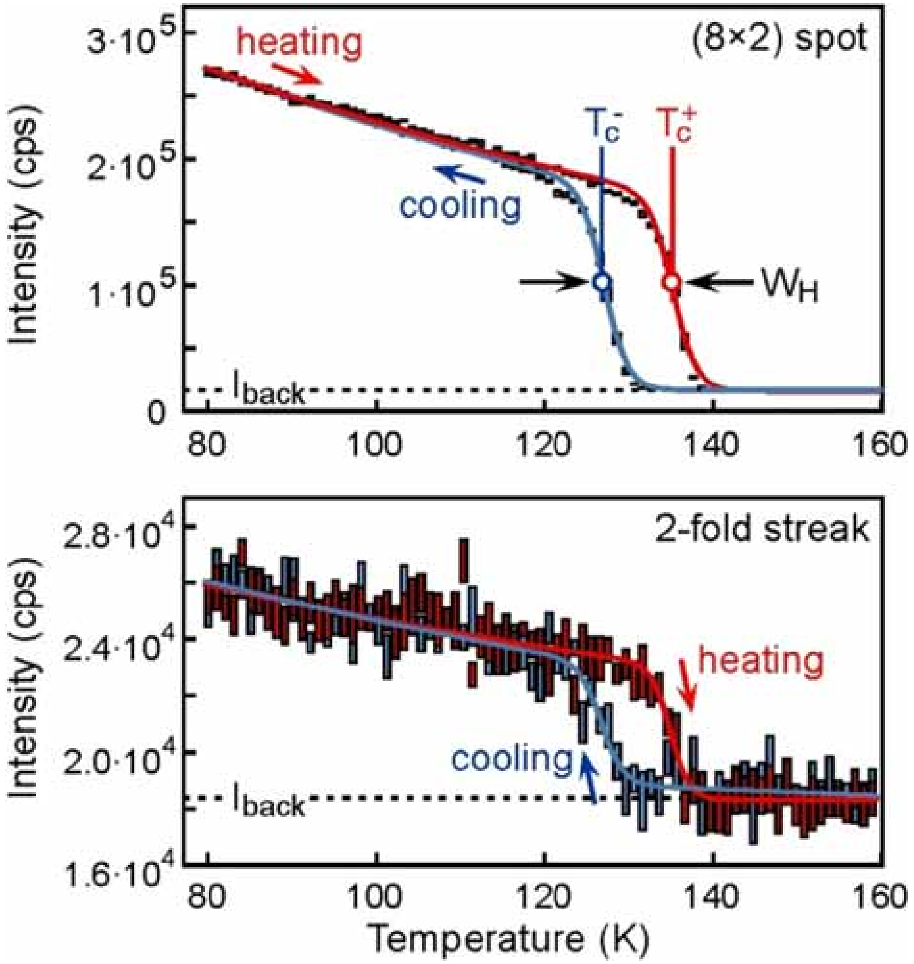


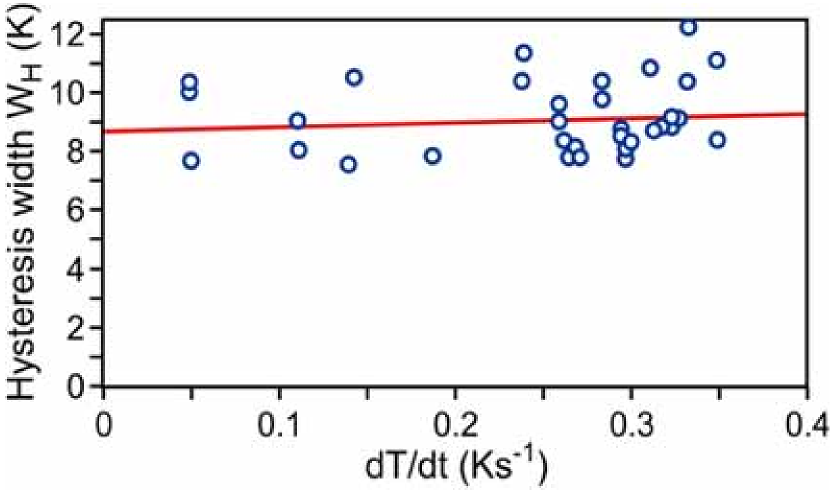




Robust Hysteresis upon T-cycling

- Phase transition temperature $T_c = 130$ K
- Hysteresis width $W_H = 9$ K





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)

1st Order Transition

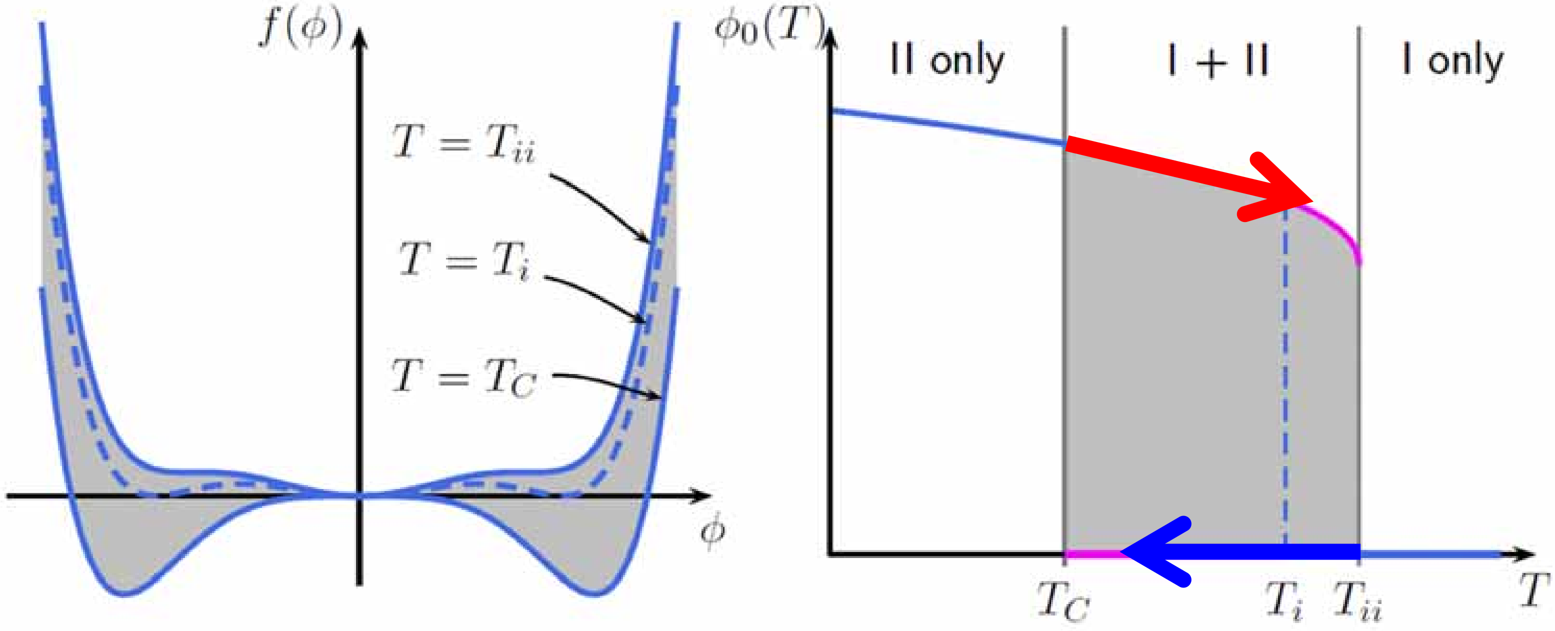
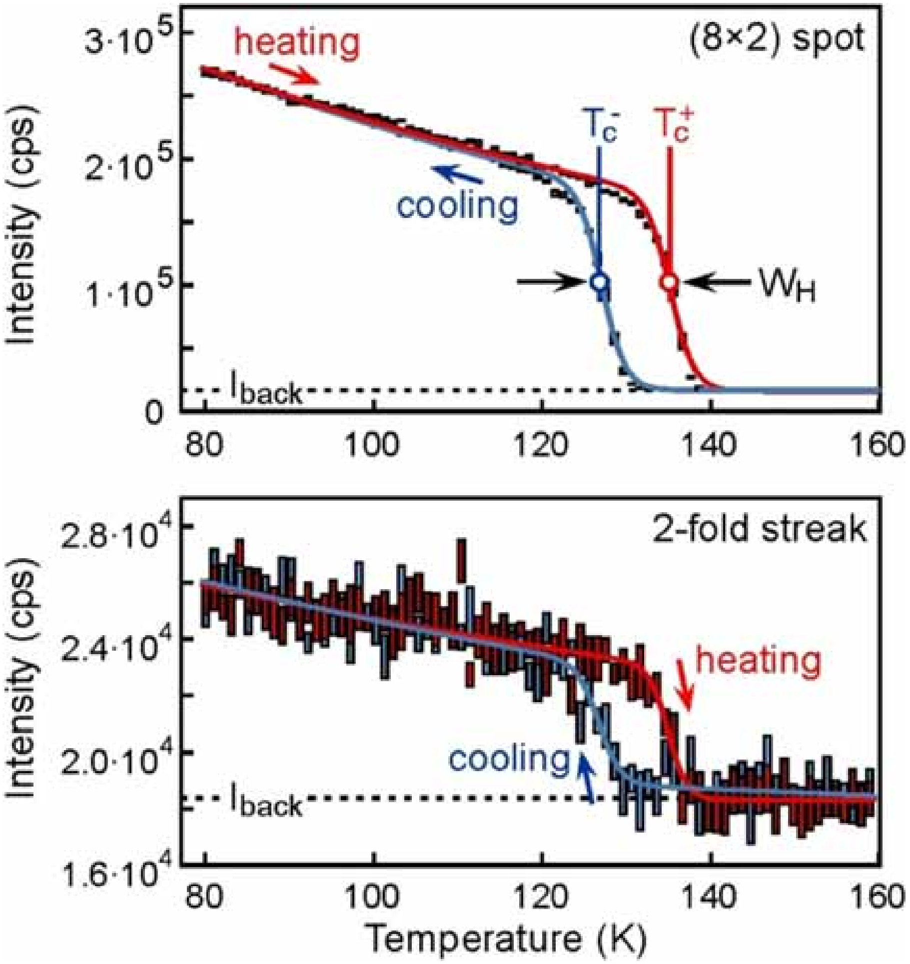
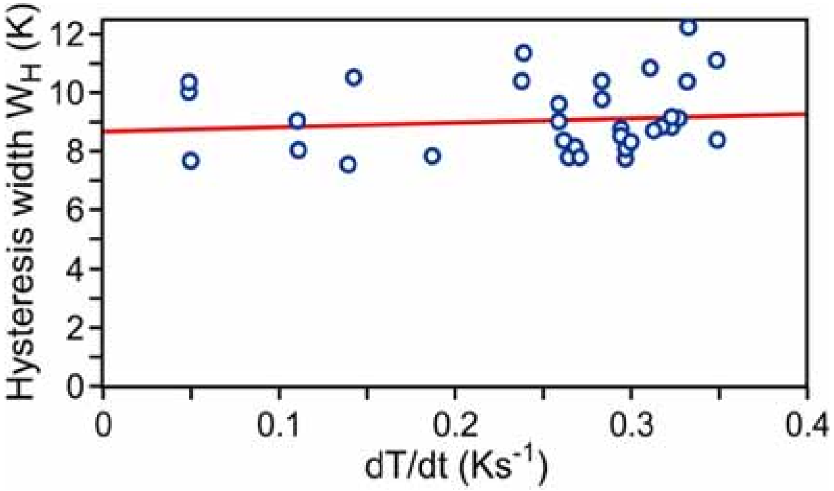


Figure 1.17: First order free energy $f(\phi)$ and $\phi(T)$. Left: Free energy f as function of the order-parameter ϕ. The red curves show the free energy for the 3 characteristic temperatures, i.e. T_C, T_i and T_{ii}. Between the solid red curves, i.e. between $T = T_C$ and $T = T_{ii}$, two stable states exist one of them being meta-stable at a time. The dashed red curve marks the temperature where both states are equal in potential. **Right:** Order-parameter ϕ as function of the temperature T. Stable states, i.e. thermal equilibrium states or the global free energy minimum, are marked in red whereas meta-stable states are colored green. The shaded temperature range corresponds to the shaded area on the left hand side.

Robust Hysteresis upon T-cycling

- Phase transition temperature $T_c = 130$ K
- Hysteresis width $W_H = 9$ K
- Proof of 1st order transition
  => Peierls like distortion [*]
  => **not** order-disorder transition





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[*] 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)

What else can be done?

