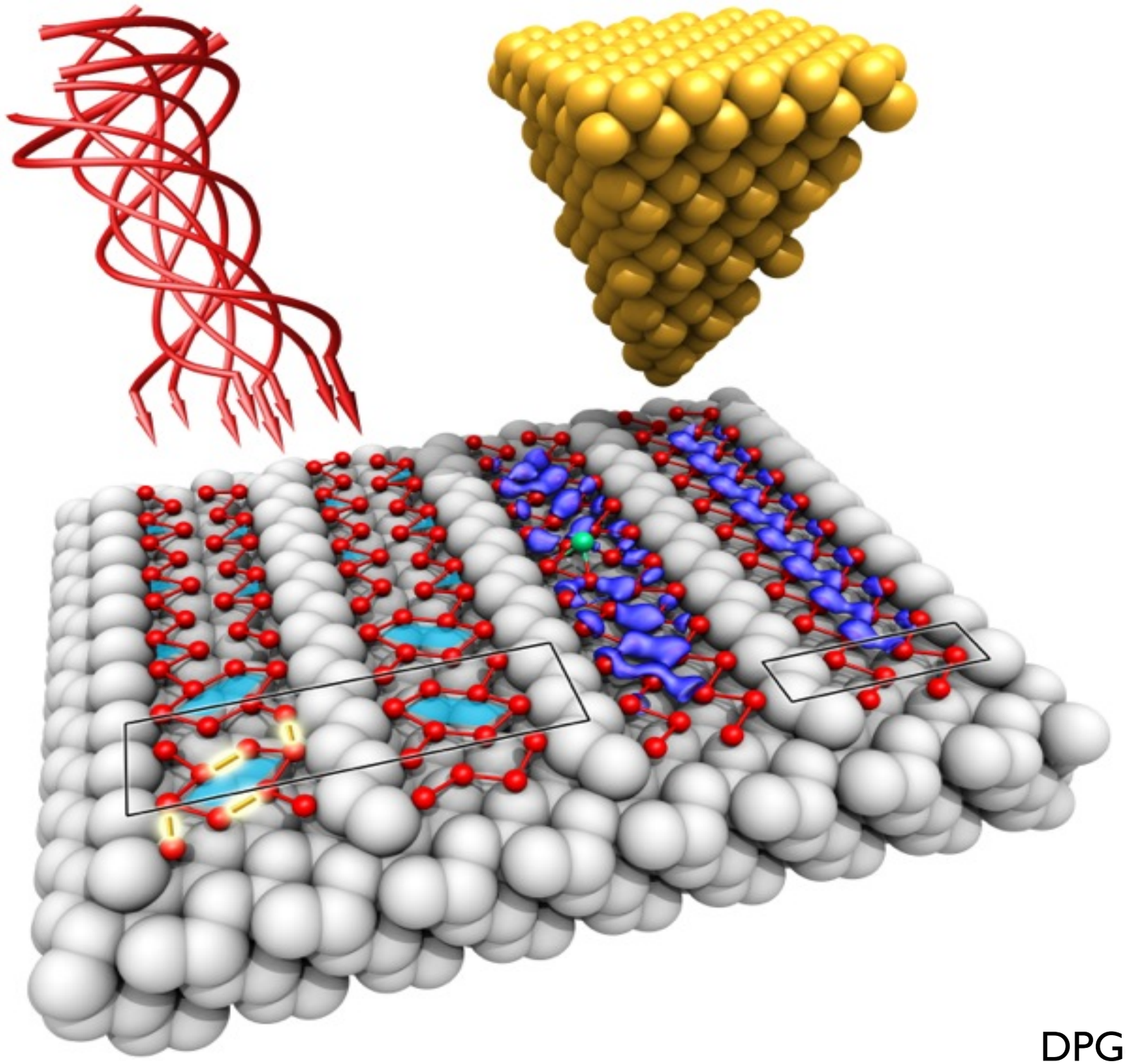
In/Si(111)-(4x1)/(8x2): a fascinating model system for one-dimensional conductors

S. Wippermann, W. G. Schmidt



DPG-2014, 04/03/2014

In/Si(111)-(4x1): atomic scale wires on semiconductors

- Model system to study (quasi) 1D physics: In-induced (4x1) surface reconstruction of Si(111) [Landers and Morrison, J. Appl. Phys. 36, 1706 (1965)]
- At borderline between semiconducting low In coverage and metallic high In coverage phases

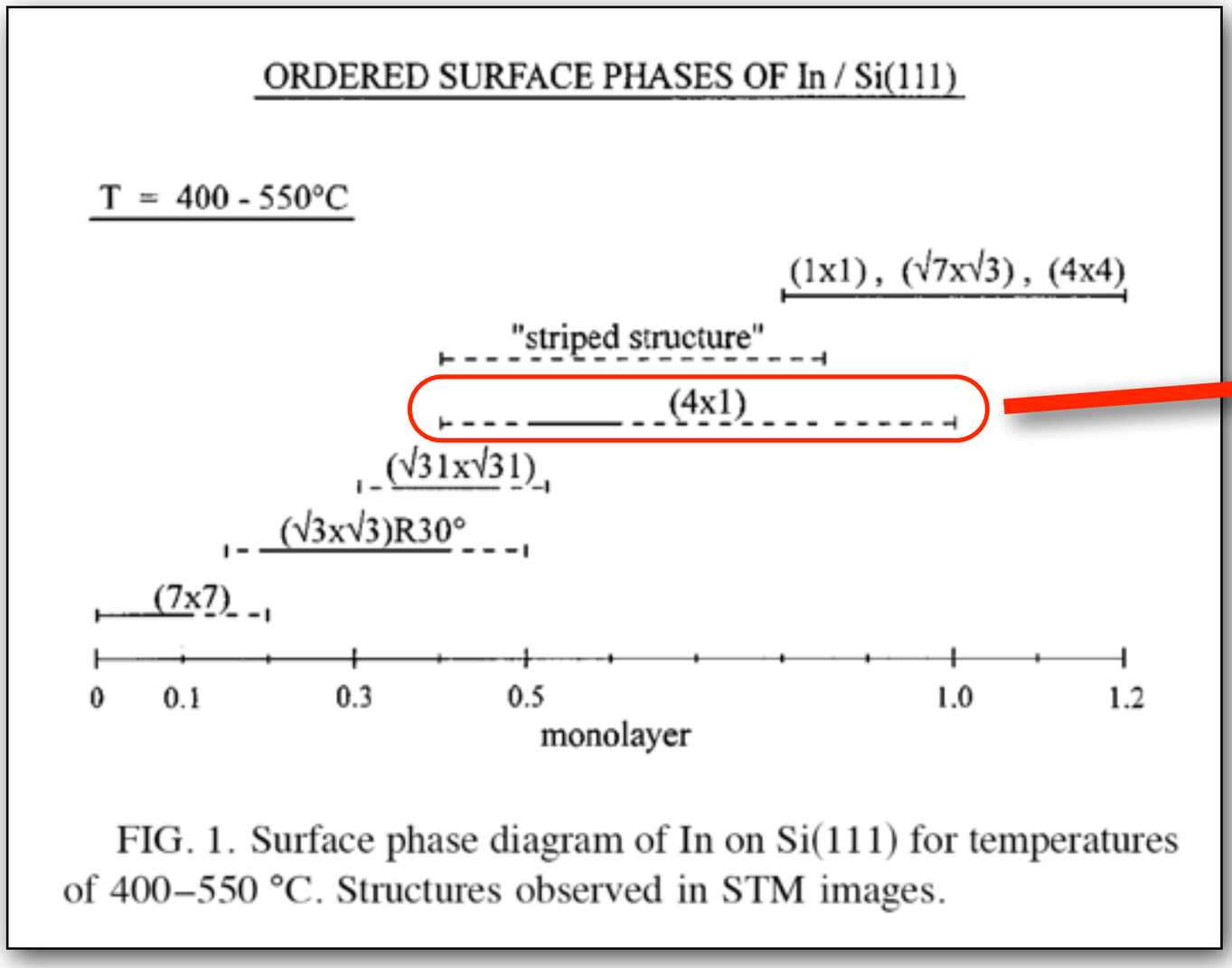
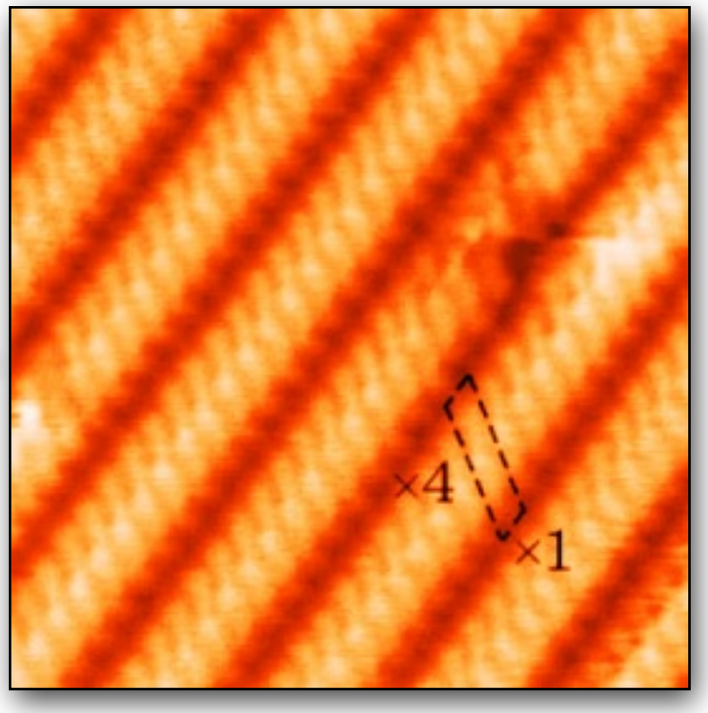


FIG. 1. Surface phase diagram of In on Si(111) for temperatures of 400–550 °C. Structures observed in STM images.

[J Kraft, MG Ramsey, FP Netzer, **PRB 55**, 5384 (1997)]

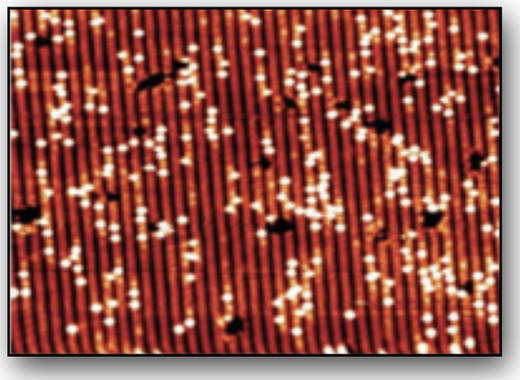


[H. W. Yeom *et al.*, **PRL 82**, 4898 (1999)]

What is special about this system?

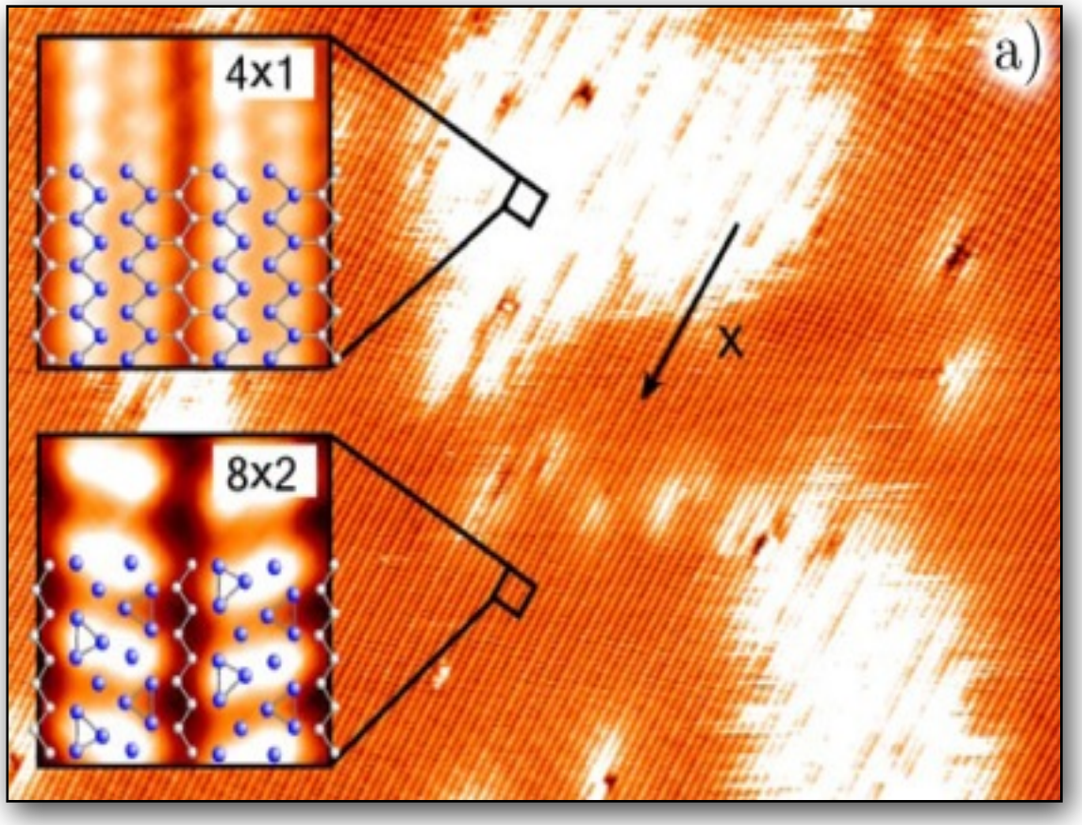
Peierls Condensation?

- Metallic RT (4x1) phase:
  - ➜ structure basically understood
  - ➜ real-world example for quasi-1D conductor



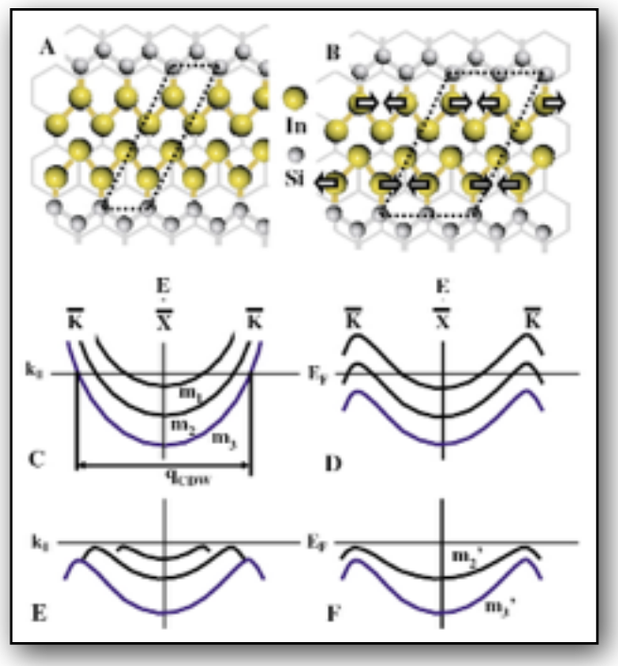
In 4x1 structure covered with 0.007 ML of Pb [Hupalo et al., **PRB 76**, 045415 (2007)]

- Temperature-induced phase transition at ~120 K



[H.W.Yeom *et al.*, **PRL 95**, 12601 (2005)]

- (presumably) semi-conducting LT (8x2) phase:
  - ➜ structure not really understood
  - ➜ mechanism of phase transition not really understood - Peierls instability??



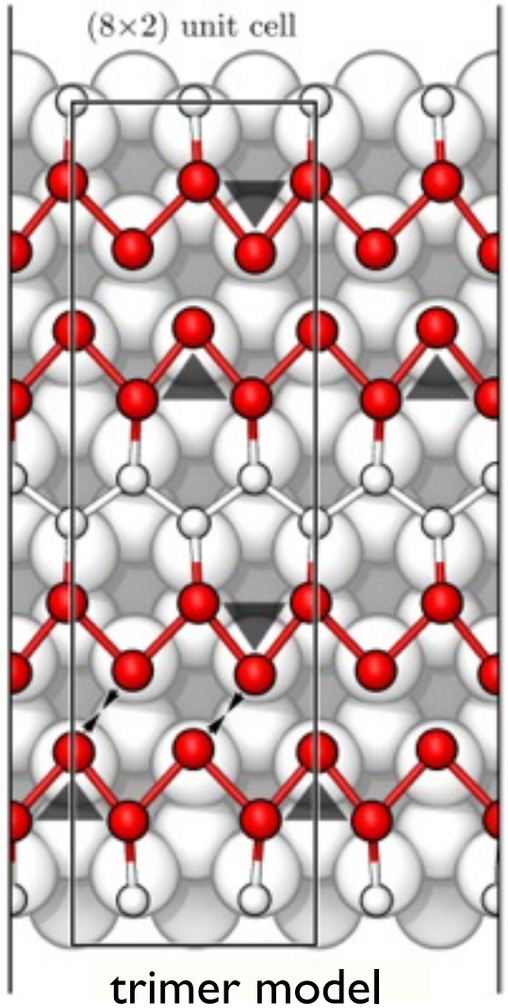
[Ahn et al., **PRL 93**, 106401 (2004)]

Competing structural models

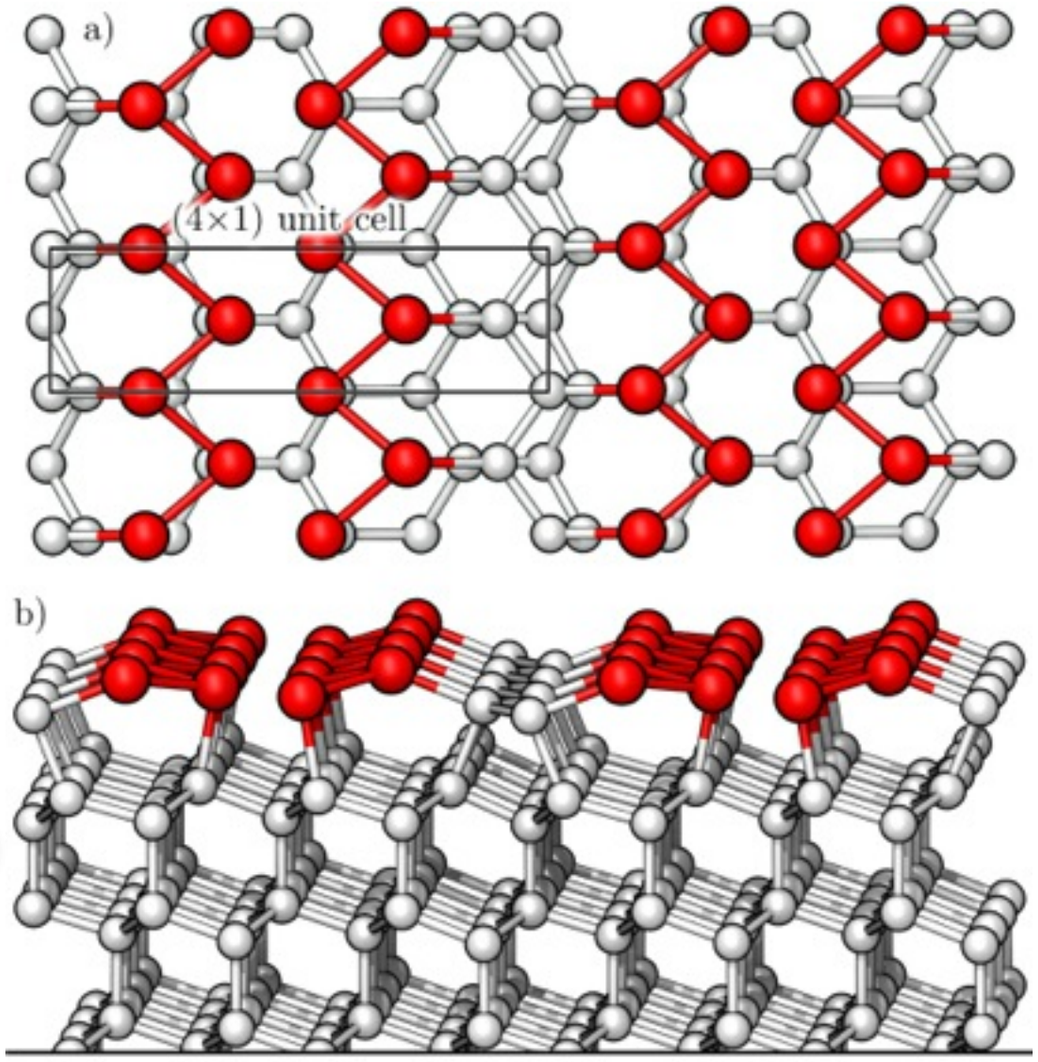
surface X-ray diffraction
Kumpf et al. PRL 85, 4916 (2000)

photoemission
Yeom et al. PRB 65, 241307 (2002)

DFT calculations
Cho et al. PRB 64, 235302 (2001);
Tsay, PRB 71, 035207 (2005);
Lopez-Lozano et al., PRB 73, 035430 (2006);
Cho and Lee, PRB 76, 033405 (2007);
...



trimer model



?

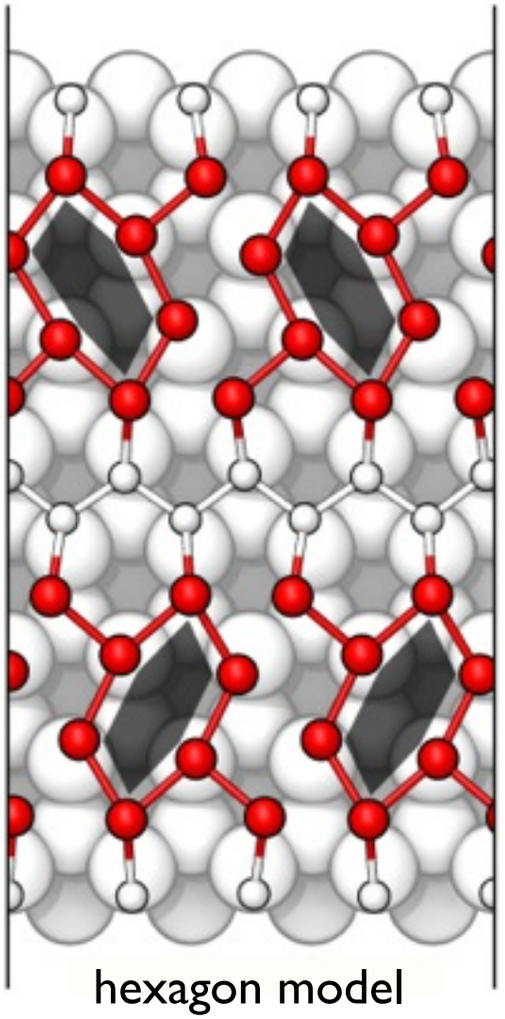
surface X-ray diffraction
Bunk et al. PRB 59, 12228 (1999)

DFT calculations
Cho et al. PRB 64, 235302 (2001);
Miwa and Srivastava, Surf. Sci. 473, 123 (2001);
Nakamura et al. PRB 63, 193307 (2001);
WGS et al. PRB 68, 035329 (2003);
...

?

DFT calculations
Gonzalez et al. PRL 96, 136101 (2006)

positron diffraction
Fukaya et al. Surf. Sci. 602, 2448 (2008)



hexagon model

GGA ← ground state → LDA

[S. Wippermann, WGS *et al.*, PRL **98**, 026105 (2007)]

Obtain Structure from Reflectance Anisotropy Spectroscopy

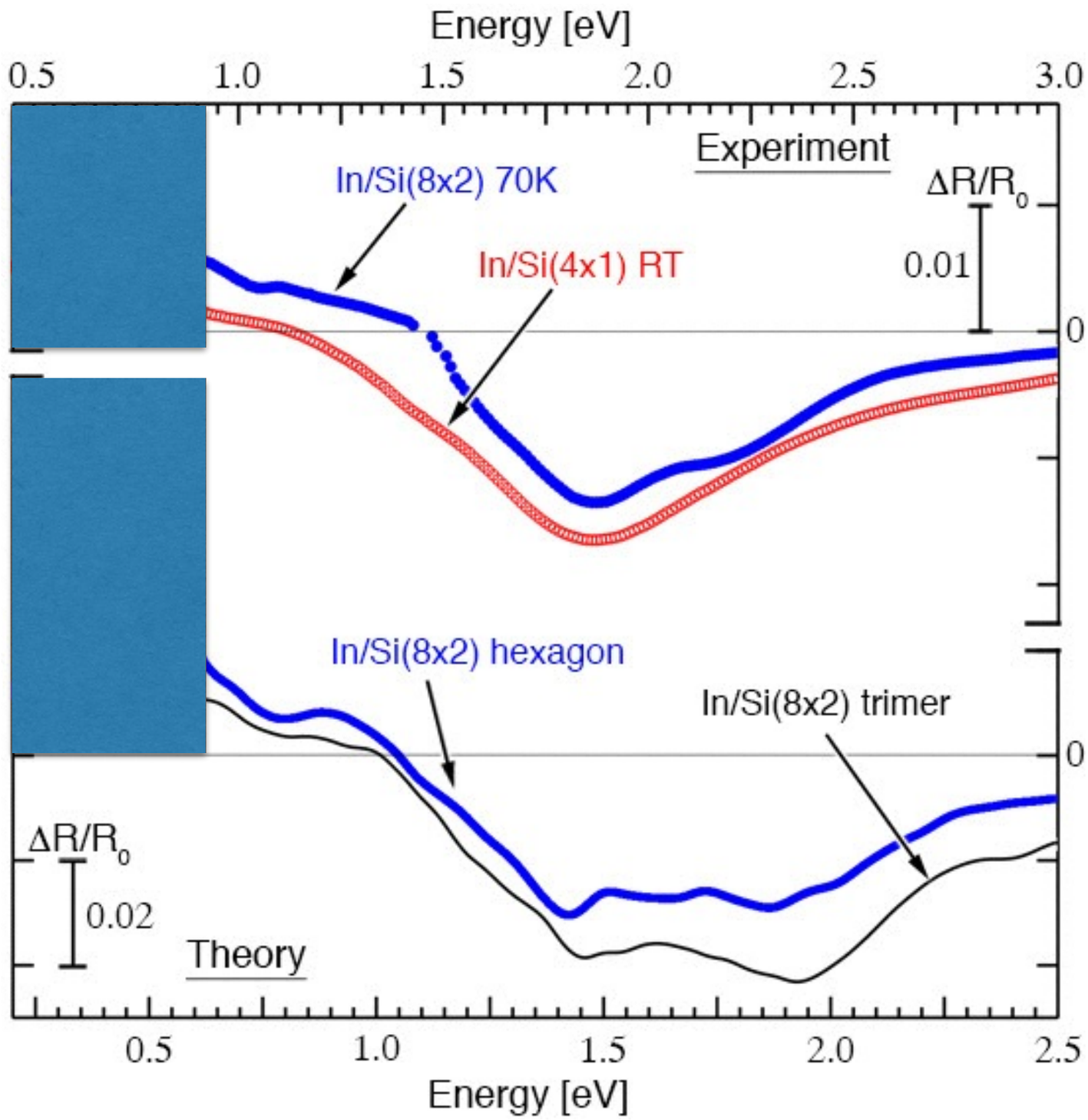
- Shoulder observed experimentally at 2 eV upon cooling, signature for phase transition?