So far equilibrium thermodynamics…

Now:

Non-equilibrum structrual dynamics of this phase transition
upon impulsive excitation

We will

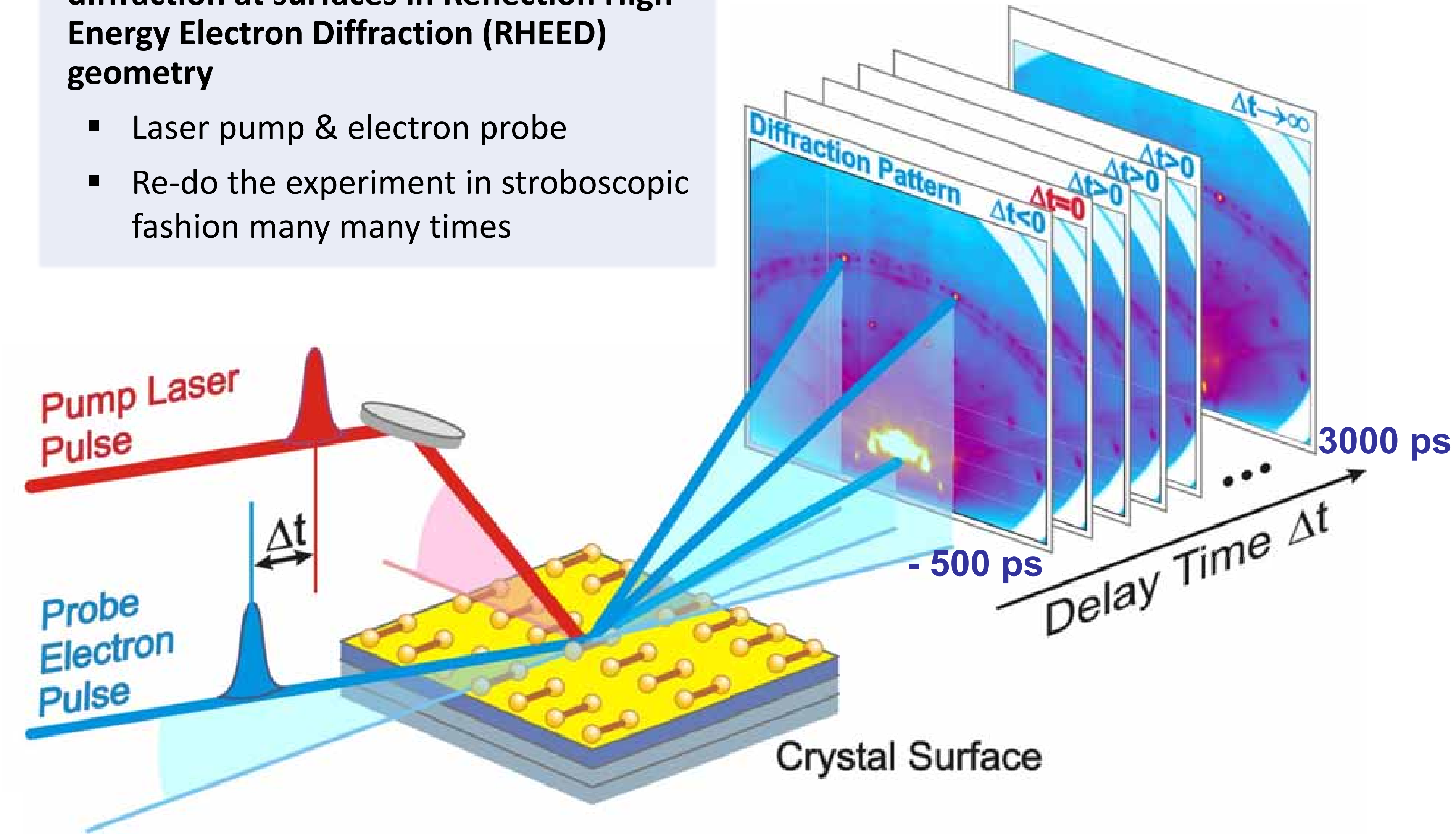
- have (analogon of) undercoolded bottles of champain on a Si surface
- will play domino day with atoms
- and answer the question how fast atoms move

We need, however, diffraction!

TR-RHEED in Pump-Probe Setup

Ultrafast time resolved femtosecond 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



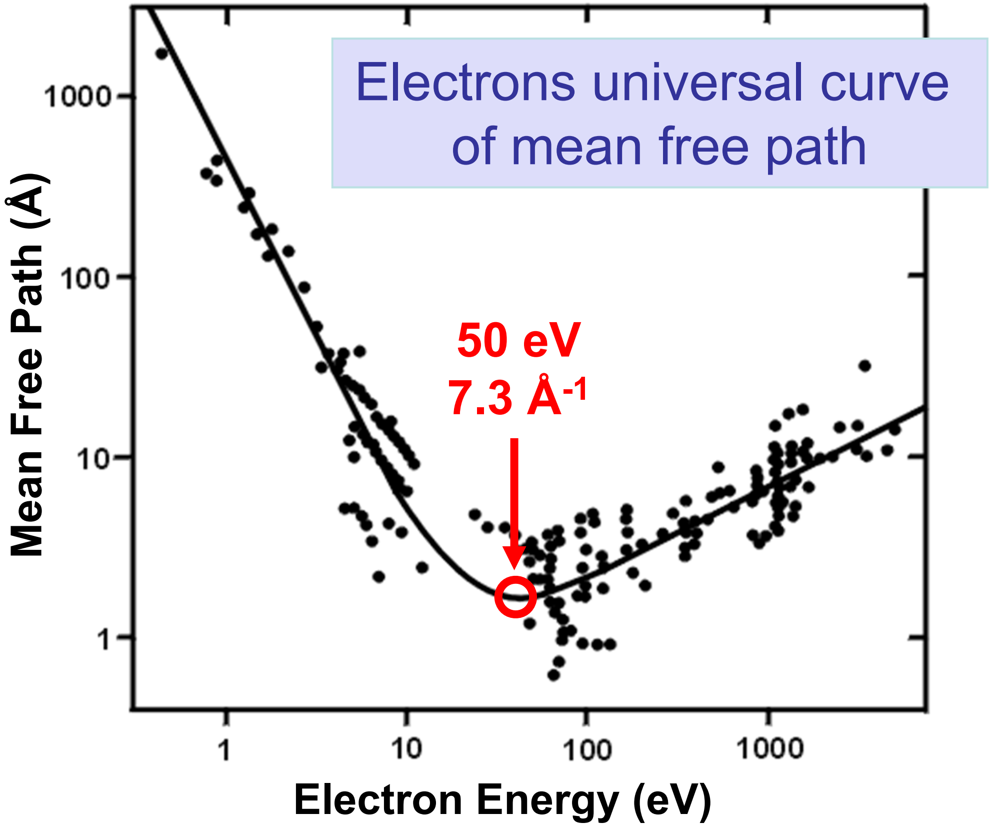
Surface Sensitivity with Electrons

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



Electrons universal curve of mean free path

Surface Sensitivity with Electrons

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

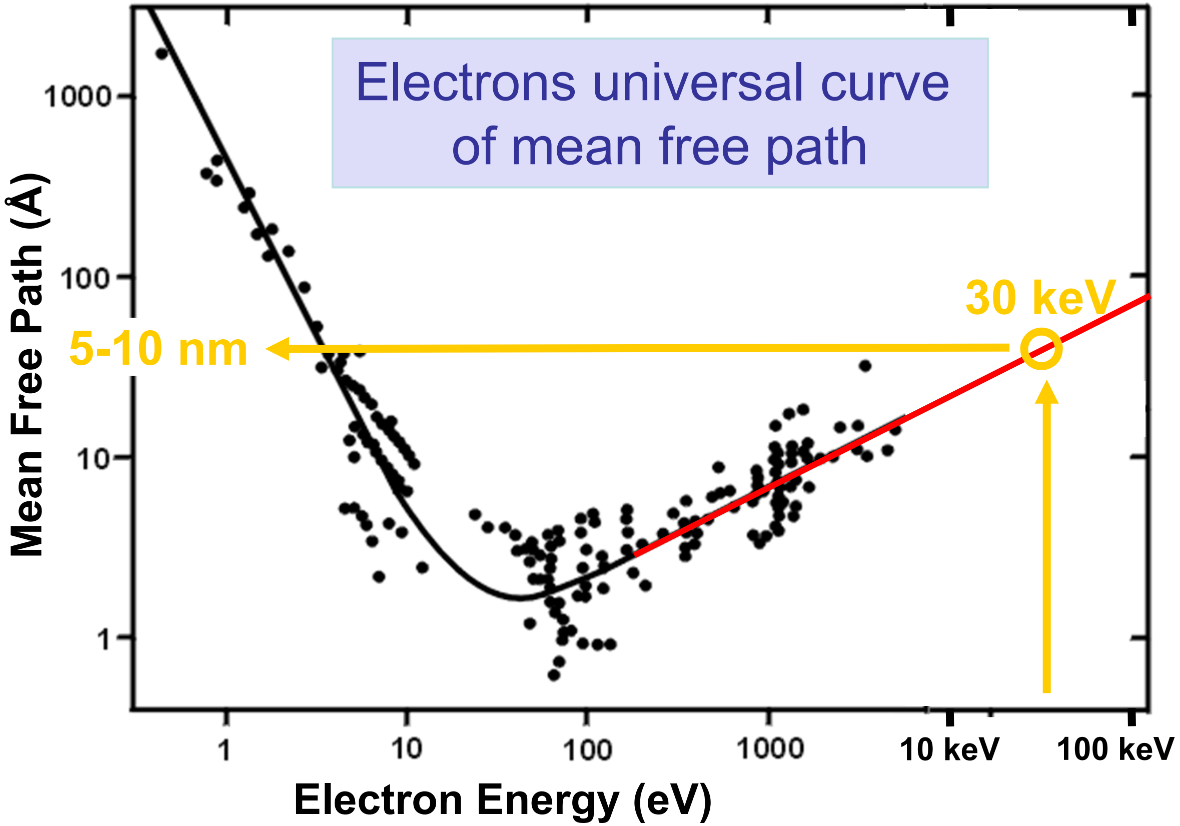
- dominant multiple scattering
  => no simple IV-analysis

=> LEED

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

=> RHEED

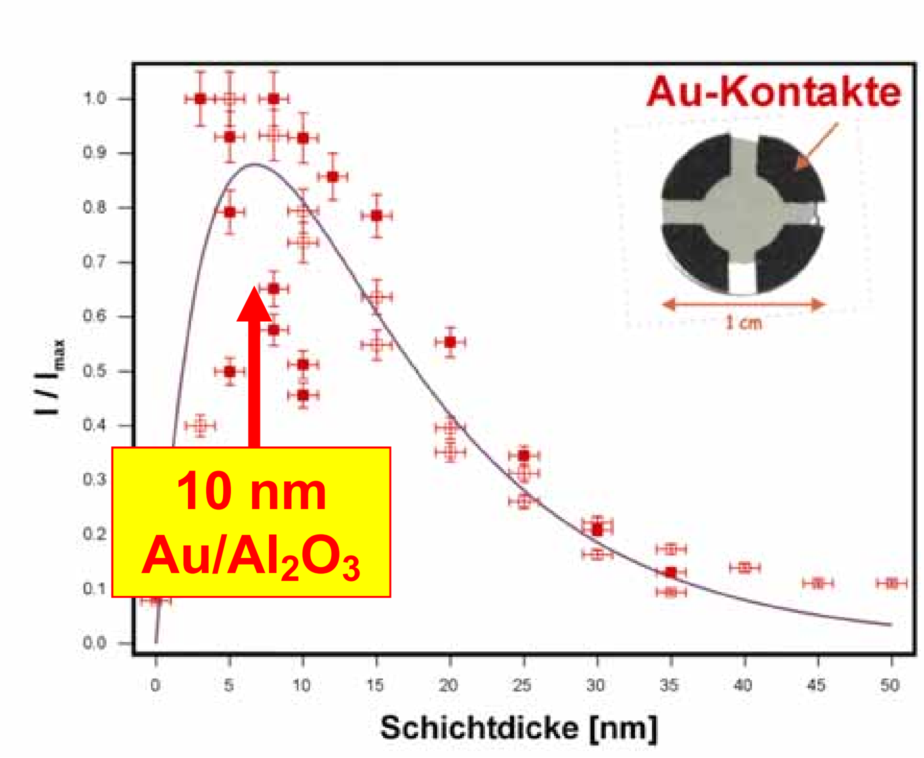
- grazing incidence
- distortion of pattern
- velocity mismatch
  degrade temporal resolution



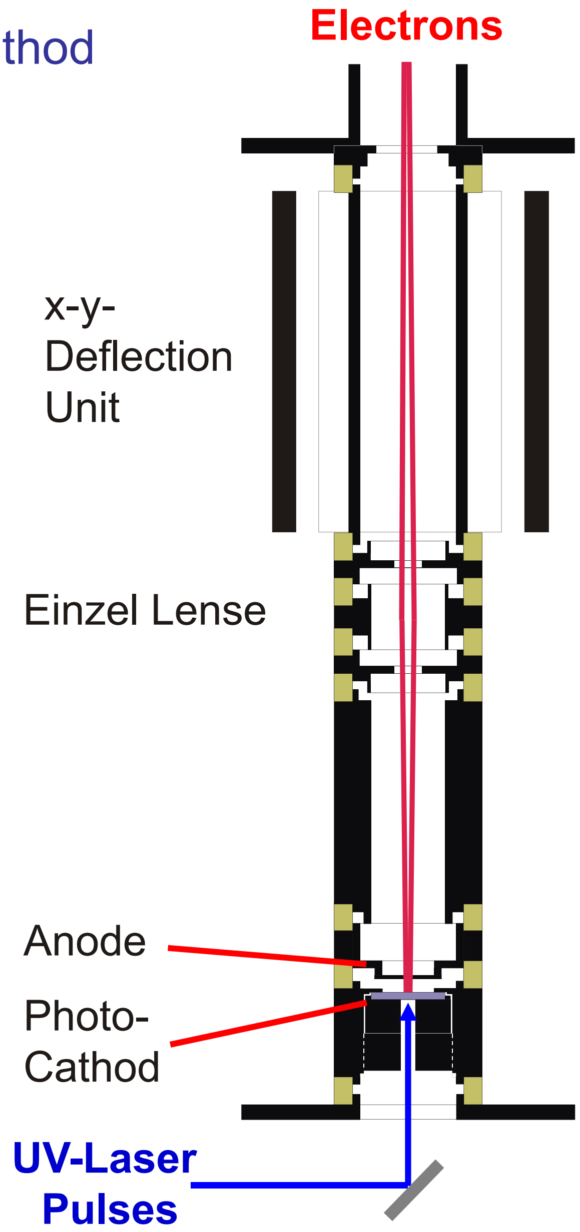
Pulsed RHEED Electron Gun

Electron pulses from backilluminated Au-photocathod

- via external photoeffect induced
  by 80 fs laser pulses at 4.6 eV
- narrow initial energy spread ΔE = 0.1 eV
- 5 – 30 keV electrons
- fine-focus RHEED gun



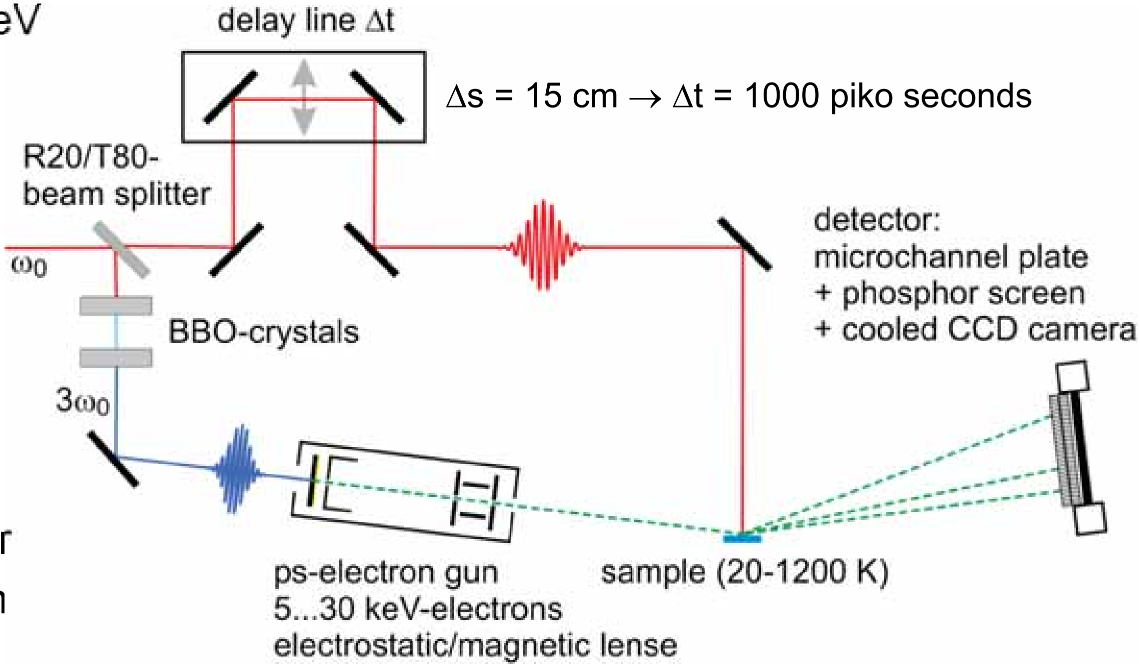
A. Janzen, M. Horn von Hoegen et al., Rev. Sci. Inst. **78**, 013906 (2007)



Surface Sensitivity with Electrons

Electron diffraction

- backilluminated 10 nm Au photocathod
- fast electrons 5 - 30 keV and narrow
  initial energy spread ΔE = 0.1 eV
  minimize temporal broadening
  of fs e-pulses



RHEED

- grazing incidence 2°- 6°
  to ensure surface sensitivity
- vertical momentum
  transfer $\Delta k_\perp = 4 - 10$ Å^{-1}
  => huge signal in Debye Waller
- reversible surface / film system
  => no radiation damage!
  More than 10^7 laserpulses / experiment
- velocity mismatch limits temporal resolution to 20 ps @ 30 keV,
  (in the meantime solved that problem!)

A. Janzen, M. Horn von Hoegen et al., Rev. Sci. Inst. **78**, 013906 (2007)

A. Hanisch-Blicharski, A. Janzen, B. Krenzer, S. Wall, F. Klasing, A. Kalus,
T. Frigge, M. Kammler, M. Horn-von Hoegen, Ultramicroscopy **127**, 2 (2013)

Experimental Setup

fs Laser Pulses

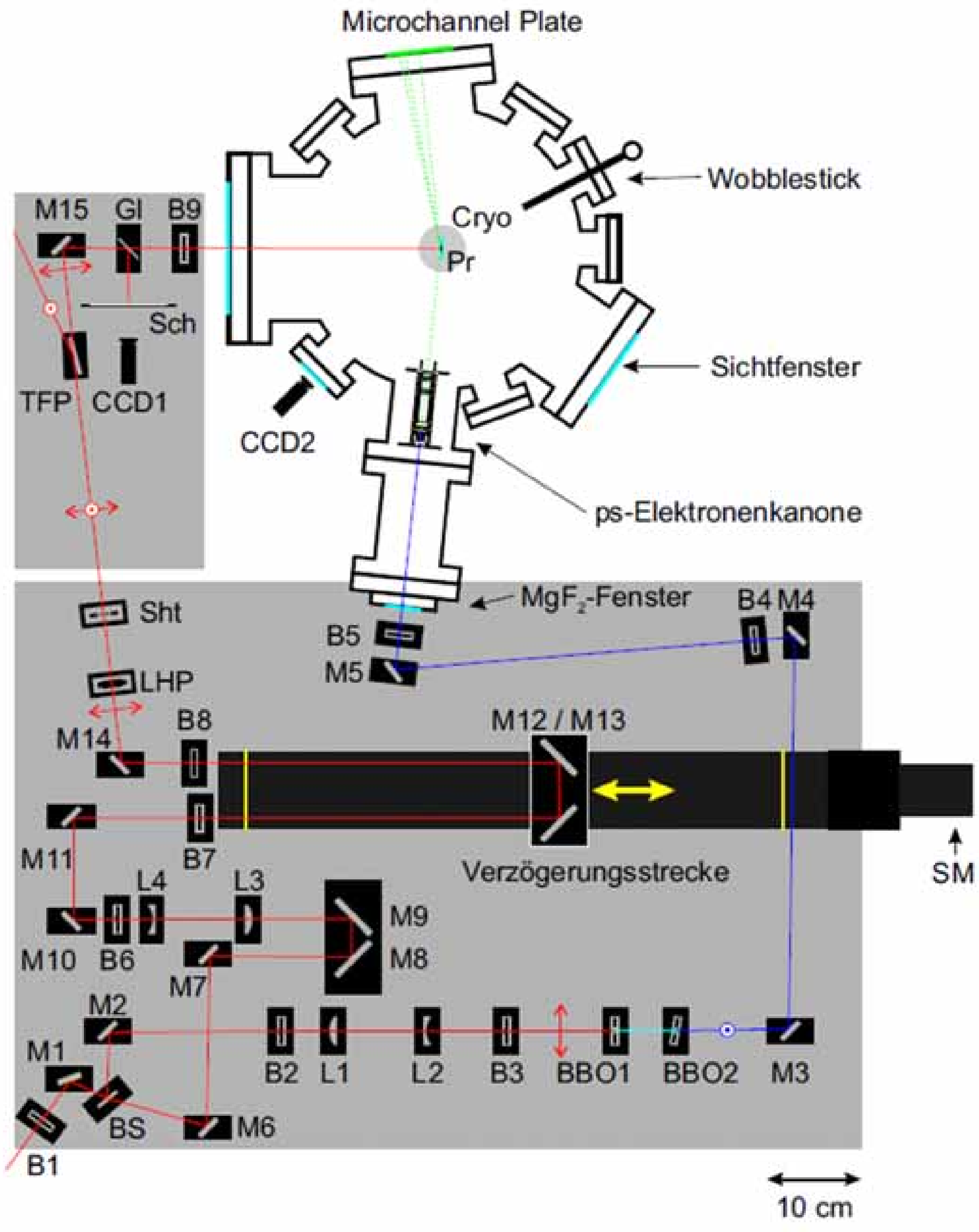
- Ti-Saphire amplifier system
- λ = 800 nm, $\hbar\omega$ = 1.55 eV
- 80 fs, 1 mJ per pulse
- Fluence of up to 10 mJ/cm^2, i.e., 10^{12} W/cm^2
- 5 kHz repetition rate

UHV-System

- $p < 1 \times 10^{-10}$ mbar
- Sample 20 K – 1200 °C
- In-situ deposition of Bi, Pb, In …

e-Diffraction

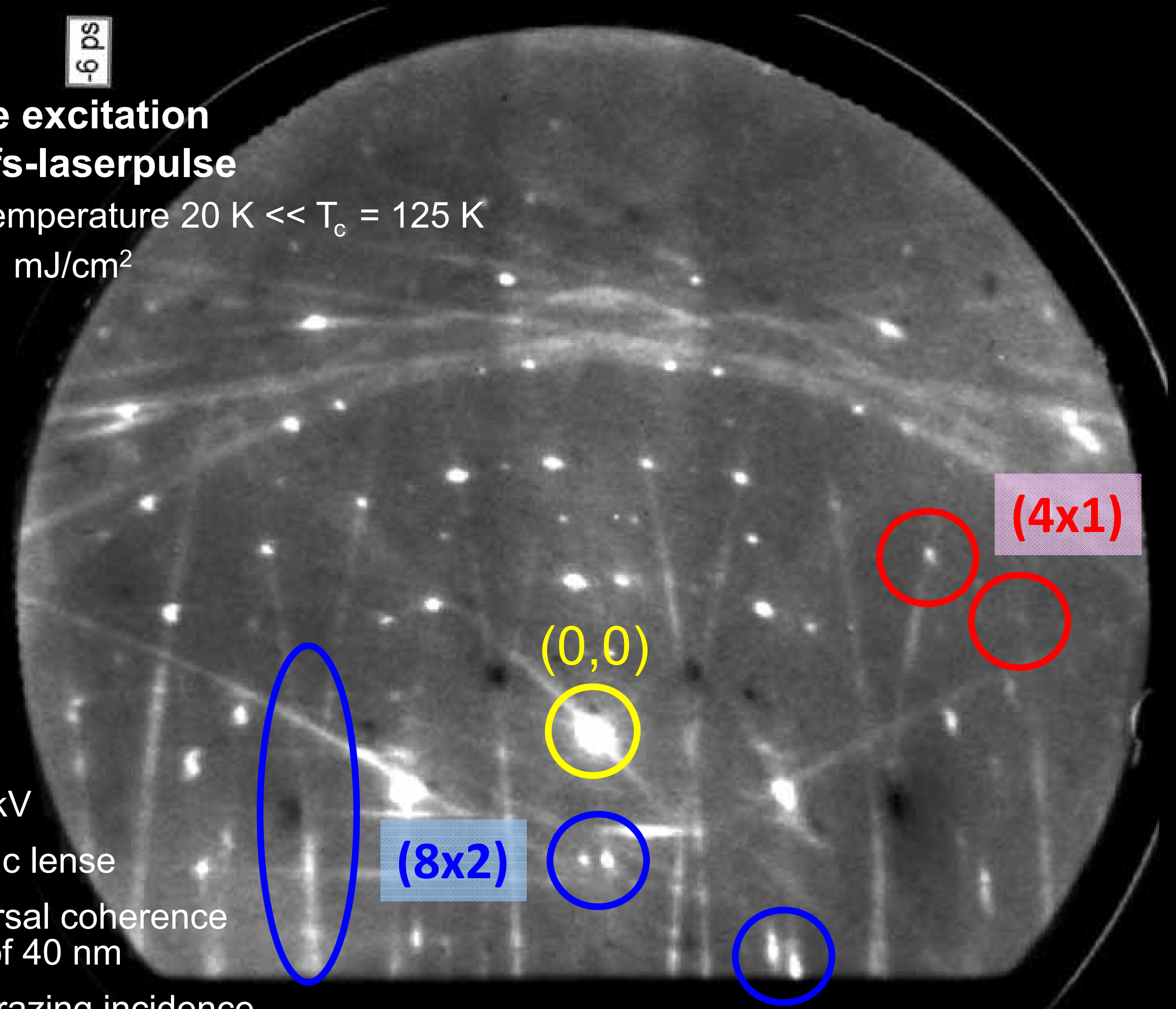
- RHEED 5 – 30 keV
- Image amplification by MCP
- Cooled 16 bit CCD camera