  → No, reproduced by both hexagon & trimer models

- Mid-infrared regime: anisotropic Drude tail replaced by two distinct peaks upon cooling

- Only hexagon model agrees with measured data

  → Structure determined! Now understand mechanism of phase transition



[S. Chandola, K. Hinrichs, M. Gensch, N. Esser, S. Wippermann, WGS *et al.*, PRL **102**, 226805 (2009)]

Phonon Modes: Theory vs. Experiment

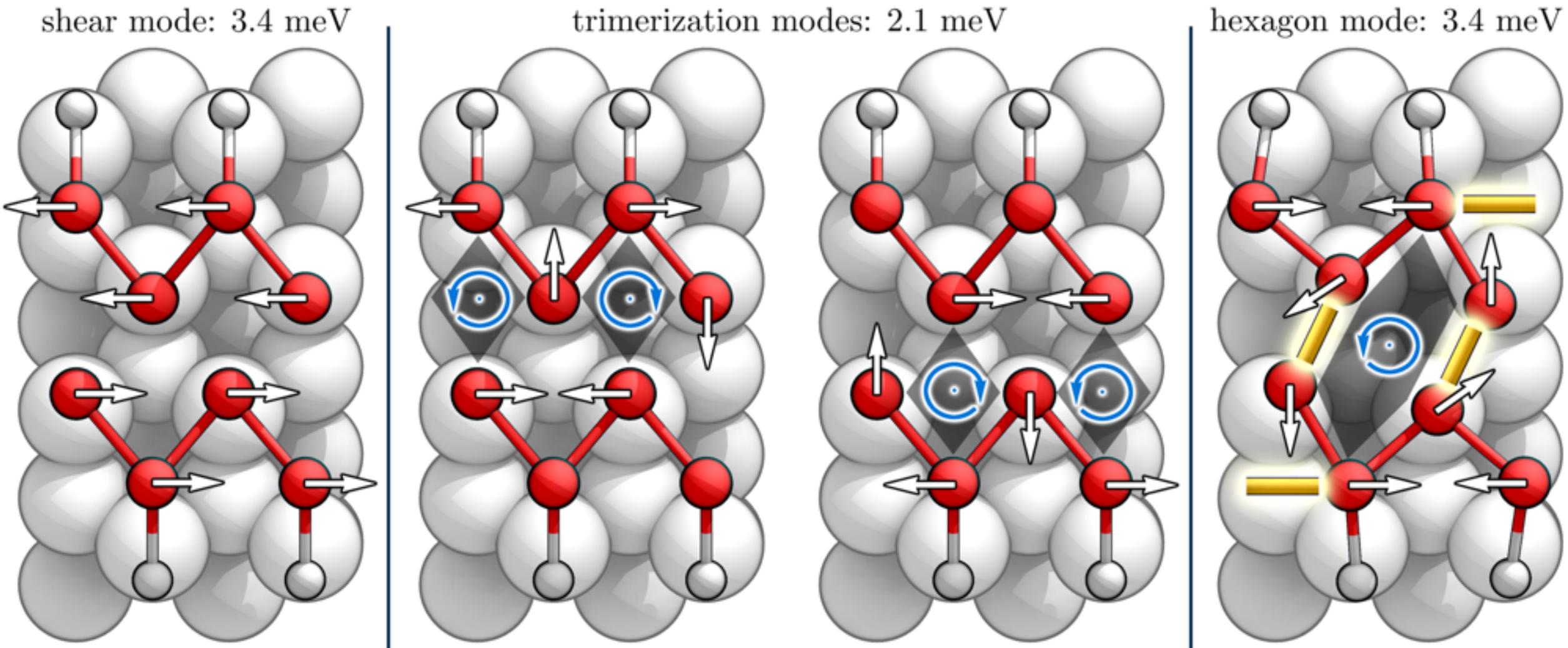
Theory ω_0 $[cm^{-1}]$			Experiment ω_0 $[cm^{-1}]$		
(4×1)	→	(8×2)	(4×1)	→	(8×2)
22	→	20	31 ± 1	→	21 ± 1.6
		27			28 ± 1.3
		hexagon rotary mode			
44	→	47	36 ± 2	→	41 ± 2
51	→	53	52 ± 0.6	→	57 ± 0.7
62	→	58, 69	61 ± 1.3	→	62, 69 ± 1.5
65, 68	→	70, 69, 78, 82	2·72 ± 3.3	→	83 ± 2.3
100, 104	→	97, 106, 113, 142	105 ± 1	→	100–130
129, 131	→	137, 142	118 ± 1	→	139 ± 1.2
143, 145	→	139, 145, 146, 147	2·148 ± 7	→	139, 2·154±2
28	→	18, 19	28 ± 0.9	→	2·23.5 ± 0.8
shear mode					
→ antisym./sym. shear mode					
		35			3·42 ± 3.5
		51			2·59 ± 3
		75			69 ± 1.5
		82			85 ± 1.7

TABLE I: Calculated Γ-point frequencies for strongly surface localized A' (upper part) and A" phonon modes (lower part) of the Si(111)-(4×1)/(8×2)-In phases in comparison with experimental data [26]. The symmetry assignment of the (8×2) modes is only approximate, due to the reduced surface symmetry.

- calculate phonon frequencies and modes
- in general good agreement with experiment [K Fleischer et al., Phys. Rev. B 76, 205406 (2007)]
- (4x1) and (8x2) structures are well defined local minima on potential energy surface
- no soft (imaginary) modes at T = 0 K
- experimental spectra and assigned calculated phonon modes on backup slide

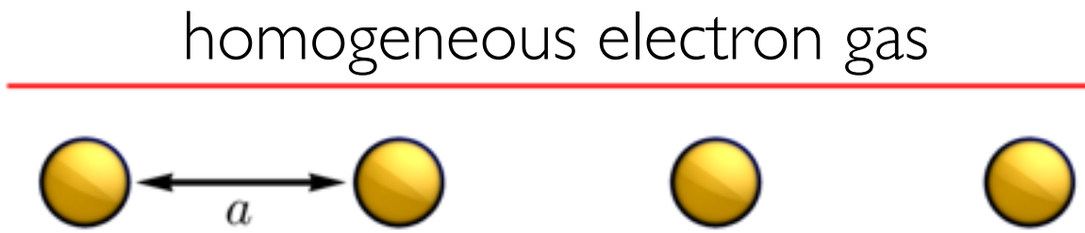
Transition path: phonon modes show the way

- (4x1) ↔ (8x2) transition path well-described by low energy phonon eigenvectors
- Linear combination of (4×1) shear and trimer modes yield (8×2) hexagon
- (8×2) shear and hexagon modes yield (4×1) ideal reconstruction
- Rearrangement of In atoms leads to formation of new bonds => Peierls instability?



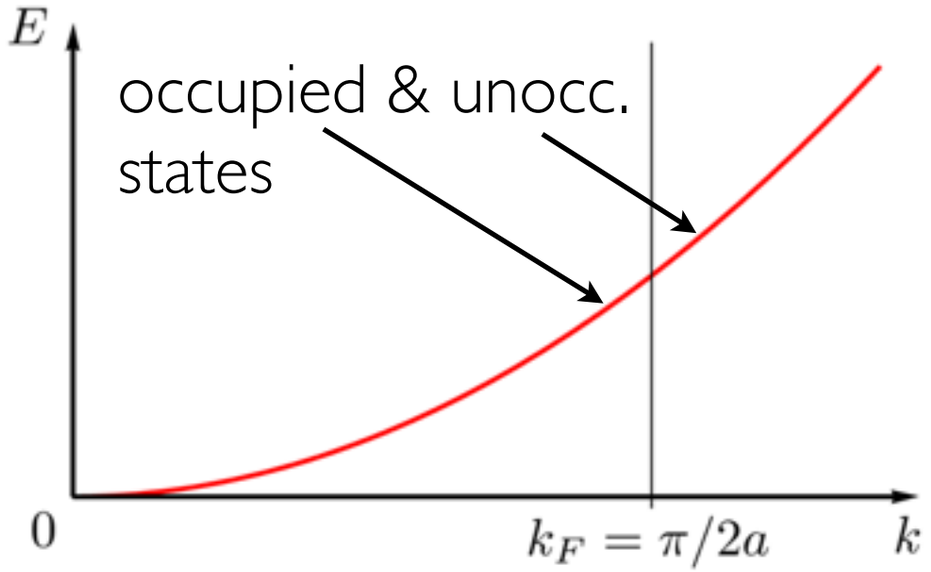
Peierls instability

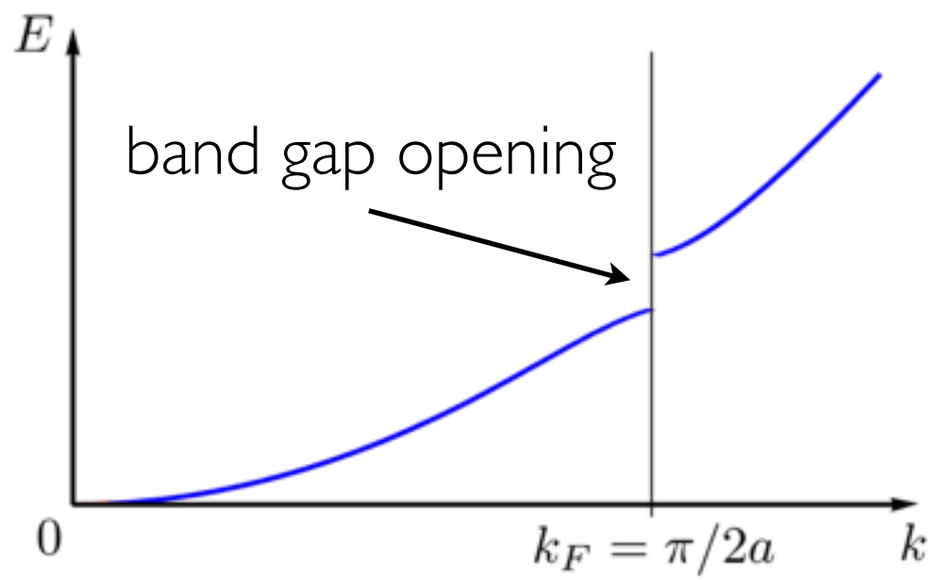
- 1D-metals *a priori* unstable
- Free energy lowered by phonon-driven metal-insulator (MI) transition



Peierls MI transition

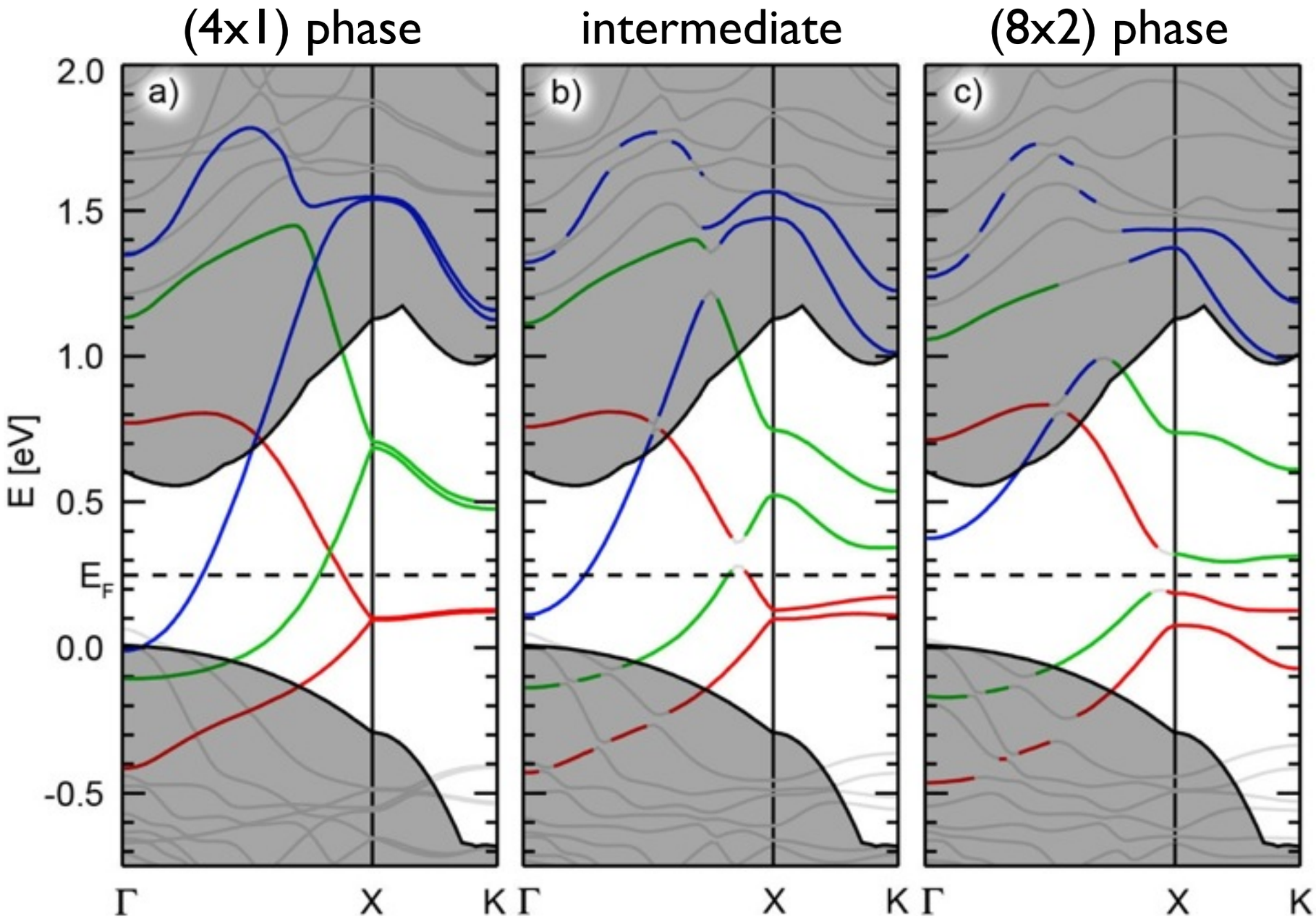
charge density wave (CDW) formation





No Peierls transition in In/Si(111) in the original sense

- Follow transition path defined by soft phonon eigenvectors and calculate band structures
- Formation of band-gap leads to energy gain *in analogy* to Peierls transition, but poor nesting and does not occur at edge of Brillouin zone



Why phase transition from semiconducting (8x2) ground state to metallic (4x1)?