Movie of transition

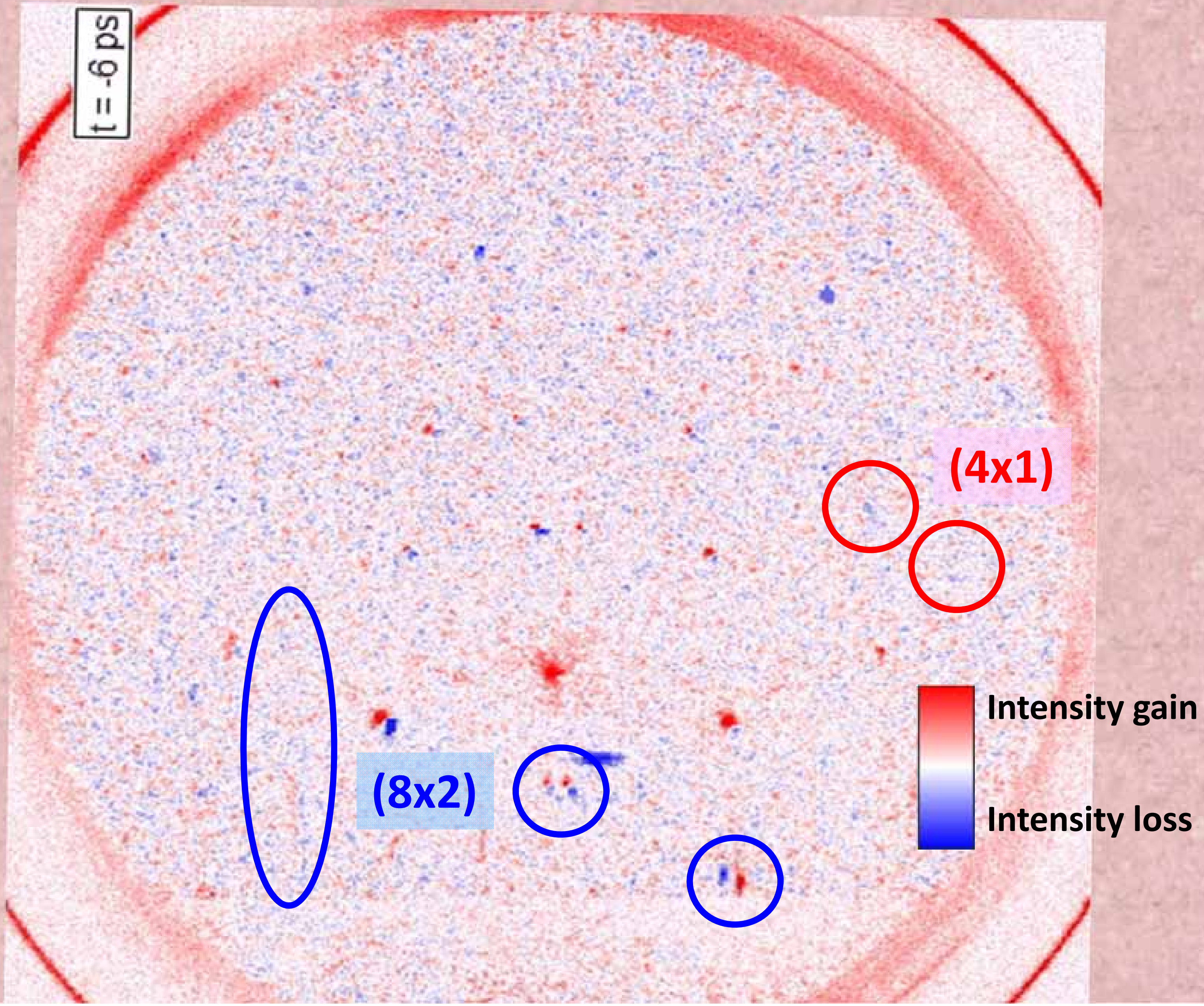
Impulsive excitation through fs-laserpulse

- Base temperature 20 K << T_c = 125 K
- Φ = 2.1 mJ/cm^2

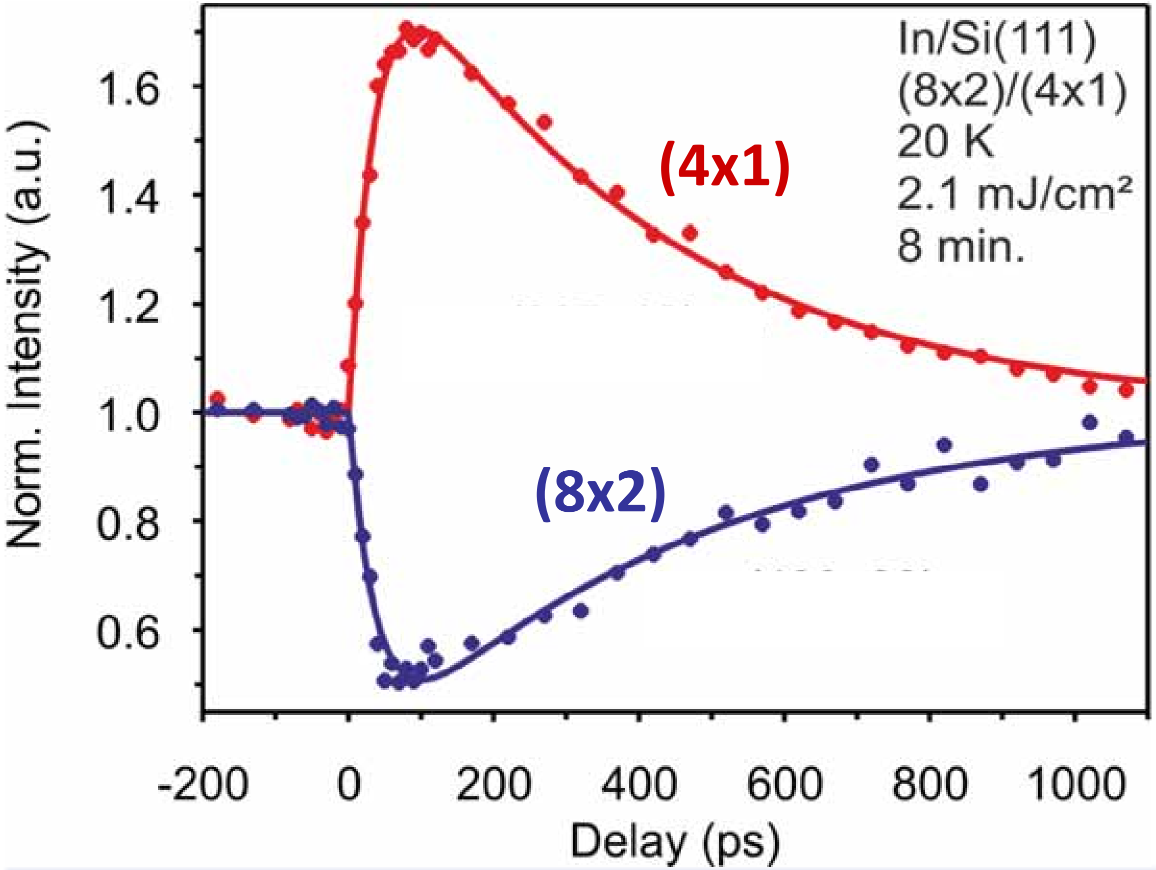


- E = 30 kV
- magnetic lense
- transversal coherence length of 40 nm
- 2°- 4° grazing incidence

Movie of transition – gains & losses



TR-RHEED: In/Si(111)

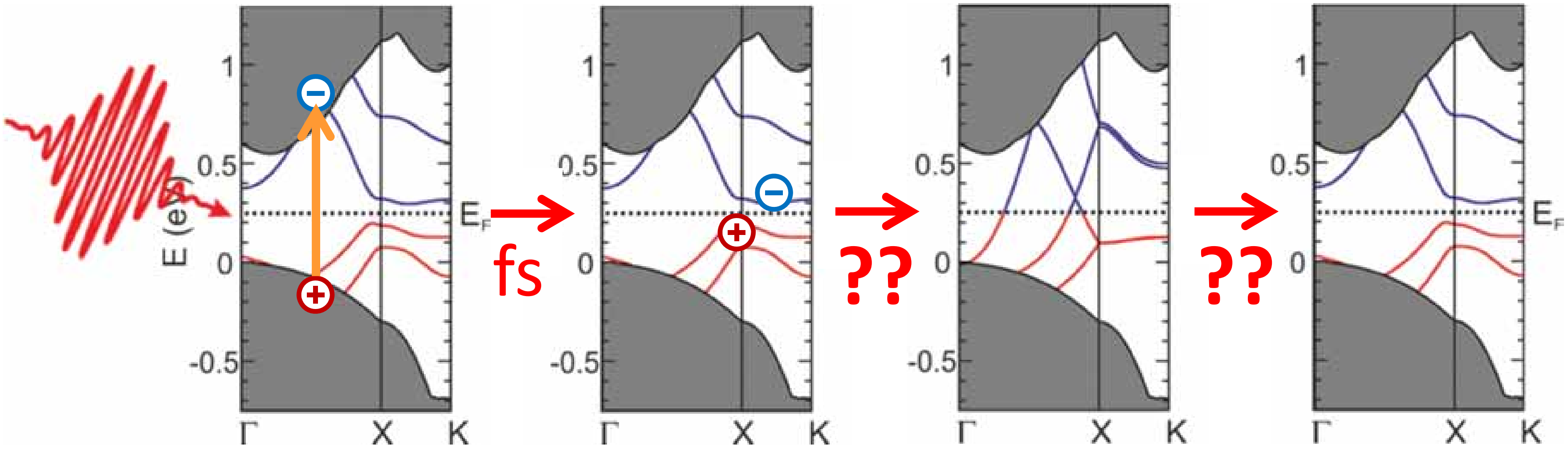


Displacive structural phase transition

- Surface at 20 K well below $T_c = 130$ K
- Confirmed that almost no heating of surface $\Delta T < 30$ K
- Photo induced, electronic (and not a thermal) excitation of phase transition

S. Möllenbeck, A. Hanisch-Blicharski, … M. Horn-von Hoegen, MRS Symp. Proc. **1230**, 3 (2009

Electronic Excitation



(4x1)

(8x2)

Photo Excitation

Carrier Relaxation

Excited state

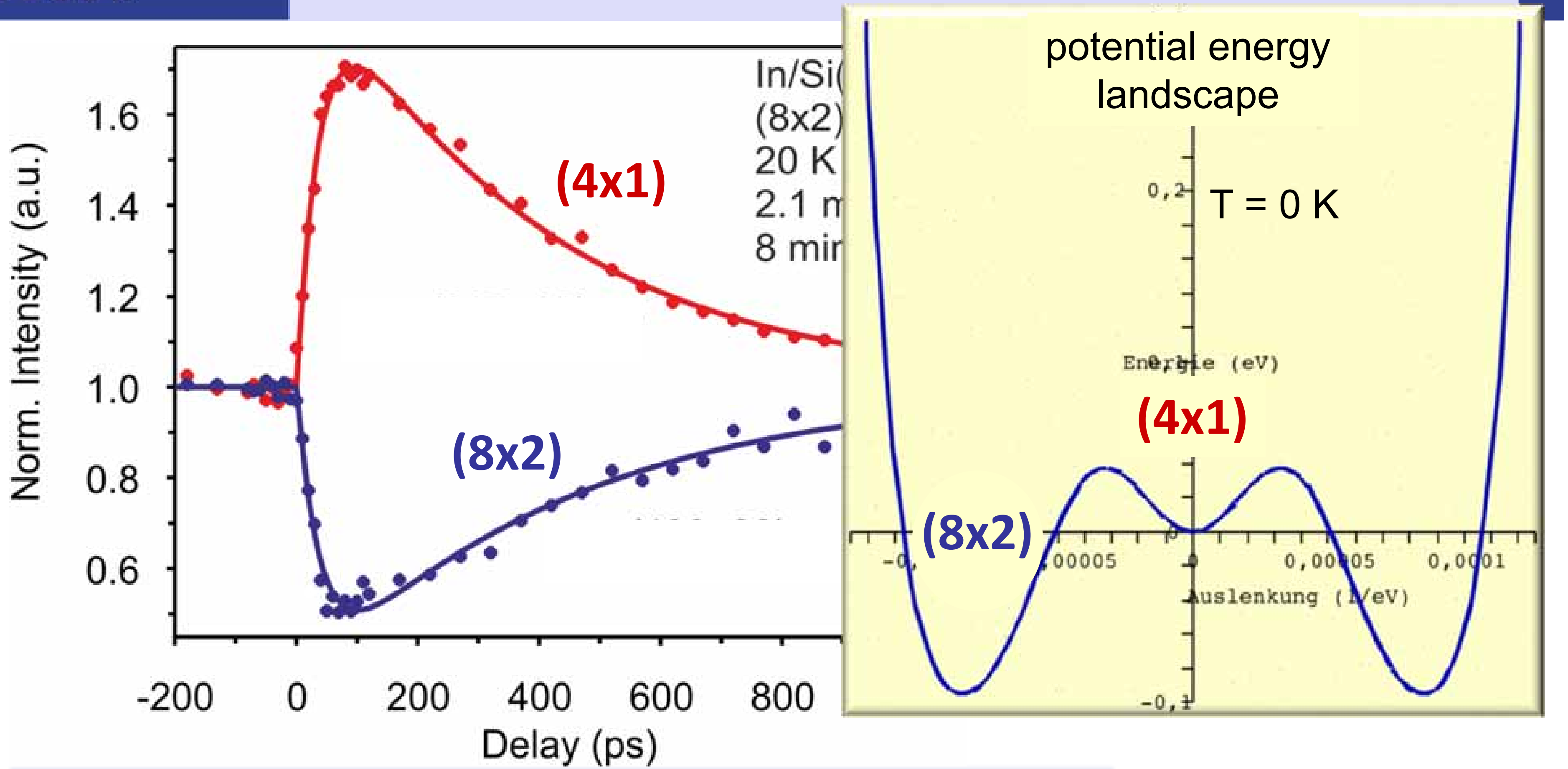
Ground state

Electronic excitation:

- Laser excited electron-hole pairs
- Relaxation of hot carriers to top and bottom of bands
- Depopulation of states responsible for Peierls transition
- Lifting of (8x2) Peierls distortion, closing of bandgap, melting of CDW, and transition to (4x1) excited state

Band structure calculation: W.G. Schmidt, M. Babilon, C. Thierfelder, S. Sanna, S. Wippermann, Phys. Rev. B **84**, 115416 (2011)

TR-RHEED: In / Si(111)

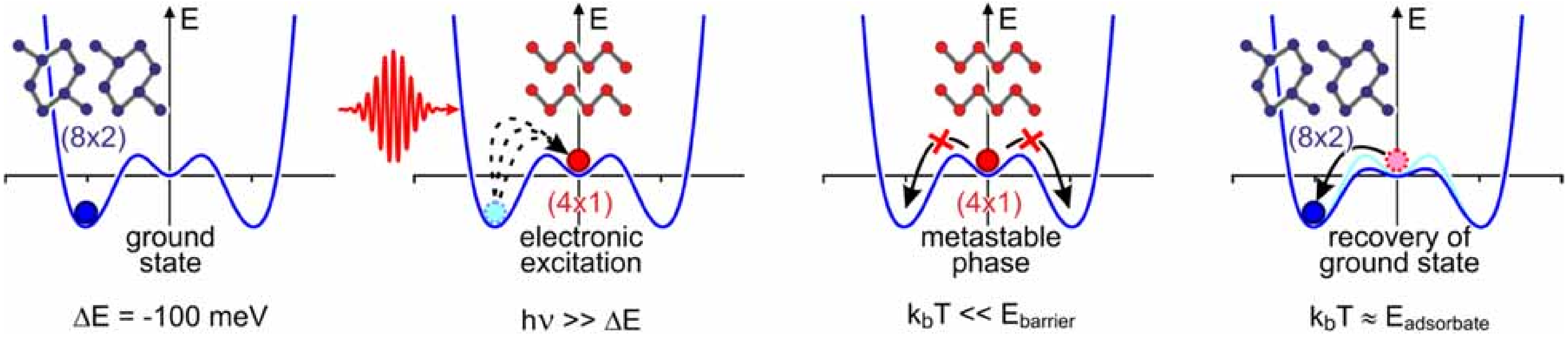


Why does the excited (4x1) phase survive that long at such low temperature?