=> *Calculate free energy at finite temperature*

[S. Wippermann, WGS *et al.*, PRB **84**, 115416 (2011)]

Atomistic Thermodynamics

- calculate **free energy** from *first principles*

$$F(V,T) = F_{el}(V,T) + F_{vib}(V,T)$$

$$F_{el} = E_{tot} - TS_{el}$$

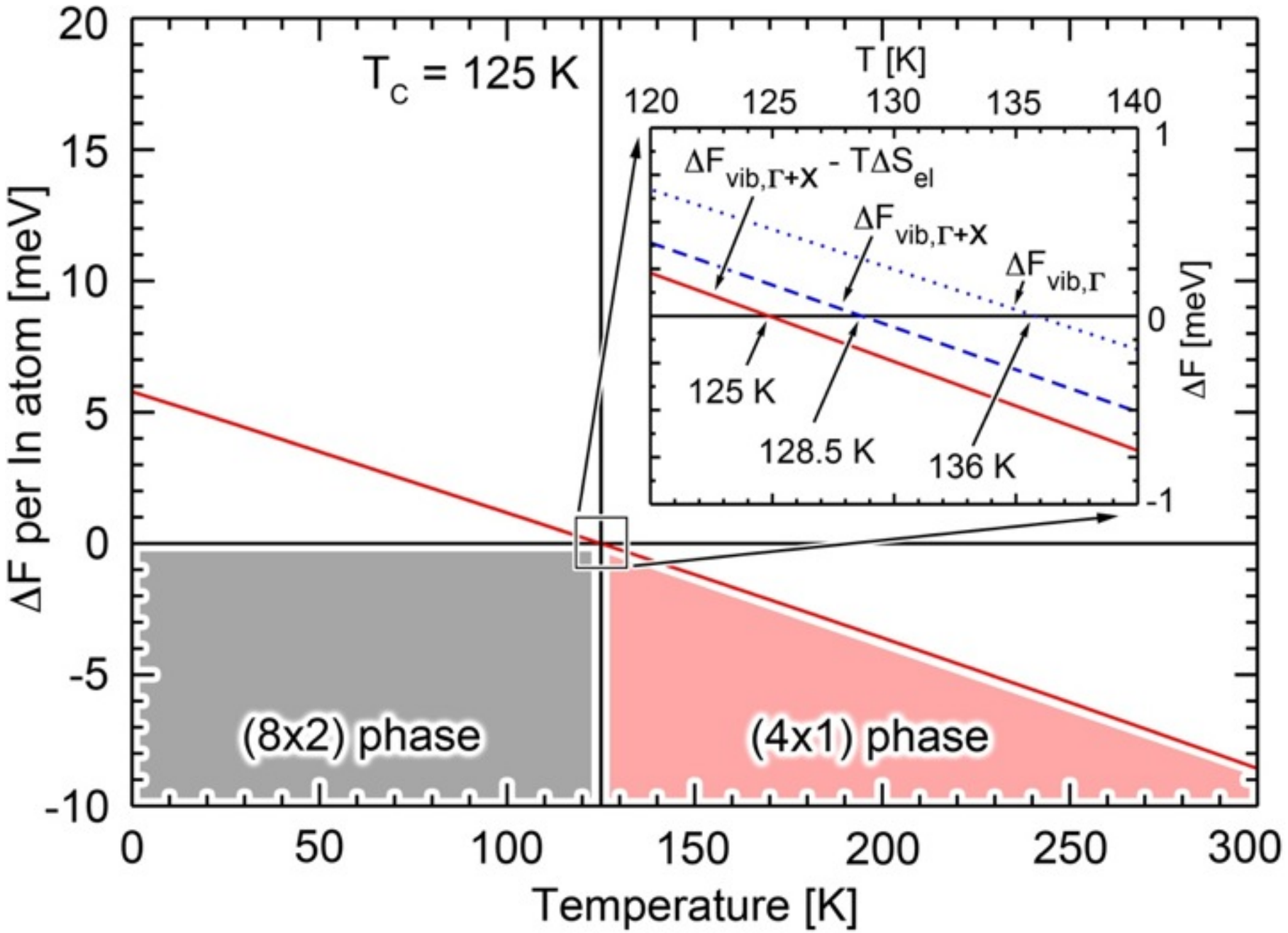
- approximate the total energy $\mathbf{E_{tot}}$ by the zero-temperature DFT value and calculate the electronic entropy $\mathbf{S_{el}}$ from

$$S_{el} = k_B \int dE \; n_F [f \ln f + (1-f)\ln(1-f)]$$

- vibrational entropy of the periodically repeated supercell with volume $\mathbf{\Omega}$ is calculated in harmonic approximation

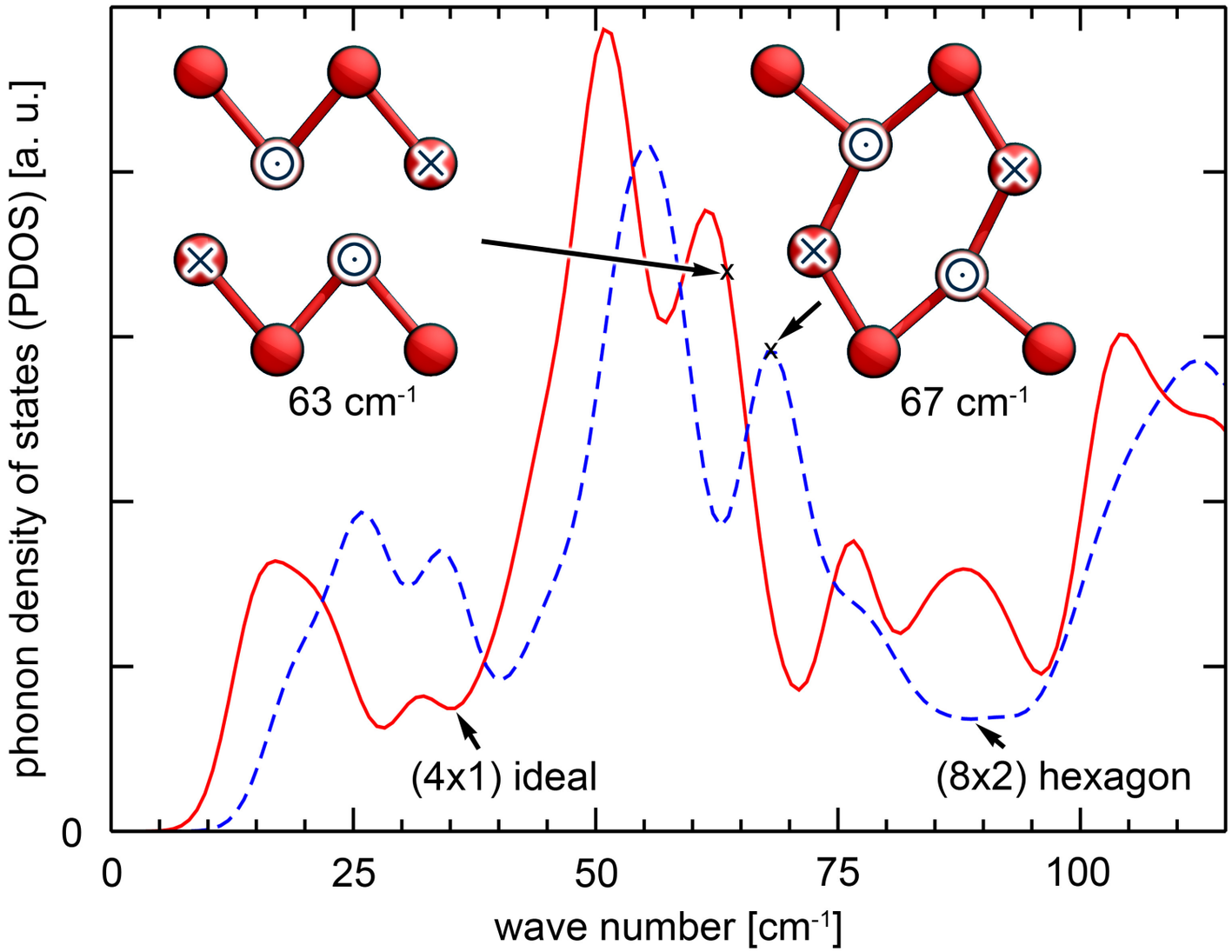
$$F_{vib} = \frac{\Omega}{8\pi^3} \int d^3\mathbf{k} \sum_i (\frac{1}{2}\hbar\omega_i(\mathbf{k}) + k_B T \ln(1 - e^{-\frac{\hbar\omega_i(\mathbf{k})}{k_B T}}))$$

Free energy of the (4x1) and (8x2) phase …



- ... explains phase transition at 125 K (experiment: 120K)
- Simple explanation possible?