- Life time of electronic excitations: few 10 to some 100 fs
- Here: hundreds of ps

W.G. Schmidt,
S. Sanna et al.,
University Paderborn

Supercooled Surface Phase

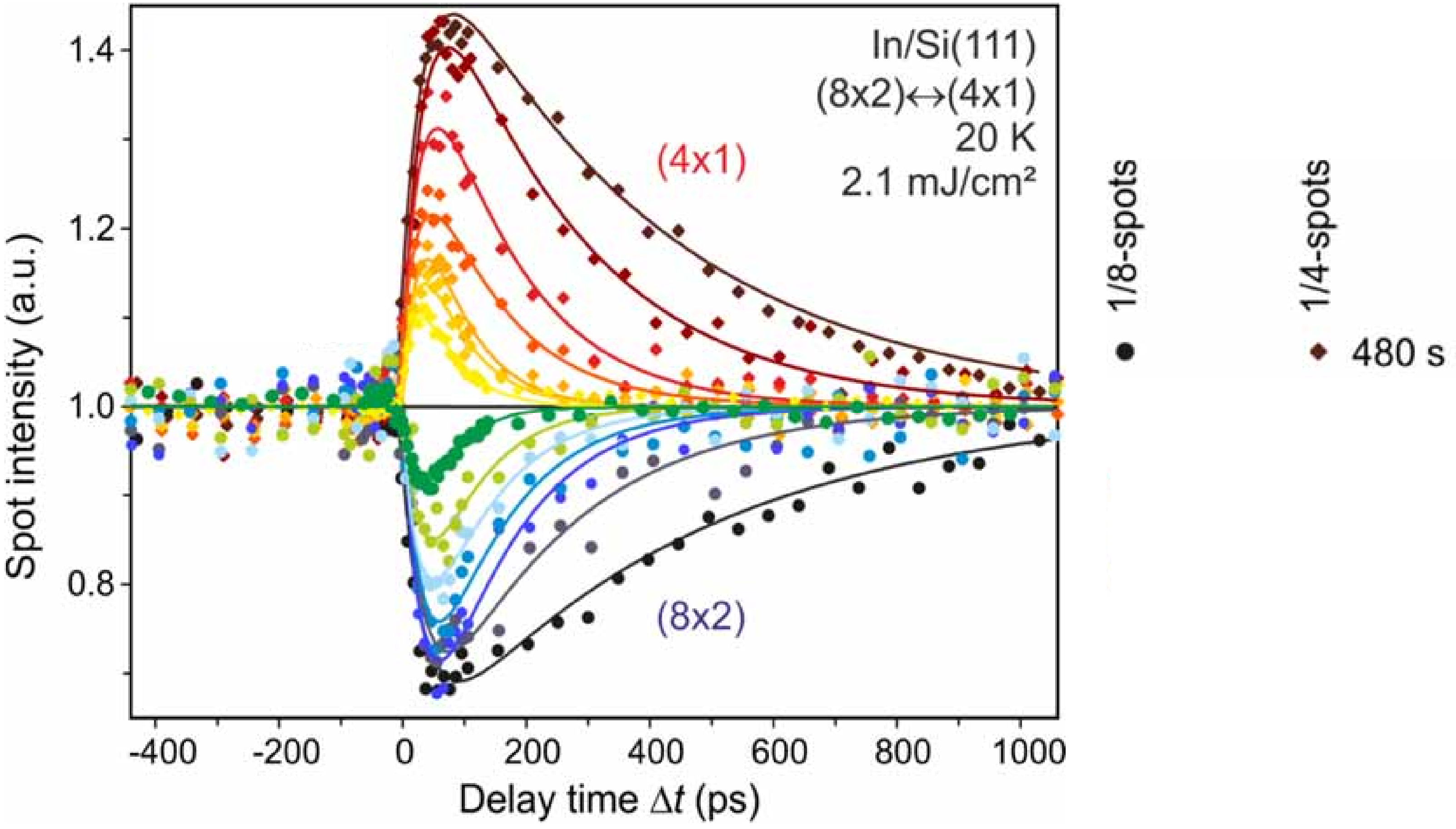


Trapped in a supercooled metastable surface phase:

- 40 meV barrier hinders recovery of low temperature (8x2) groundstate
- State far away from equilibrium – unaccessible under equilibrium conditions

Hidden State of Matter !

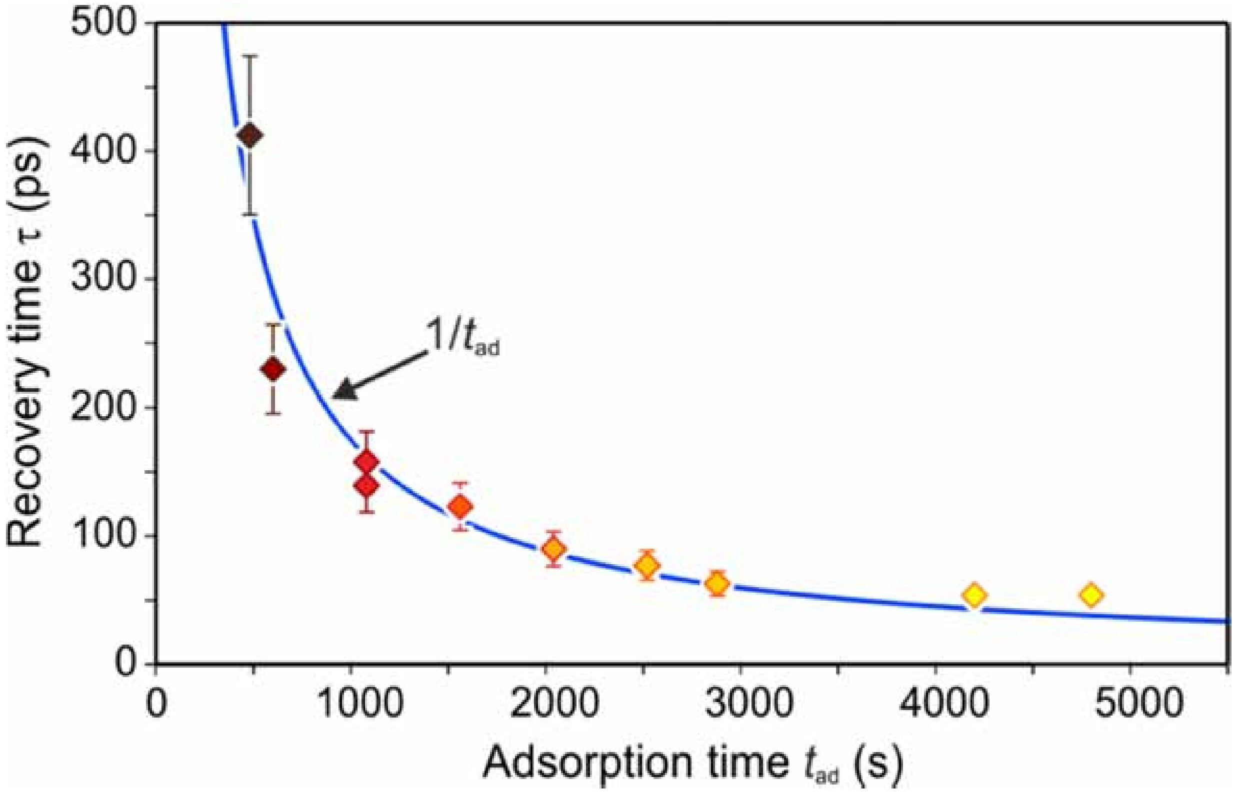
Relaxation Dynamics



Recovery of groundstate sensitive to

- Adsorption from residual gas in UHV, most likely H$_2$0 acting as seeds
- 1-dim. atomic wire system: expect an (adsorption time)$^{-1}$ behavior

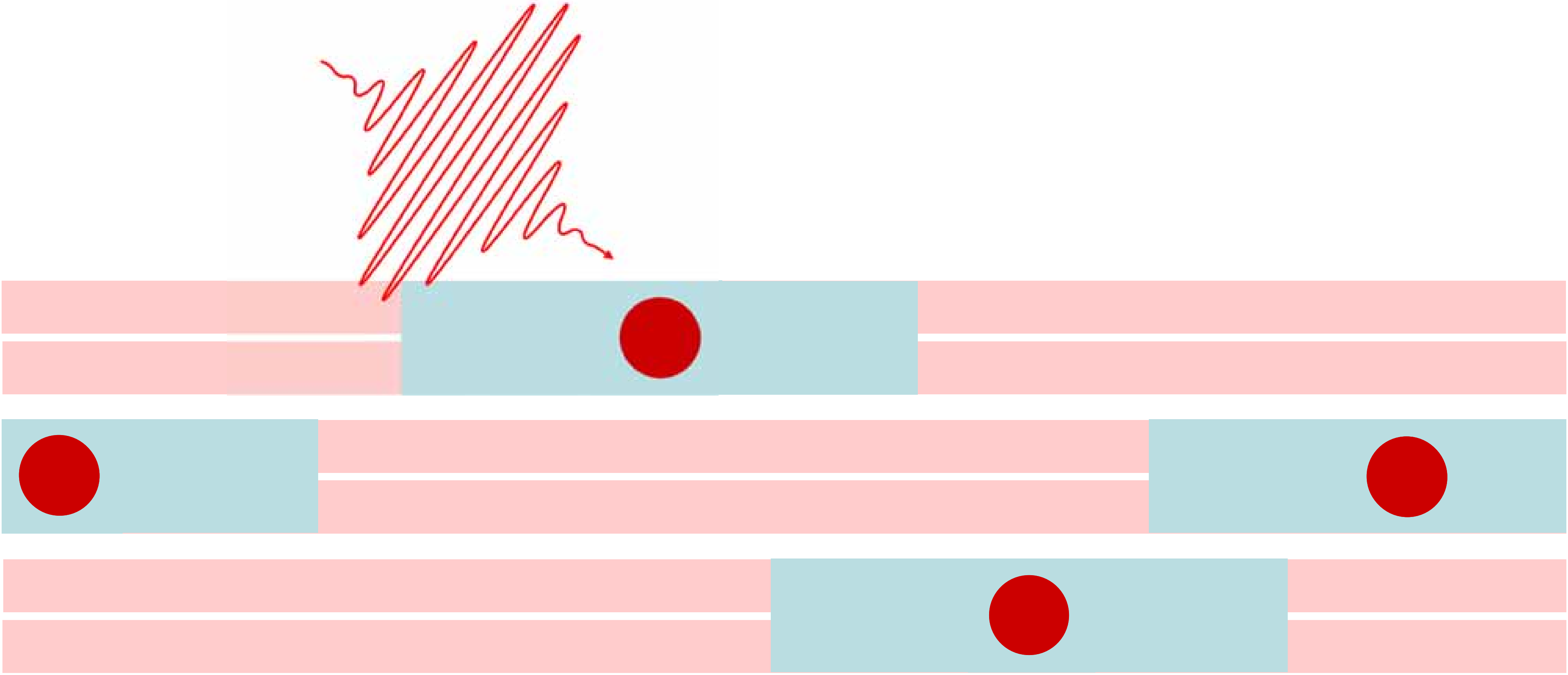
Relaxation Dynamics



Recovery of groundstate sensitive to

- Adsorption from residual gas in UHV, most likely H_20 acting as seeds
- 1-dim. atomic wire system: expect an (adsorption time)$^{-1}$ behavior

Relaxation Dynamics



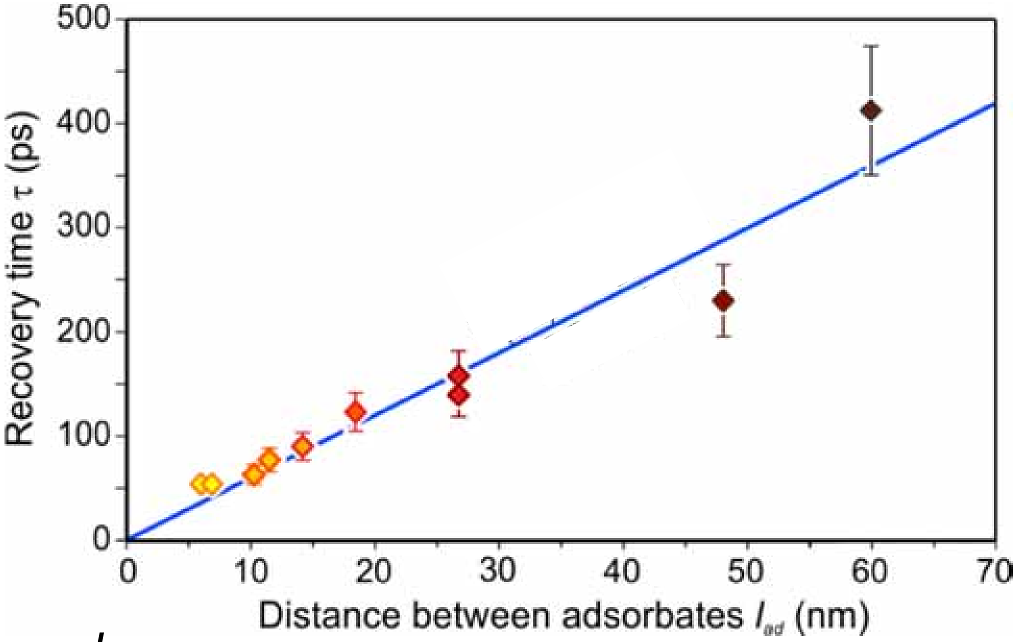
(8x2) (4x1) Adsorbates

Relaxation Dynamics

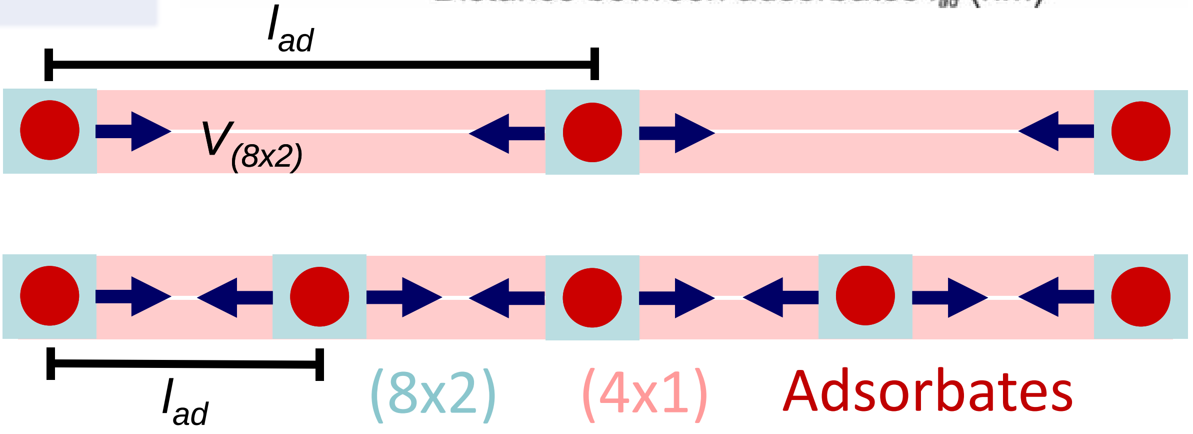
Adsorbates trigger phase transition

- Adsorbates act as seed for recovery into (8x2) groundstate
- Recovery front propagates only 1-dimensionally:

  => constant velocity
- Take density of adsorbates from literature [1),2)] and correlate with change of T_c :
- **velocity of phase front $\approx$ 100 m/s**

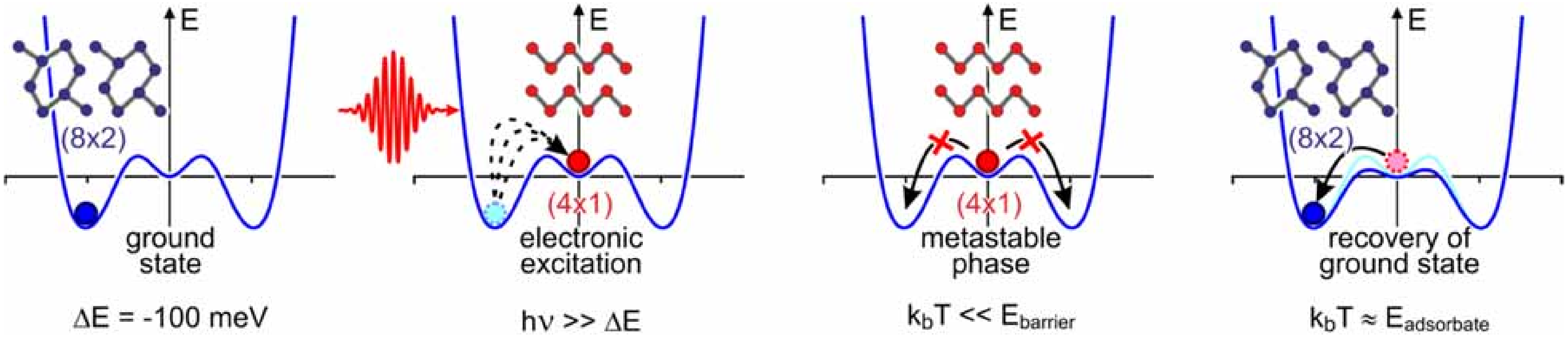


1) G. Lee, S.-Y. Yu, H. Shim, W. Lee, J.-Y. Koo, Phys. Rev. B **80**, 075411 (2009)
2) T. Shibasaki et al., Phys. Rev. B **81**, 035314 (2010)



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)

Supercooled Surface Phase



Supercooled metastable surface phase:

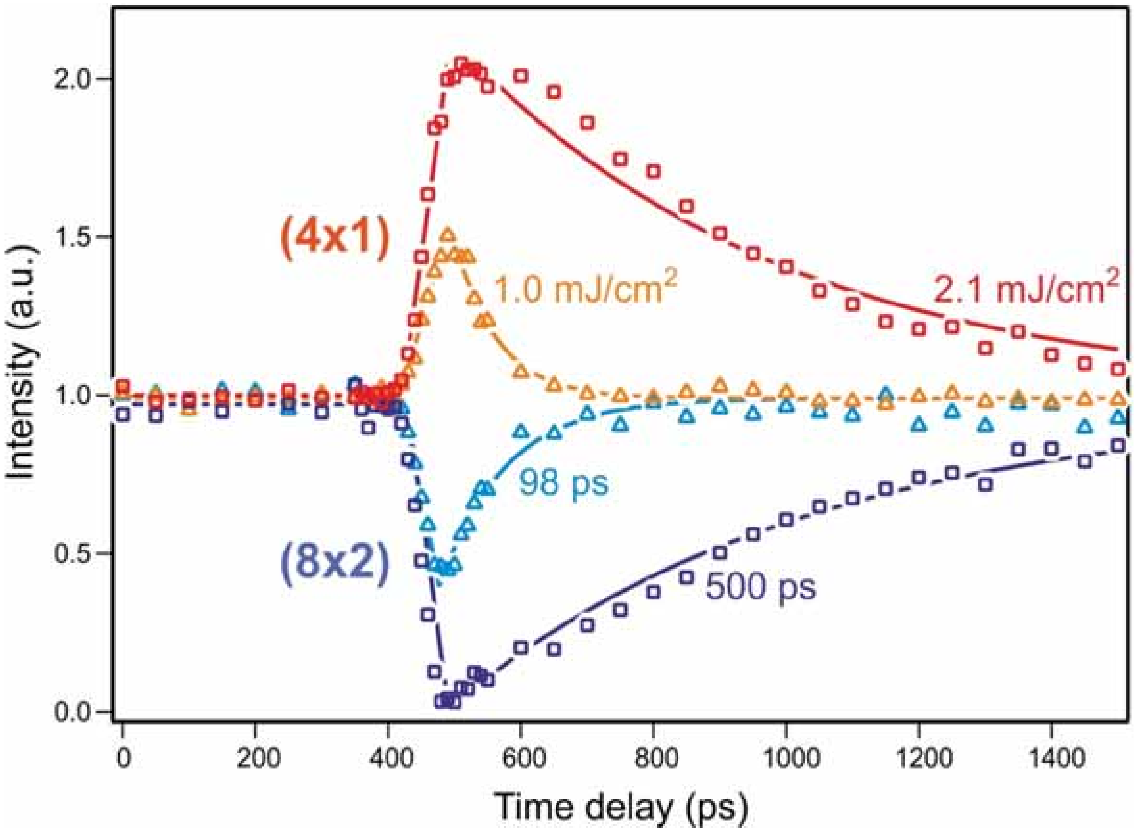
- 40 meV barrier hinders recovery of low temperature (8x2) groundstate
- State far away from equilibrium – unaccessible under equilibrium

Adsorbates trigger phase transition

- Pre-existing adsorbates act as seed for recovery into (8x2) groundstate
- Recovery front propagates only 1-dimensionally @ 100 m/s
- Like a row of falling dominos …

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)

Transient Spot Profile Analysis



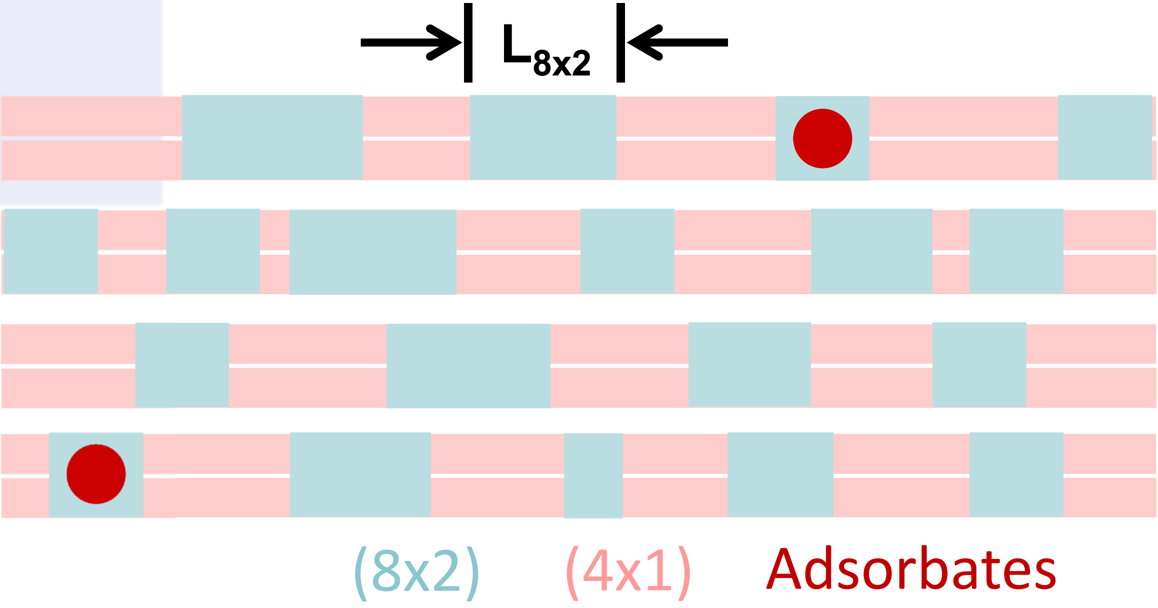
Phase transition is incomplete due to weak laser excitation

- Only ~50% of (8x2) is converted into (4x1)
- Recovery time **independent** on adsorbate coverage and always 50-100 ps

Transient Spot Profile Analysis

Pattern of small (8x2) and (4x1) domains on surface

- Remnant (8x2) groundstate expands linear in time – no seeds necessary
- $L_{8x2} = 2 \cdot v_{8x2} \cdot t$
- (8x2) regions act as slit
  for electron diffraction
  => broadening of (8x2) spots
- FWHM ~ $(L_{8x2})^{-1}$ ~ $(2\ v_{8x2}\ t)^{-1}$