Harder phonons counterbalance band structure energy gain

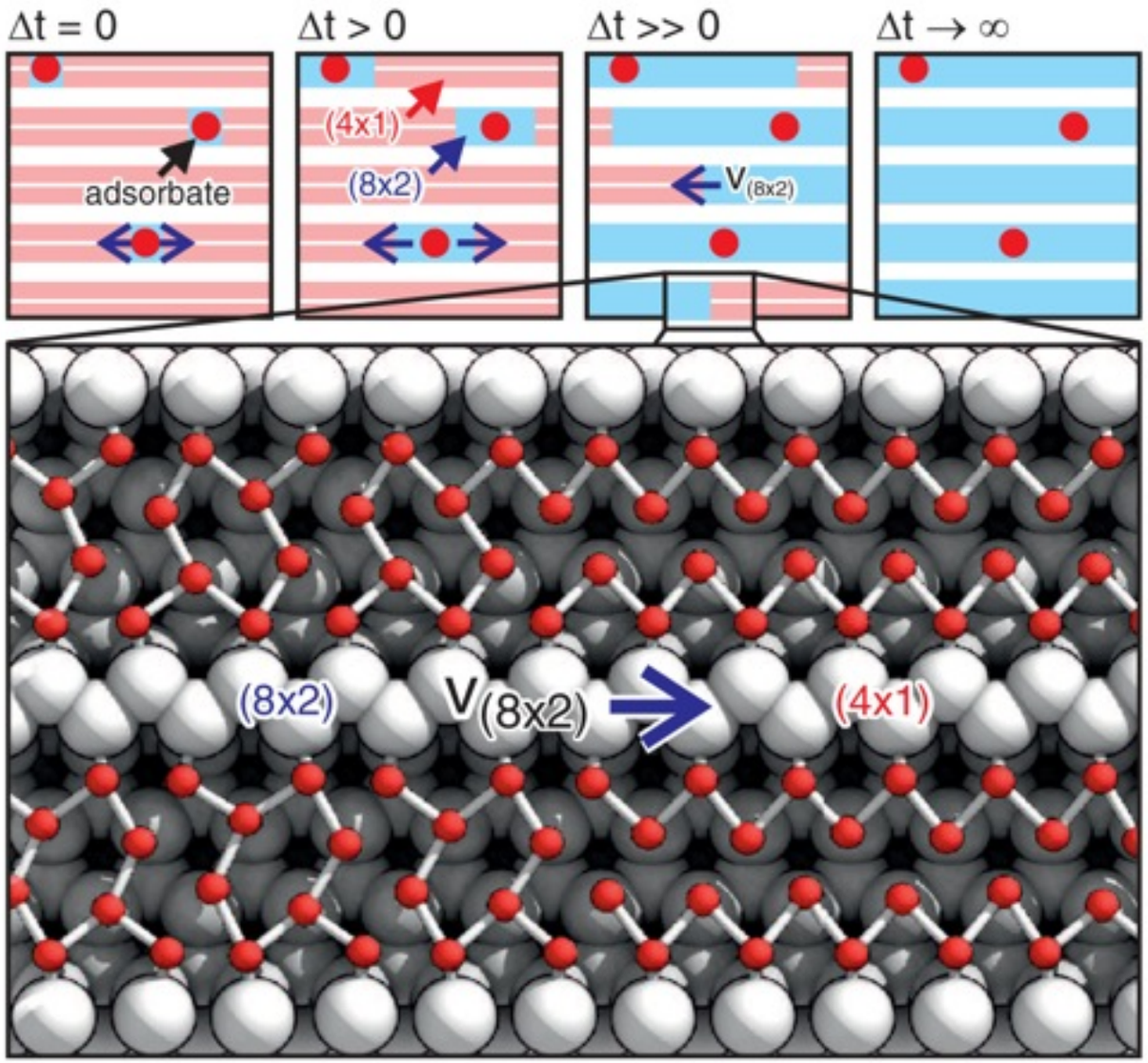


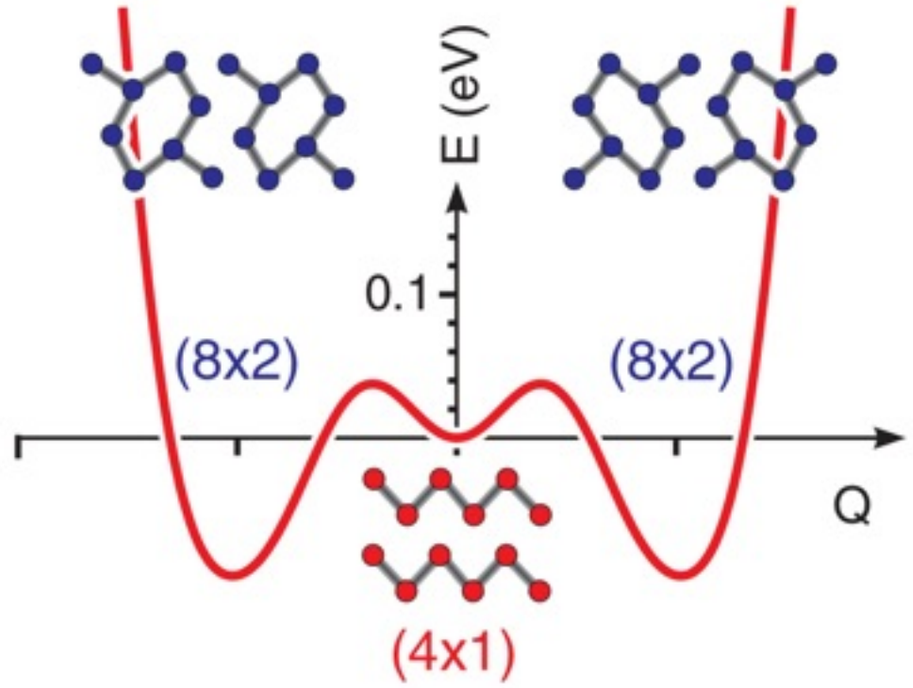
- Hardening of phonon modes upon bond formation in (8x2) hexamer model lowers vibrational entropy...
- ...compared to metallic (4x1) model with soft bonds
- For finite temperatures entropy contributions dominate and cause (8x2) ➜ (4x1) phase transition

[S. Wippermann, WGS, PRL **105**, 126102 (2010)]

Phase transition triggered by condensation nuclei

- energetics along (4x1) -> (8x2) transition path obtained from phonon calculations
- hampered by energy barrier of 20 meV per (8x2) unit cell





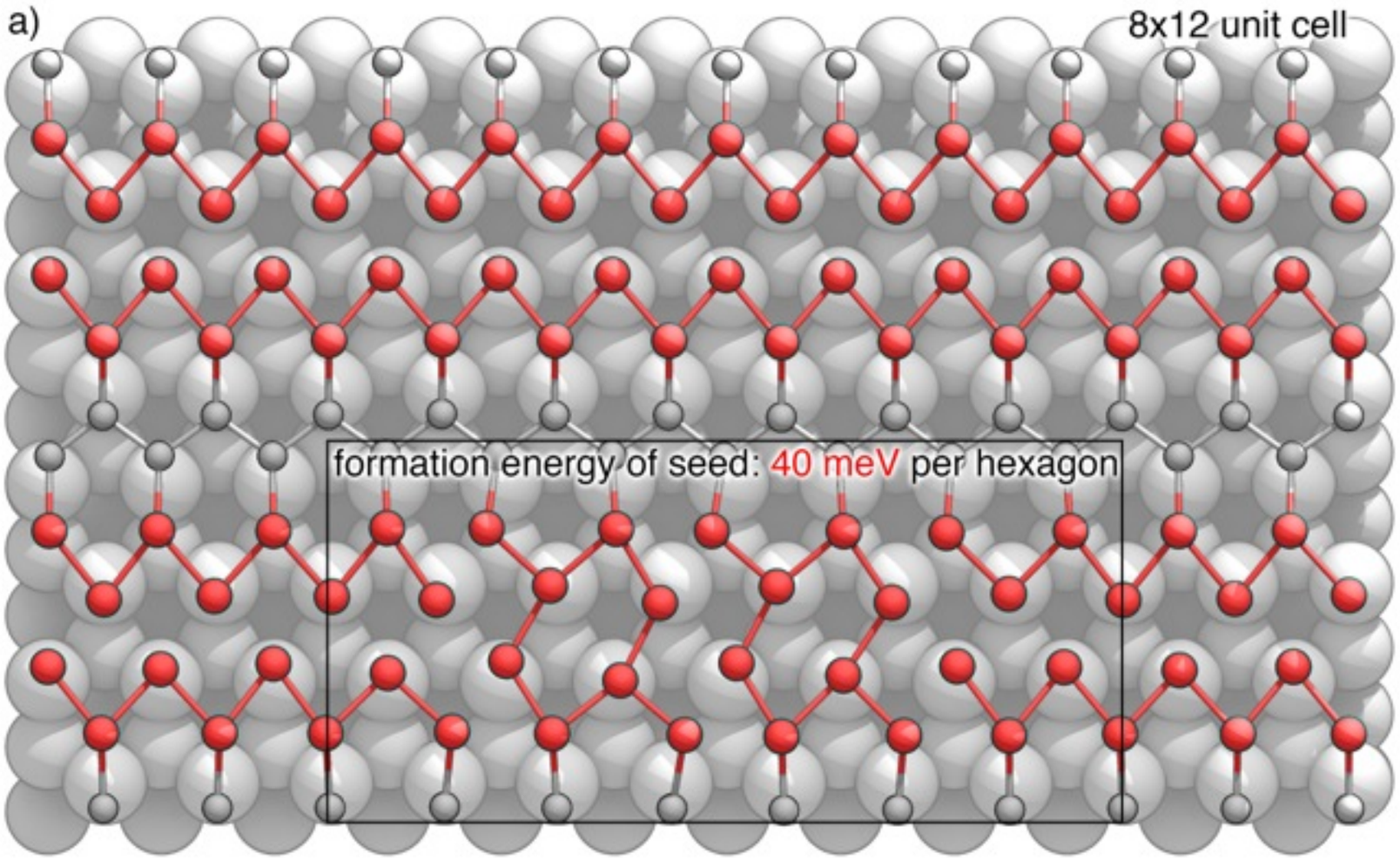
- time-resolved electron diffraction measurements (M. Horn von Hoegen group) and *ab initio* molecular dynamics calculations show freezing triggered by heterogeneous nucleation of ground state at adsorbates

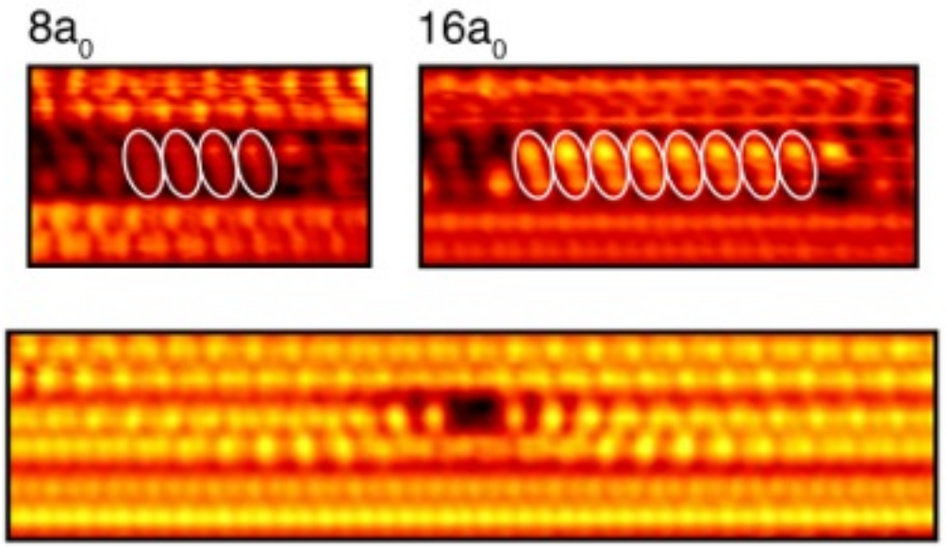
First order transition propagating from seeds at speed of sound (850m/s), in analogy to falling row of dominoes

[S. Wall, B. Krenzer, S. Wippermann, S. Sanna, WGS, M. Horn von Hoegen, *et al.*, PRL **109**, 186101 (2012)]

Nature of condensation nuclei?

- so far used hexagons as condensation nuclei
- local minimum on potential energy surface, but formation costs 40 meV per hexagon
- attempts to use adatoms, e. g. O, as nuclei resulted in no observable condensation





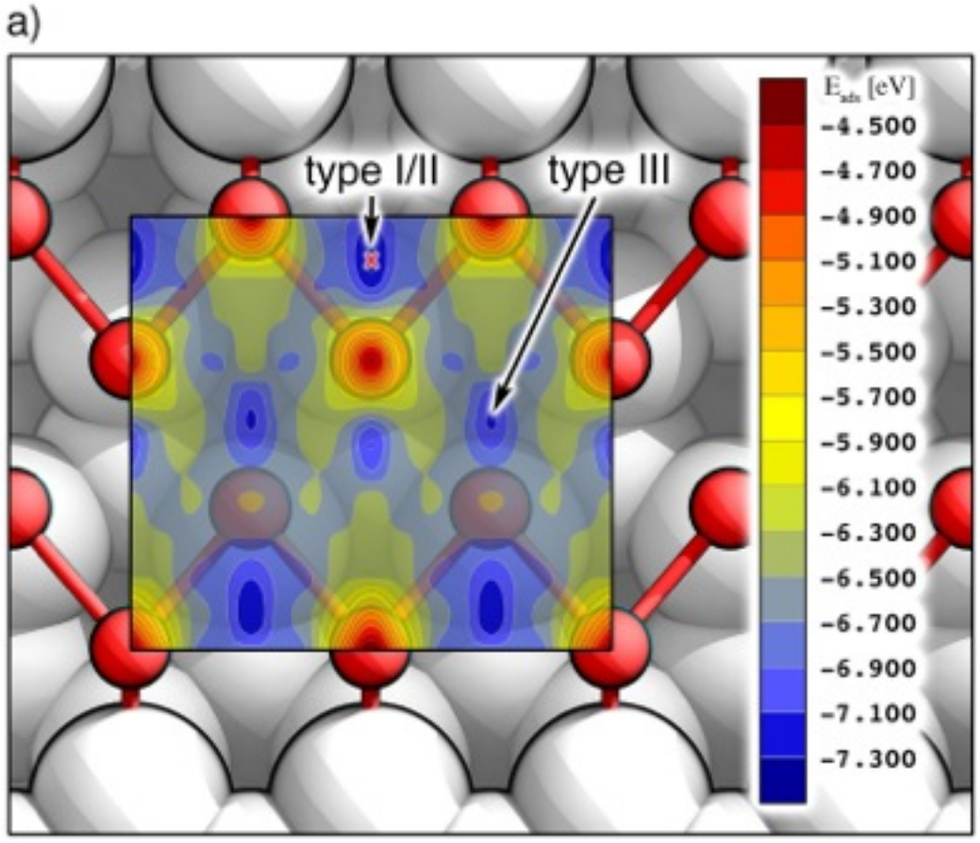
- Recent experiment by H. W. Yeom shows oxygen to facilitate phase transition, but only for pair-wise oxygen coadsorption!

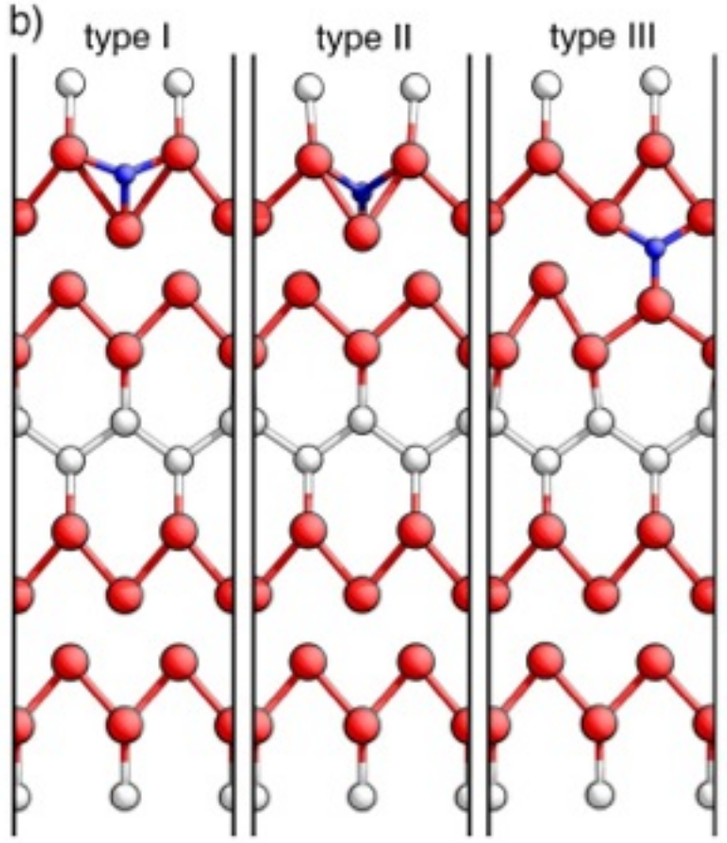
=> Investigate O adatoms on In/Si(111)

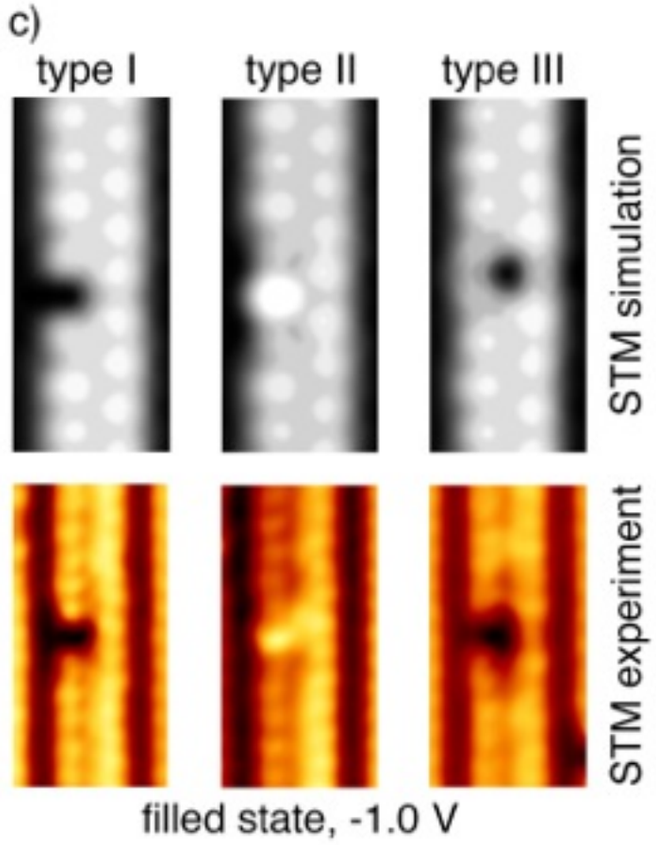
Oxygen on In/Si(111)

- 3 dominant types of defects observed experimentally, labeled type I, II and III
- Calculate adsorption energy surface, pick 3 energetically most favourable and calculate STM images

=> good agreement with measured STM images, basic adsorption understood

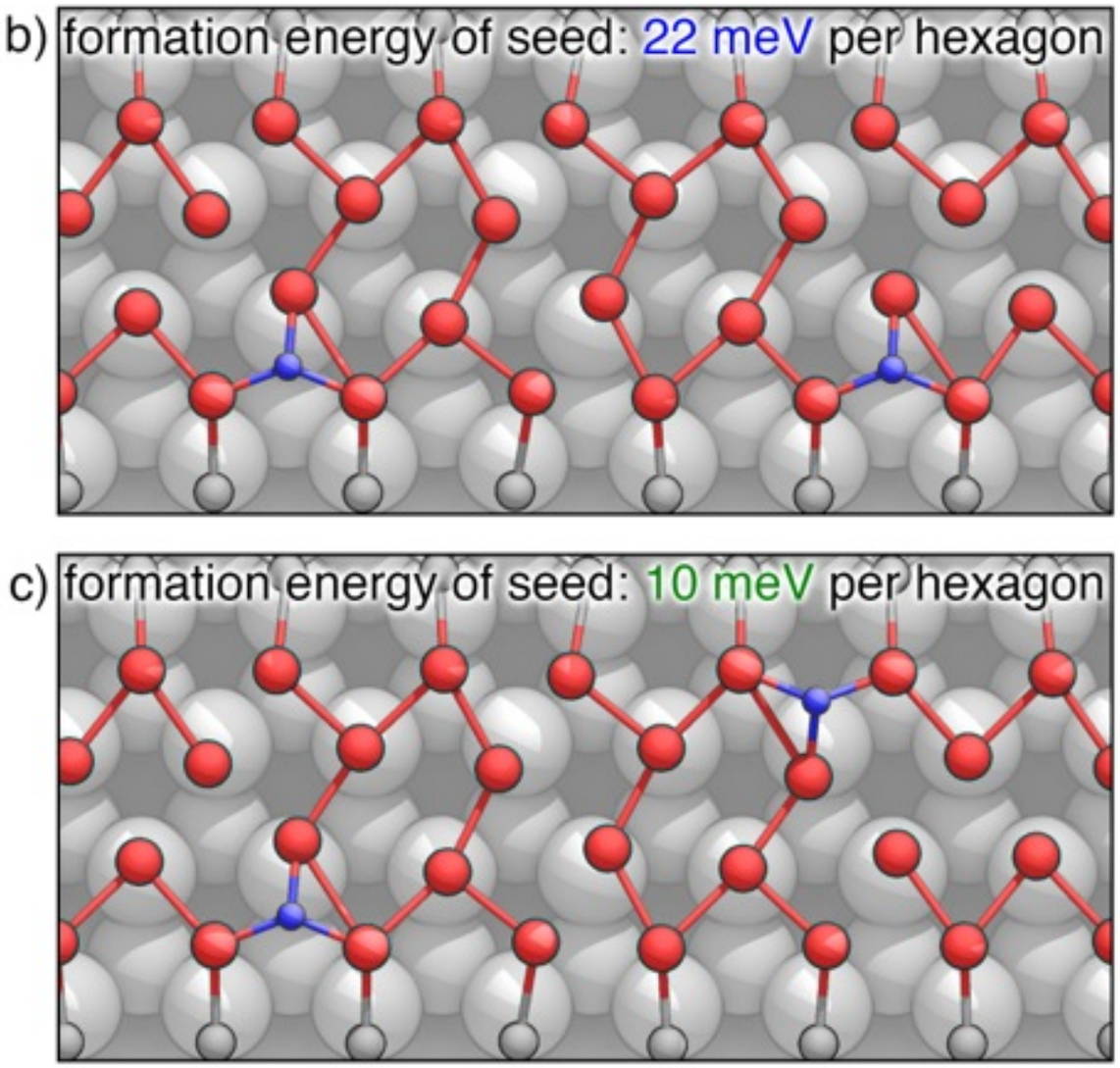






Oxygen reduces formation energy of seeds

- Experimentally, only type I defects with a spacing of even multiples of a_0 = 3.86 A observed to trigger phase transition
- Calculate impact of O adatoms with x4 distance in type I position in (8x12) unit cell
- O coadsorption at odd multiples of a_0 pulls trimers within hexagons apart by chemical strain, locking structure in (4x1)
- O coadsorption at even multiples of a0 reduces energy cost for hexagon formation from 40 meV to 22 meV (same chain) or even 10 meV (opposite chain sides)
- Formation energy still positive, (4x4) hexagon still unstable contrary to experimental observation
- 10 meV per (4x2) hexagon
  = 2.5 meV per In atom
- finite size effects, accuracy of DFT-LDA? => could try hybrid DFT with self interaction correction



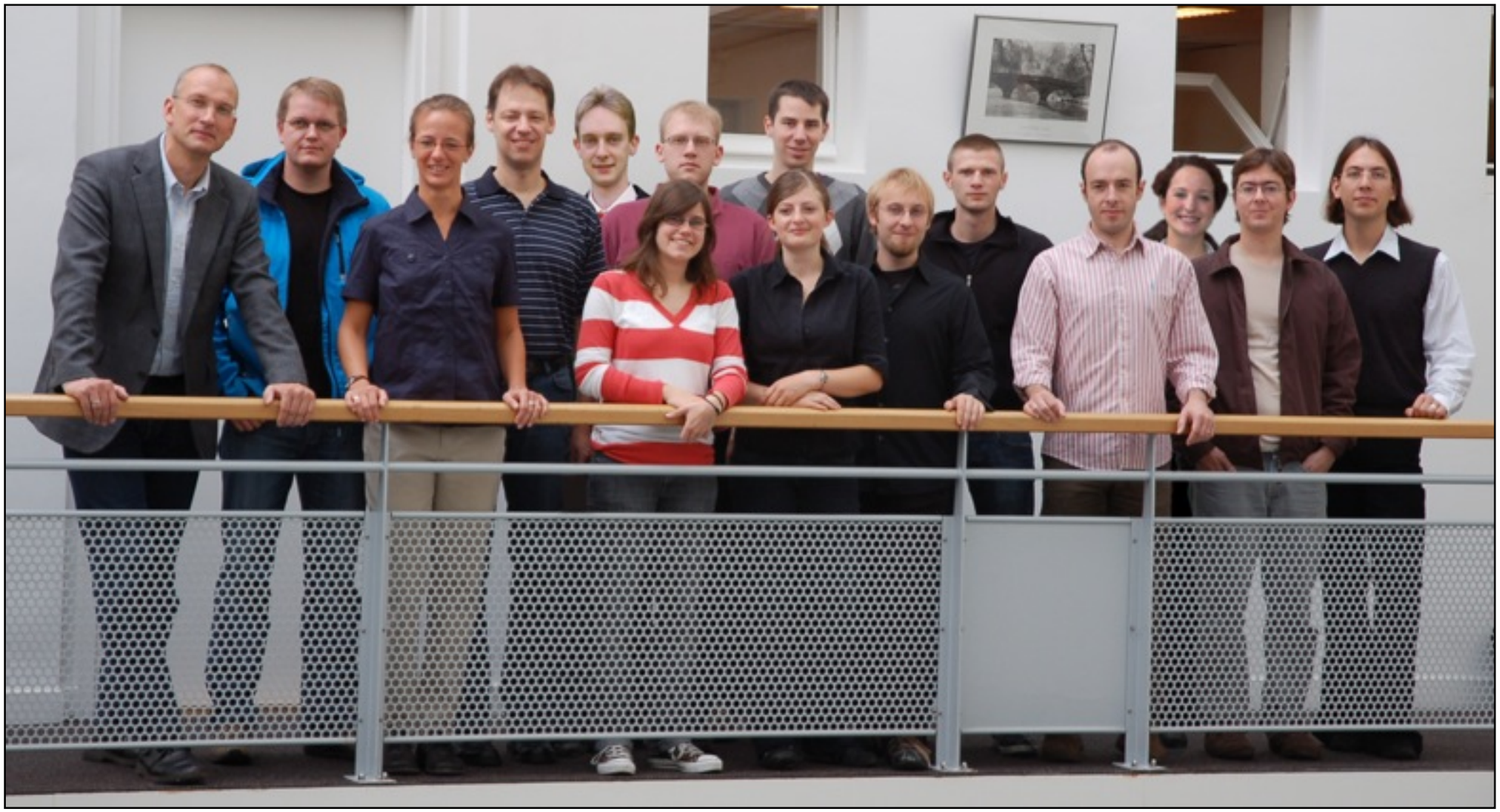
Summary

- Determined structure of ground state from mid-infrared response => (8x2) hexagon
- Phase transition path described by phonon eigenvectors
- Transition (4x1) ➜ (8x2) is strictly NOT a Peierls transition, but energy gain due to band gap opening in analogy to Peierls transition
- (8x2) ➜ (4x1) transition at finite temperatures explained as subtle interplay between lower total energy of insulating (8x2) hexagon and higher vibrational & electronic entropy of metallic and less tightly bound (4x1) zigzag chain structure
- Phase transition is of first order, propagating from condensation nuclei similar to a row of falling dominoes
- Condensation seeds not consisting of single adsorbates, but two adsorbates acting together (work in progress)

PRL **98**, 026105 (2007), PRL **100**, 106802 (2008),
PRL **102**, 226805 (2009), PRL **105**, 126102 (2010),
PRB **84**, 115416 (2011), PRL **109**, 186101(2012)

Acknowledgements

Thanks to my coworkers, especially to Wolf Gero Schmidt, his group, and Simone Sanna



Thanks to our collaborators Friedhelm Bechstedt, John McGilp, Norbert Esser and Han Woong Yeom