Transient Spot Profile Analysis

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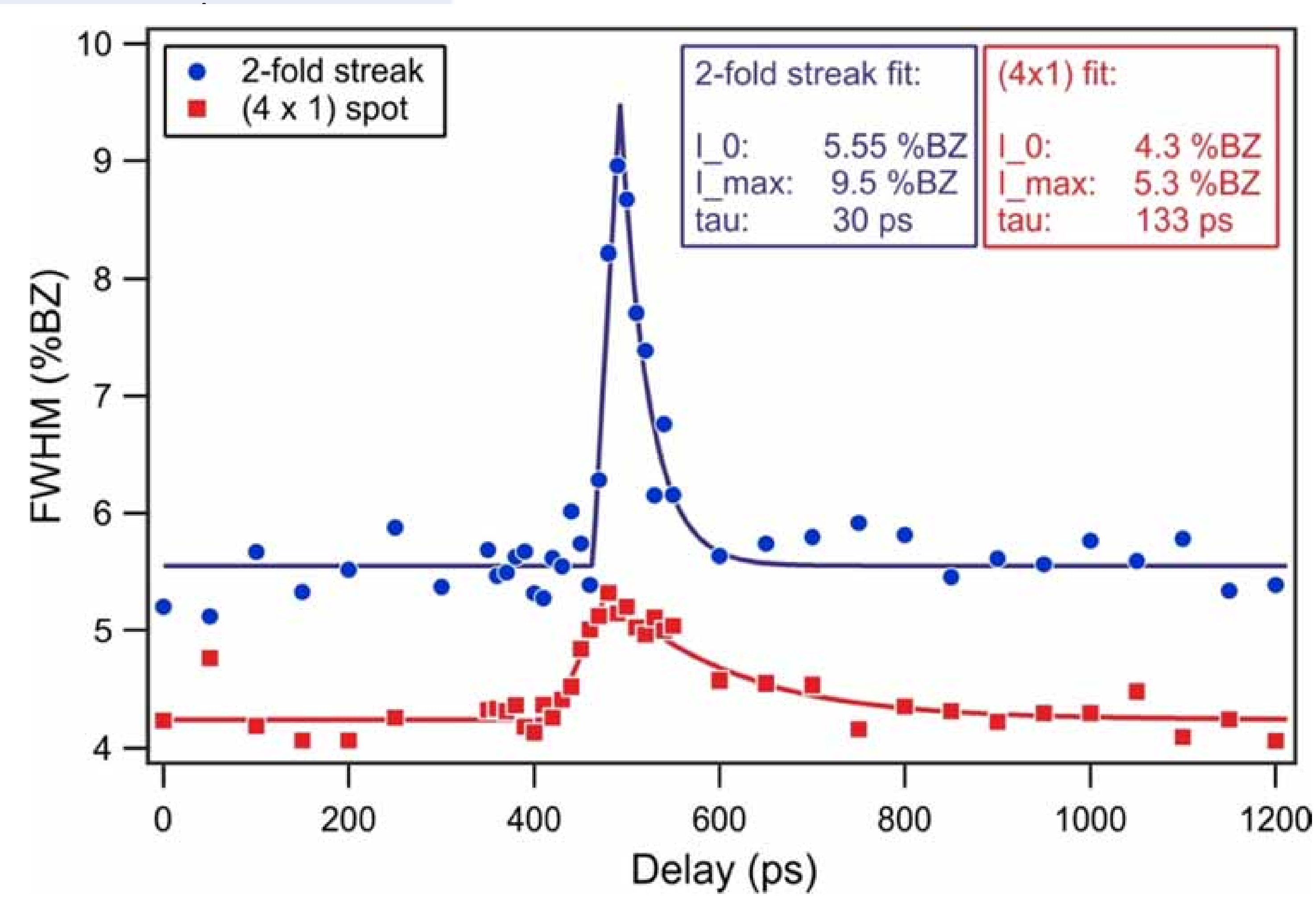
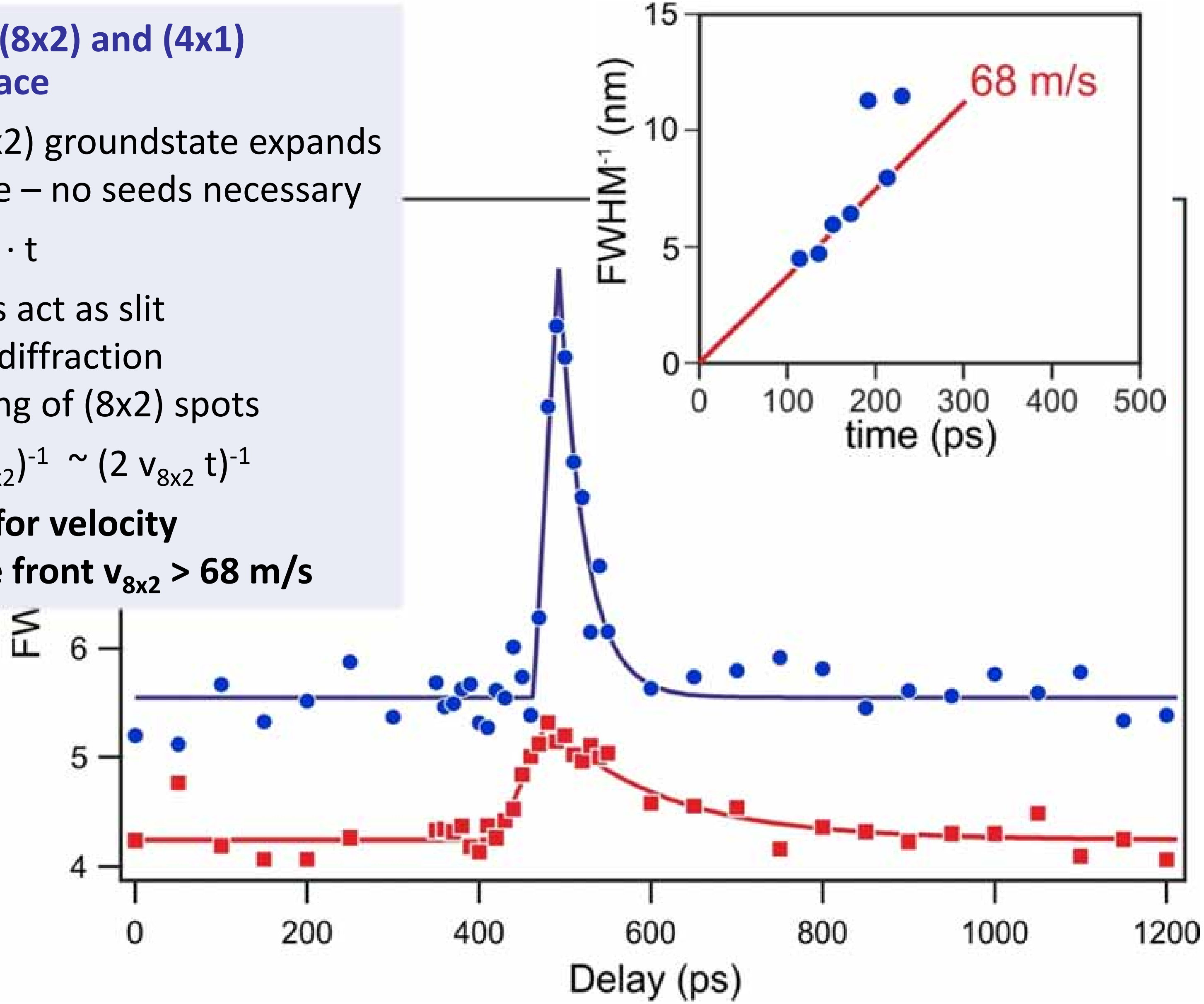
- FWHM ~ (L



Transient Spot Profile Analysis

Pattern of small (8x2) and (4x1) domains on surface

- Remnant (8x2) groundstate expands linear in time – no seeds necessary
- $L_{8x2} = 2 \cdot v_{8x2} \cdot t$
- (8x2) regions act as slit for electron diffraction => broadening of (8x2) spots
- FWHM ~ $(L_{8x2})^{-1}$ ~ $(2\, v_{8x2}\, t)^{-1}$
- **Lower limit for velocity of the phase front v_{8x2} > 68 m/s**



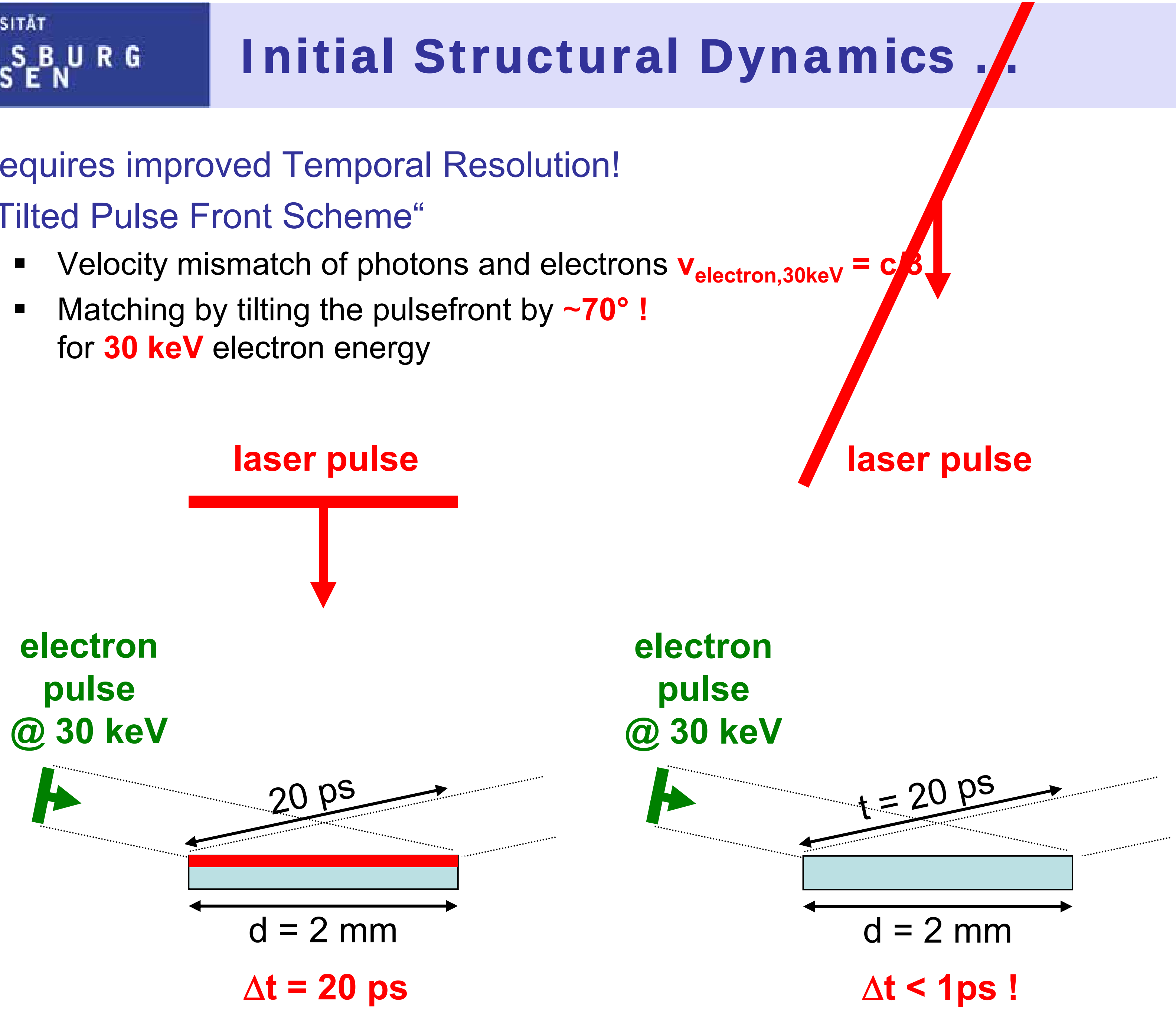
Recovery Dynamics

Initial Structural Dynamics …

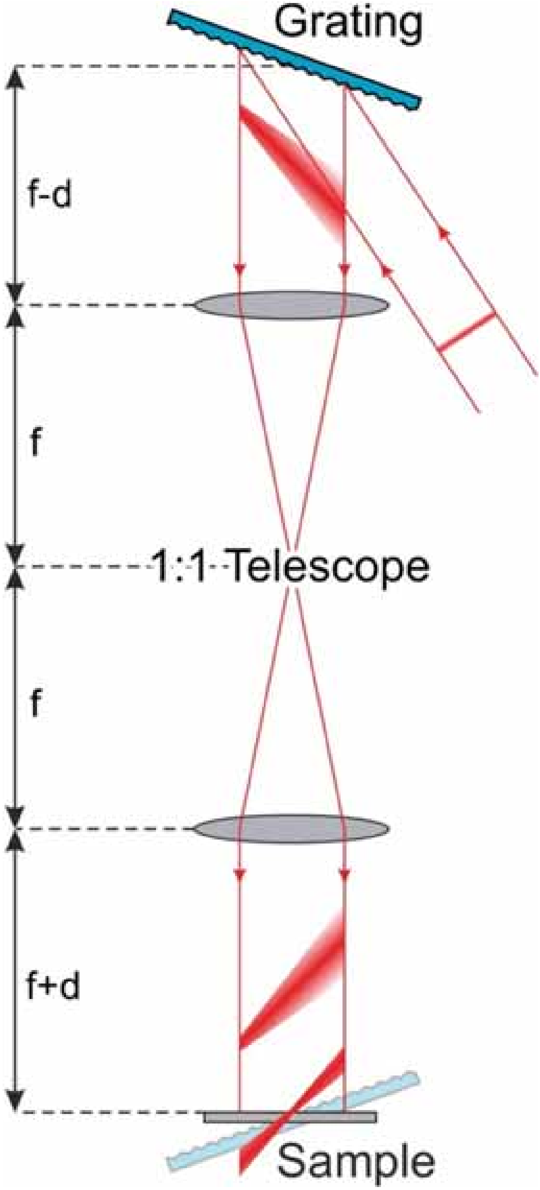
… requires improved Temporal Resolution!