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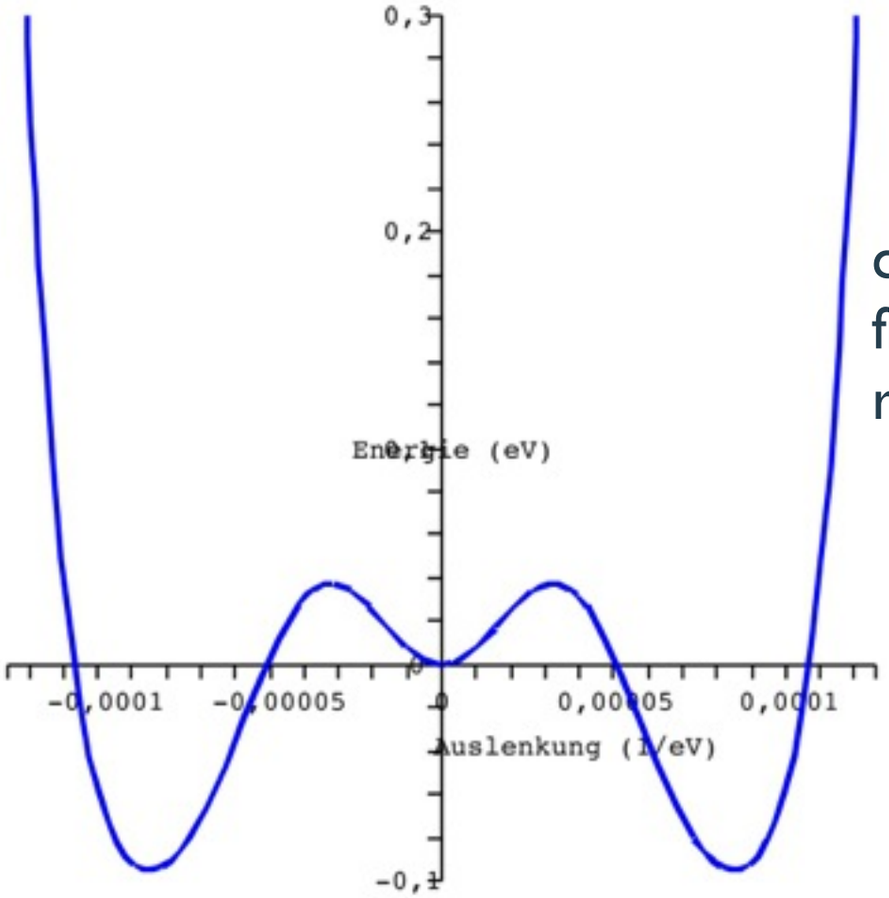
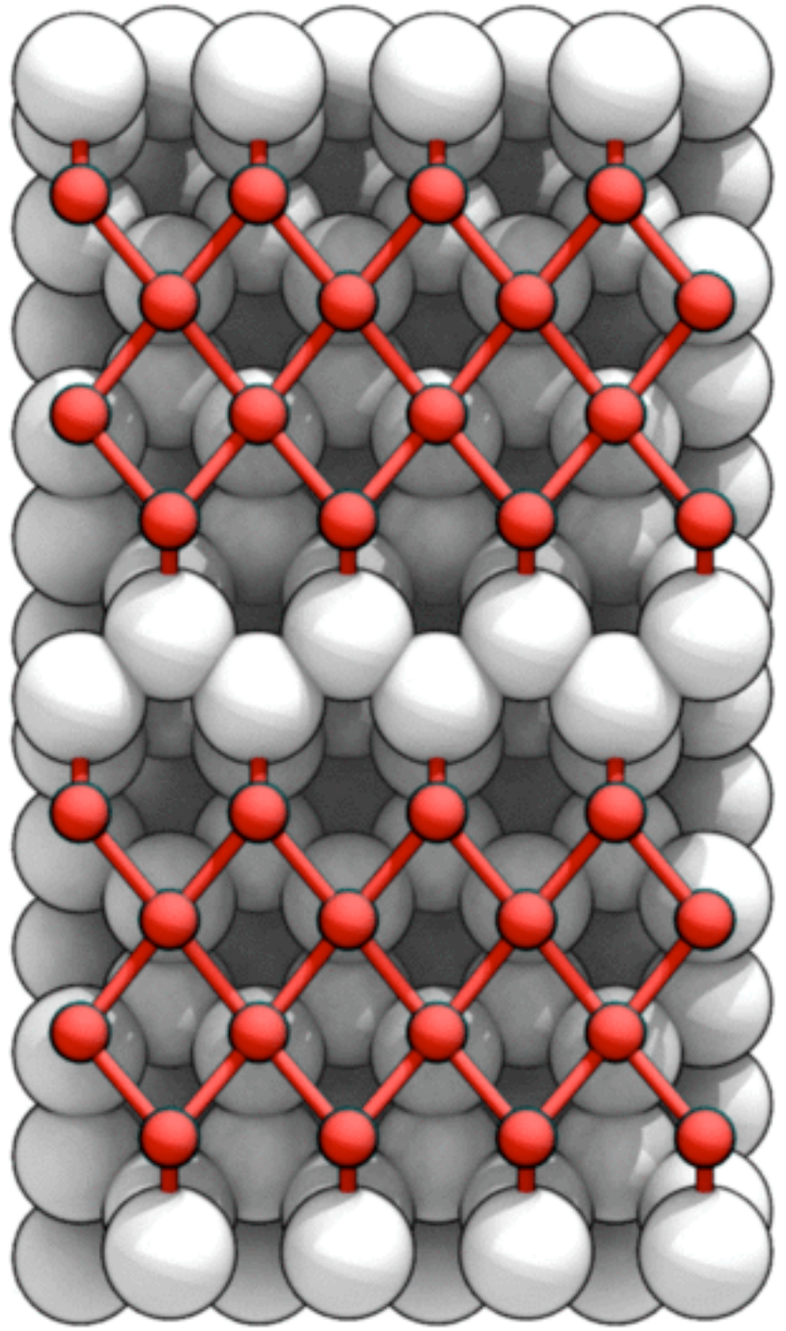
(4x1) <-> (8x2) Transition path

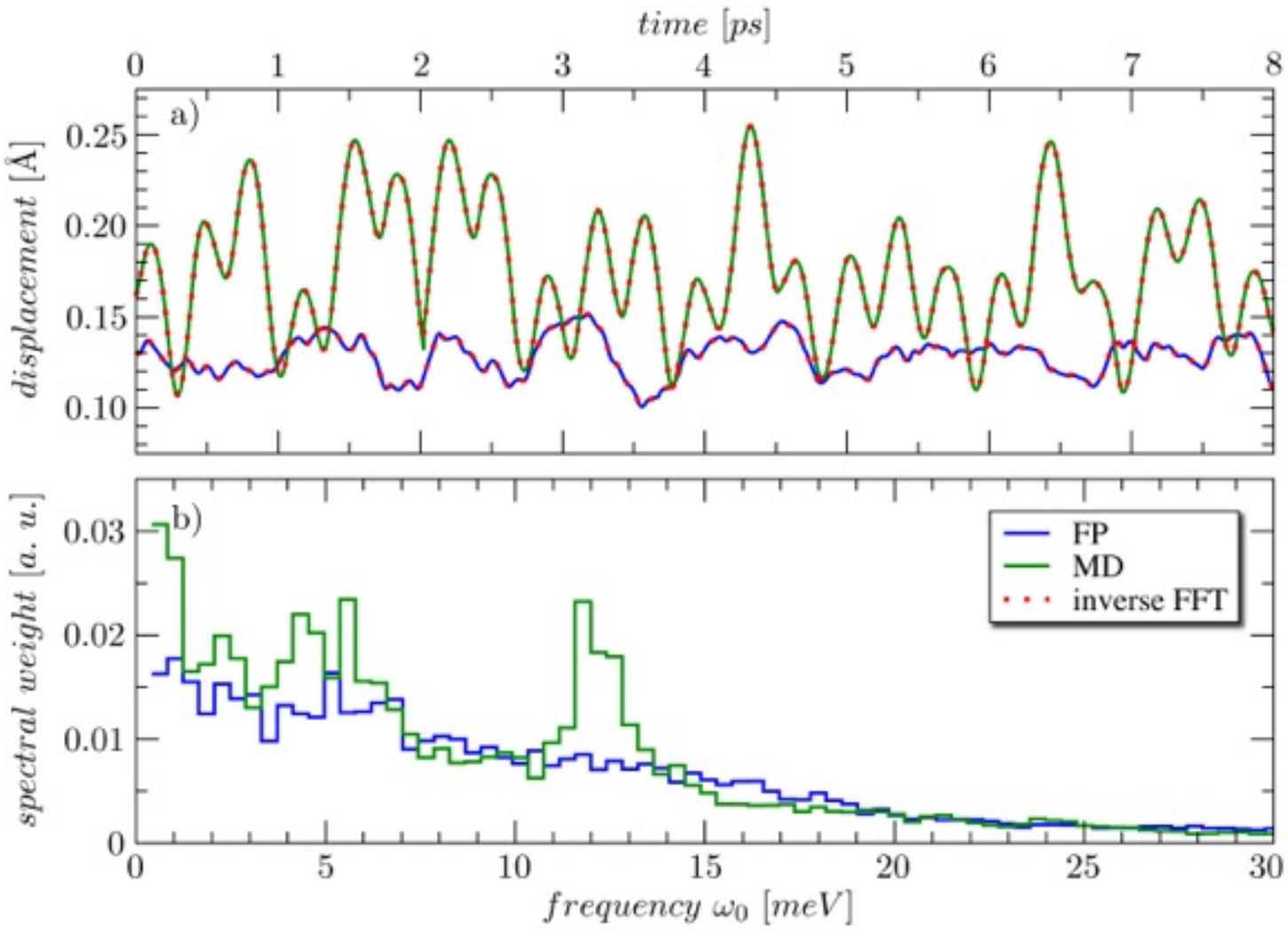
- Obtain transition path from linear combination of frozen-phonon eigenvectors
- Anharmonic effects lead to fluctuation frequency of 16 cm^{-1}

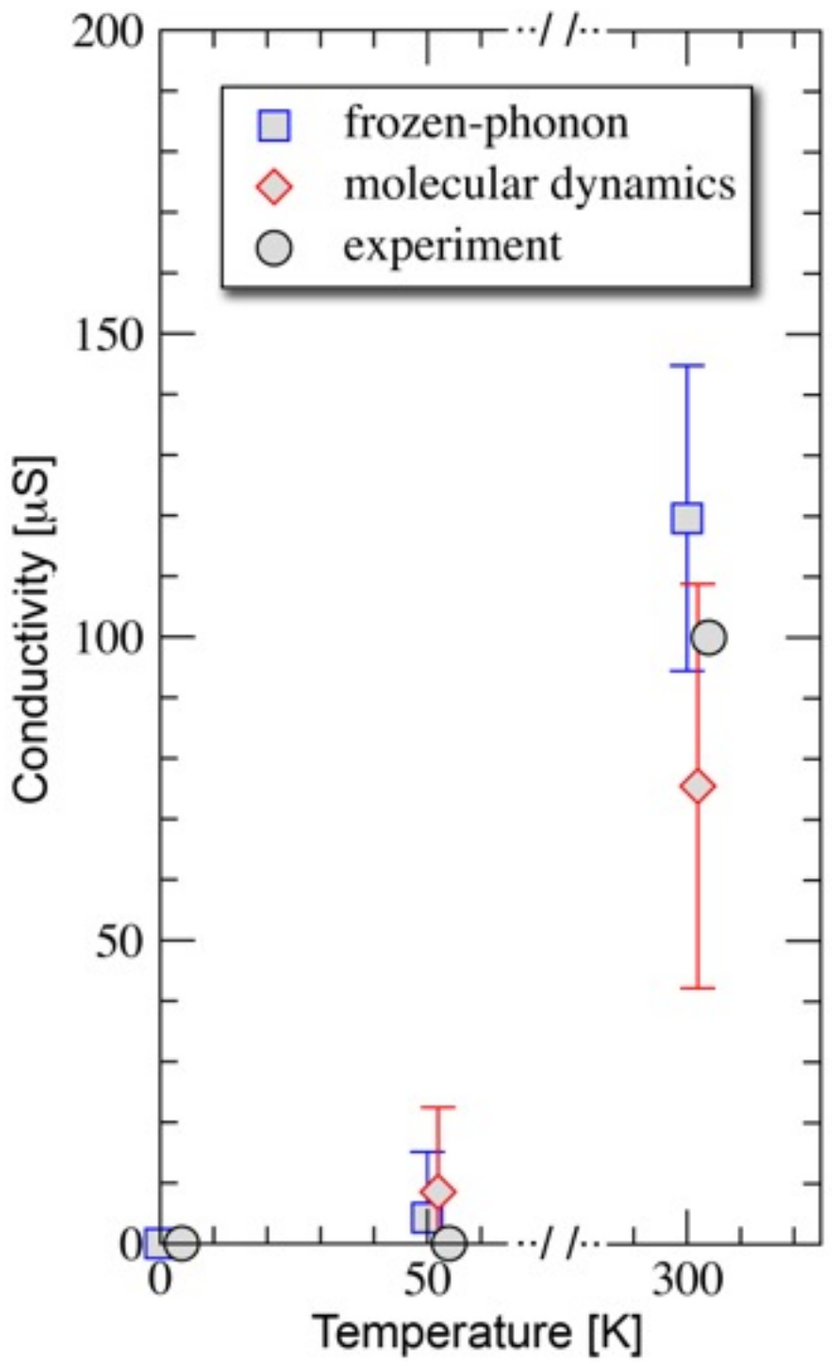


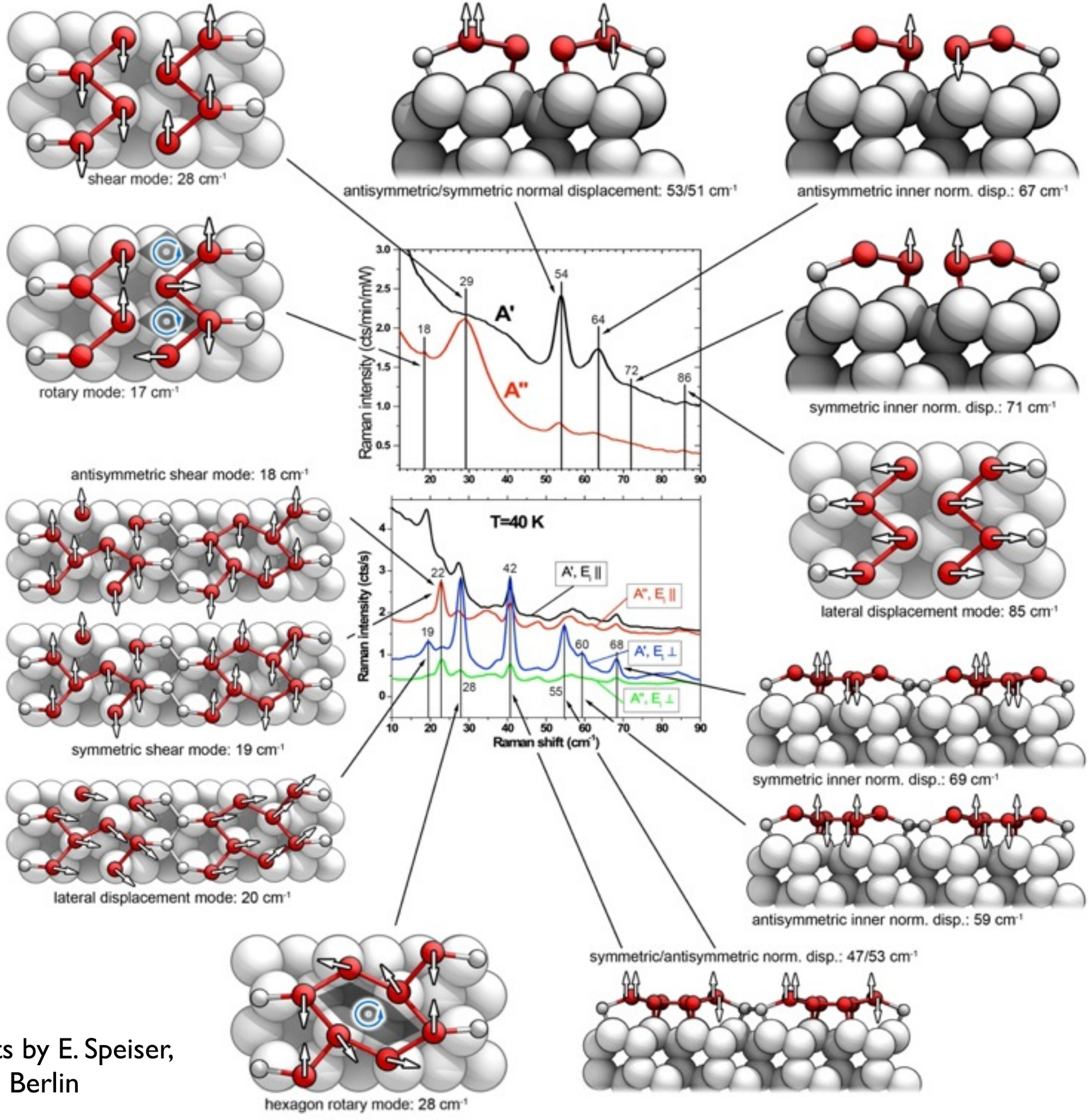
composite potential from shear mode + rot I + rot II + remaining modes



Shear Mode	(8×2) $[cm^{-1}]$	$\rightarrow$	(4×1) $[cm^{-1}]$
Experiment	$2{\cdot}23.5 \pm 0.8$	$\rightarrow$	28 ± 0.9
harmonic approx.	18, 19	$\rightarrow$	28
anharmonicities	20	$\rightarrow$	16


time [ps]
a)
displacement [Å]
b)
spectral weight [a. u.]
FP
MD
inverse FFT
frequency ω_0 [meV]


frozen-phonon
molecular dynamics
experiment
Conductivity [μS]
Temperature [K]



measurements by E. Speiser,
N. Esser, ISAS Berlin

Density functional theory (DFT):

- Hohenberg-Kohn theorem:

$$E_{XC}[n] \approx E_{XC}^{LDA}[n] = \int n(\boldsymbol{r})\epsilon_{XC}^{hom}(n(\boldsymbol{r}))d\boldsymbol{r}$$

$$E_e[n] = T_0[n] + \frac{1}{2}\int \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}d\boldsymbol{r}' + \int n(\boldsymbol{r})V(\boldsymbol{r})d\boldsymbol{r} + E_{XC}[n]$$

[Walter Kohn, Nobel Prize for chemistry in 1998]

atomic positions

Starting point: initial geometry

⇩

external potential

interatomic forces

Kohn-Sham self-consistent electron structure

$$\left\{-\frac{\nabla^2}{2} + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}' + V(\boldsymbol{r}) + \frac{\delta E_{XC}^{LDA}}{\delta n(\boldsymbol{r})}\right\}\psi_j(\boldsymbol{r}) = \epsilon_j\psi_j(\boldsymbol{r})$$

$$n(\boldsymbol{r}) = \sum_j^{occ.} |\psi_j(\boldsymbol{r})|^2$$

⇩

structurally relaxed ground-state

- vibrational and thermal properties
- electronic properties
- spectroscopic and transport properties

Excited states (GW/BSE)

- DFT disregards screened e^-–e^- interaction and e^-–h interaction for excited states => band gap underestimation, wrong distribution of spectral weights
- Perturbative approaches for including screening (GW) and e^-–h interaction (Bethe-Salpeter), starting from Quantum Liouville equation

$$i\frac{d\hat{\rho}(t)}{dt} = \left[\hat{\mathcal{H}}(t), \hat{\rho}(t)\right] \qquad \rho(\mathbf{r},\mathbf{r}',t) = \sum_v \phi_v^*(\mathbf{r},t)\phi_v(\mathbf{r}',t)$$

single particle occ. orbitals

$$\int \hat{\mathcal{H}}(\mathbf{r},\mathbf{r}',t)\phi(\mathbf{r}',t)d\mathbf{r}' = \left(-\frac{1}{2}\nabla^2 + v_H(\mathbf{r},t) + v_{ext}(\mathbf{r},t)\right)\phi(\mathbf{r},t) + \int \Sigma(\mathbf{r},\mathbf{r}',t)\phi(\mathbf{r}',t)d\mathbf{r}'$$

time-dep. perturbation, i. e. electromagn. field

self-energy

$$\Sigma_{COH}(\mathbf{r},\mathbf{r}') = \frac{1}{2}\delta(\mathbf{r}-\mathbf{r}')W_p(\mathbf{r},\mathbf{r}')$$

$$\Sigma_{SEX}(\mathbf{r},\mathbf{r}',t) = -\sum_v \phi_v(\mathbf{r},t)\phi_v^*(\mathbf{r}',t)W(\mathbf{r},\mathbf{r}')$$

statically screened Bethe-Salpeter equation (BSE)

screened Coulomb interaction

Excited states (GW/BSE)

- To correct for DFT's band gap underestimation, quasiparticle energies can be obtained in GW approximation from

$$\Sigma_{GW}(\mathbf{r},\mathbf{r}';i\omega) = \frac{1}{2\pi}\int G(\mathbf{r},\mathbf{r}';i(\omega-\omega'))W(\mathbf{r},\mathbf{r}';i\omega')d\omega'$$

- Screened Coulomb interaction required (in random phase (RPA) approx.)

$$W(\mathbf{r},\mathbf{r}') = \int \epsilon^{-1}(\mathbf{r},\mathbf{r}'')v_c(\mathbf{r}'',\mathbf{r}')d\mathbf{r}''$$

- Bottleneck: calculation, storage & inversion of dielectric matrix is very computationally demanding, involves large sums over empty states and is hard to converge
- Solution: spectral representation of RPA dielectric matrix; obtain matrix from directly calculating eigenvectors and eigenvalues

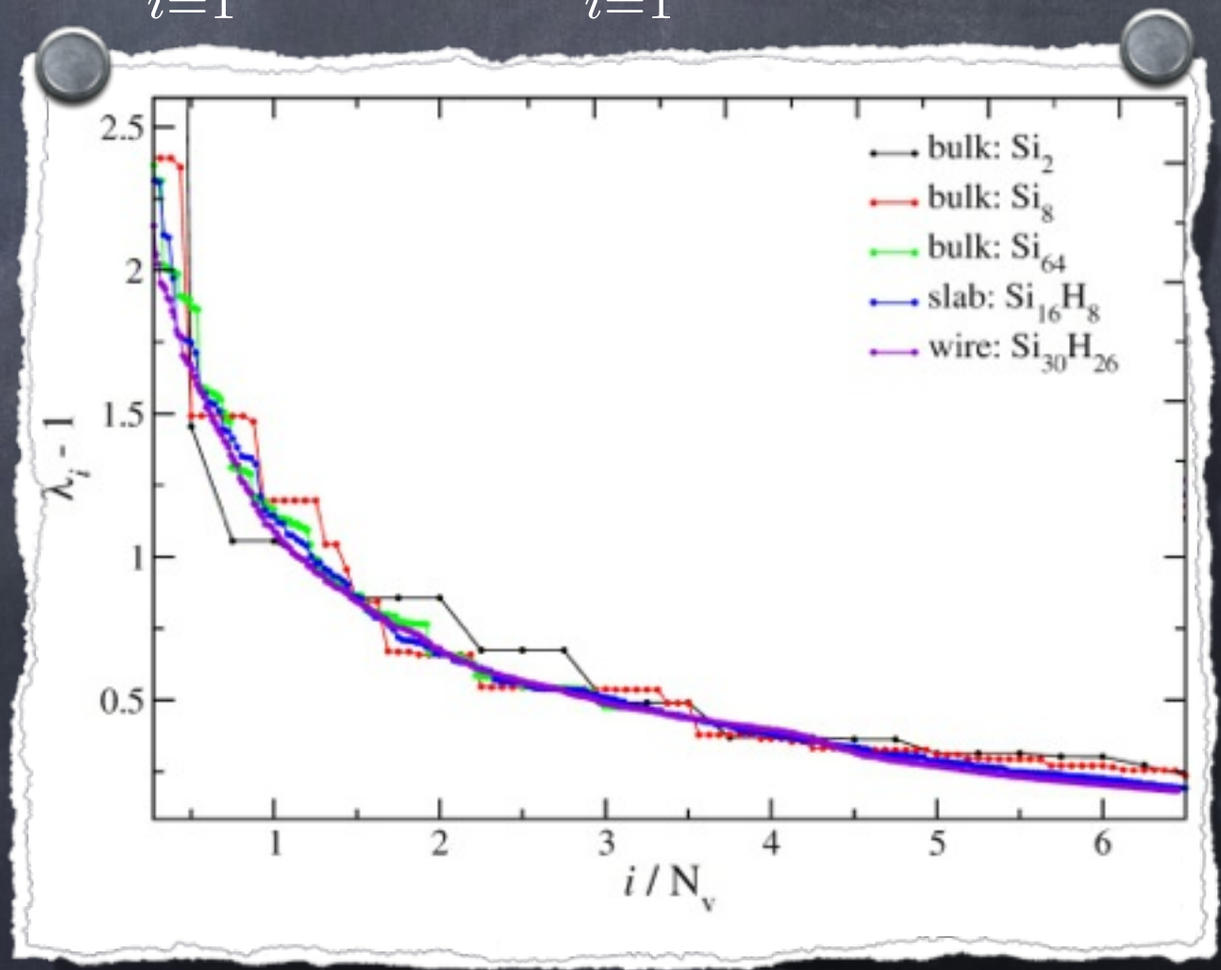
$$\tilde{\epsilon} = \sum_{i=1}^{N}\tilde{\mathbf{v}}_i\lambda_i\tilde{\mathbf{v}}_i^H = \sum_{i=1}^{N}\tilde{\mathbf{v}}_i(\lambda_i-1)\tilde{\mathbf{v}}_i^H + I$$

=> no summation over empty states, no inversion, storage of eigenvector/-value pairs only!

How to calculate the screening

- Obtaining the eigenvectors/-values does NOT require explicit knowledge of the matrix; knowledge of the action of the matrix on an arbitrary vector is sufficient!
- in linear response: $(\epsilon - I)\Delta V_{SCF} = -v_c \Delta n$
- charge density response Δn to perturbation of self-consist. field ΔV_{SCF} can be evaluated from density functional perturbation theory
- orthogonal iteration procedure to obtain eigenvectors/-values, using ΔV_{SCF} as trial potentials
- in RPA fast monotonous decay of dielectric eigenvalue spectrum
- single parameter N_{eig} to control numerical accuracy

$$\tilde{\epsilon} = \sum_{i=1}^{N} \tilde{\mathbf{v}}_i \lambda_i \tilde{\mathbf{v}}_i^H = \sum_{i=1}^{N} \tilde{\mathbf{v}}_i (\lambda_i - 1) \tilde{\mathbf{v}}_i^H + I$$



[H. Wilson *et al.*, PRB **79**, 245106 (2009); D. Rocca *et al.*, J. Chem. Phys. **133**, 164109 (2010); H.-V. Nguyen *et al.*, PRB **85**, 081101 (2012)]