„Tilted Pulse Front Scheme“

- Velocity mismatch of photons and electrons **$v_{electron,30keV} = c/3$**
- Matching by tilting the pulsefront by **~70° !**
  for **30 keV** electron energy



Tilted Pulse Fronts



„Tilted Pulse Front Scheme“

- Blazed grating
- Almost Littrow geometry
- 1:1 mapping of grating to sample

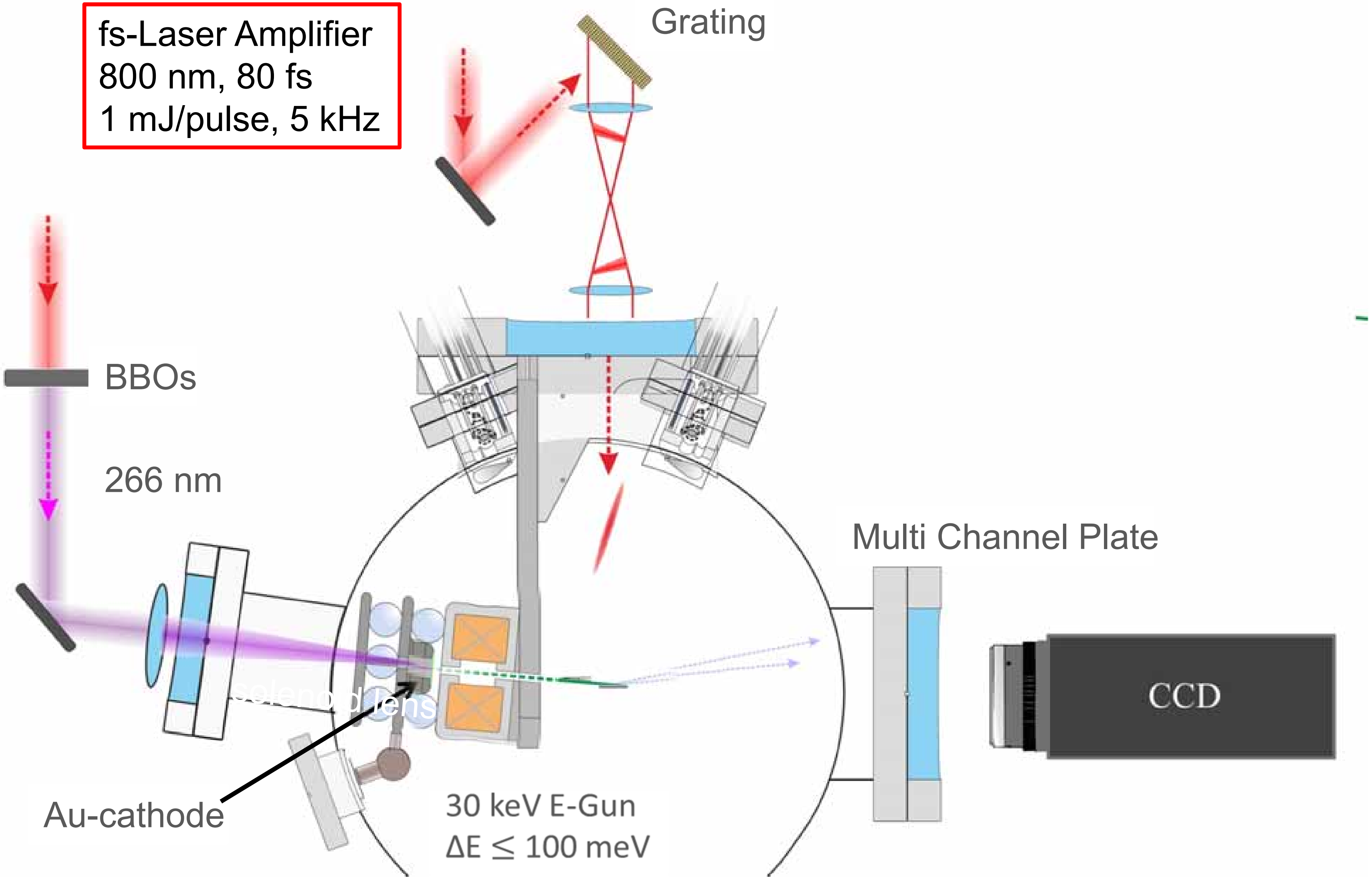
Setup realized together with group of Uwe Bovensiepen @ UDE

- Thanks to Carla Streubühr, Ping Zhou, Manuel Ligges & Dietrich von der Linde

P. Baum, D. S. Yang and A. H. Zewail, Science **318,** 788 (2007)

P. Zhou, C. Streubühr, A. Kalus, T. Frigge, S. Wall, A. Hanisch-Blicharski, M. Kammler, M. Ligges, U. Bovensiepen, D. von der Linde, M. Horn-von Hoegen,EPJ Web Conf. **41**, 10016 (2013)

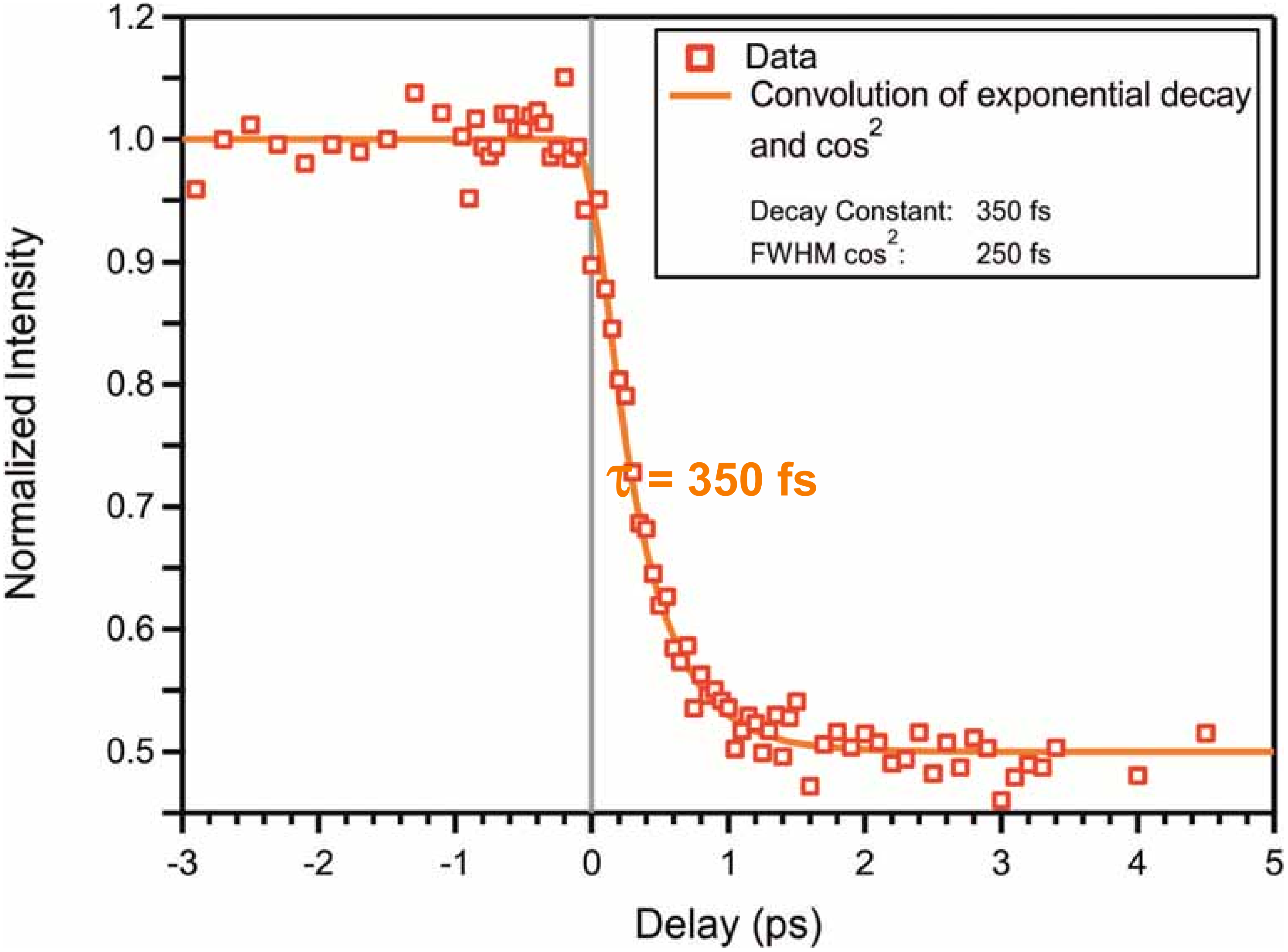
Ultrafast fs-RHEED: Advanced Setup



fs-Laser Amplifier
800 nm, 80 fs
1 mJ/pulse, 5 kHz

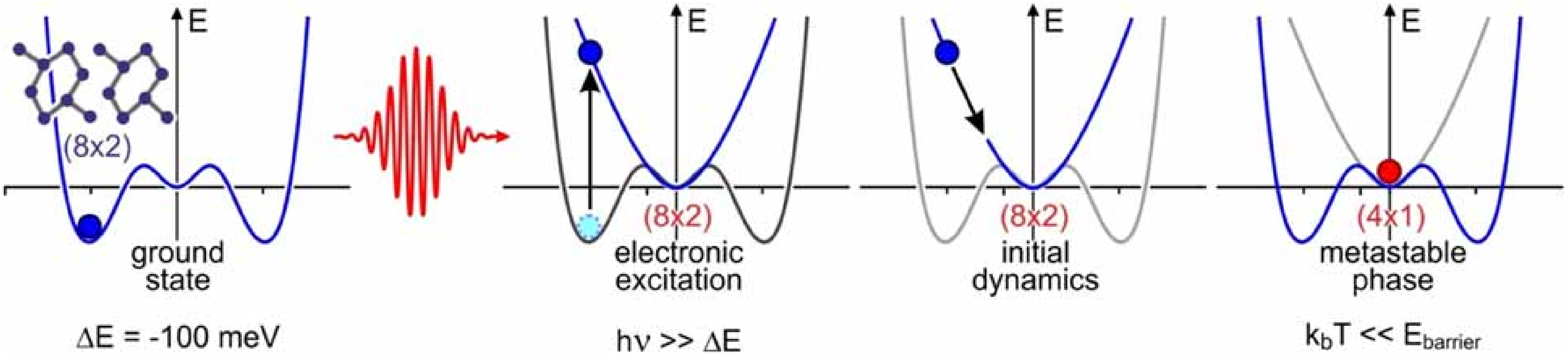
30 keV E-Gun
ΔE ≤ 100 meV

Strongly driven excitation



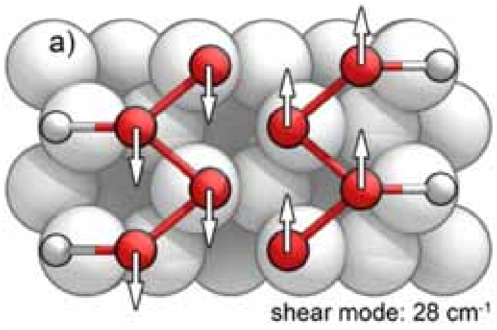
T. Frigge, B. Krenzer, B. Hafke, C. Streubühr, P. Zhou, M. Ligges,
U. Bovensiepen, D. von der Linde, M. Horn-von Hoegen (yet unpublished)

Strongly driven excitation

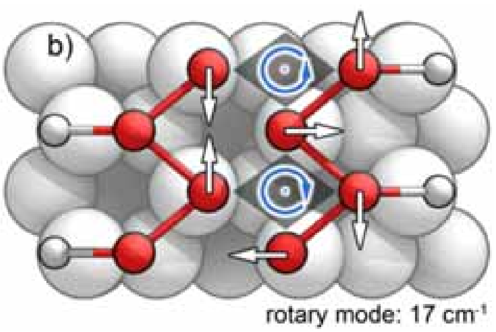


Potential energy landscape changes upon electronic excitation:

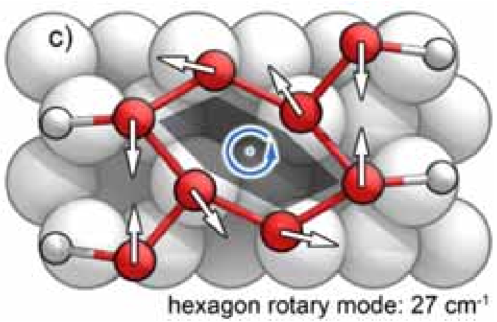
- Accelerated displacive transition from (8x2) ground state to (4x1) excited state in 350 fs – „slow“ structural transition!
- Transition in ¼ period of the characteristic shear and rotational soft phonon modes



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)

Thanks to

TR-RHEED Team:

Andreas Janzen, **Boris Krenzer**, Anja Hanisch-Blicharski, **Simone Wall**, Annika Kalus, Paul Schneider, Tobias Pelka, Friedrich Klasing, Martin Kammler, **Tim Frigge**, Verena Tinnemann, **Bernd Hafke**, Tobias Witte

Laser Team:

Carla Streubühr, Ping Zhou, Manuel Ligges, Dietrich von der Linde, Uwe Bovensiepen

Theory Team:

Wolf Gero Schmidt(1), Simone Sanna(1), Stefan Wippermann(1) (2), Andreas Lücke(1)

1) University of Paderborn
2) present adress: MPI Eisenforschung, Düsseldorf

Financial Support:

State of NRW, DFG, SFB616

Summary - Atomic Wires

Si(111)/In (8x2) ↔ (4x1)

Simple sample preparation

Peierls instabililty

1st order phase transition at 130 K

- Ultrafast electronic excitation of phase transition in 350 fs
- Formation of supercooled, metastable surface phase
- Pre-exisiting defects trigger the 1-dim propagating recovery front, which propagates at 100m/s