UPR 3346
Univ. Poitiers / ENSMA

INSTITUT P'

Fluides, thermique et combustion

Génie mécanique et systèmes complexes

Physique et mécanique des matériaux

Macro Homogénéisation

Eléments finis

Dynamique moléculaire

DFT

Electron GW, BS, ...

S. Brochard, J. Godet, J. Durinck, V. Mauchamp, C. Mastail, C. Gérard, J. Colin, L. Pizzagalli

Cloquage / adhésion

Plasticité des matériaux / nanos

Défauts liés à l'irradiation

Croissance

Pptés optiques de matériaux complexes

Is it possible to make a realistic amorphous silicon model?

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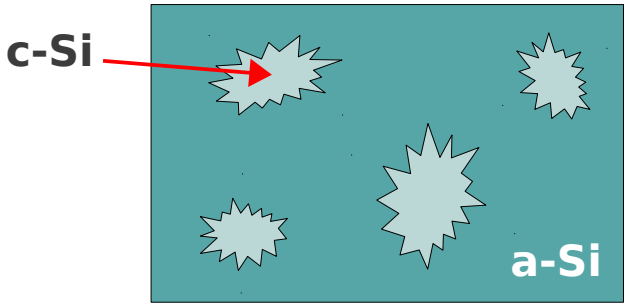
Facts from experiments and issues

a-Si → a model amorphous material with short range order

Facts

→ a-Si is less dense than c-Si (1.8%)
→ average 1st neighbors distance and angle are known (dispersion too)
→ Energy (enthalpy) difference between c-Si and a-Si ranges from 0.07 eV to 0.15 eV
→ Presence of coordination defects

The paracrystallinity assumption: is a-Si fully disordered?



→ Evidence for medium range order in a-Si (created by irradiation or indentation)
→ May be explained by paracrystallinity (RMC)

→ Do a fully disordered (no crystal grains) or perfectly relaxed (no defects) a-Si exist?

→ Is there a unique experimental a-Si state ?

→ Realistic amorphous Si models are needed.

a-Si model: the Continuous Random Network

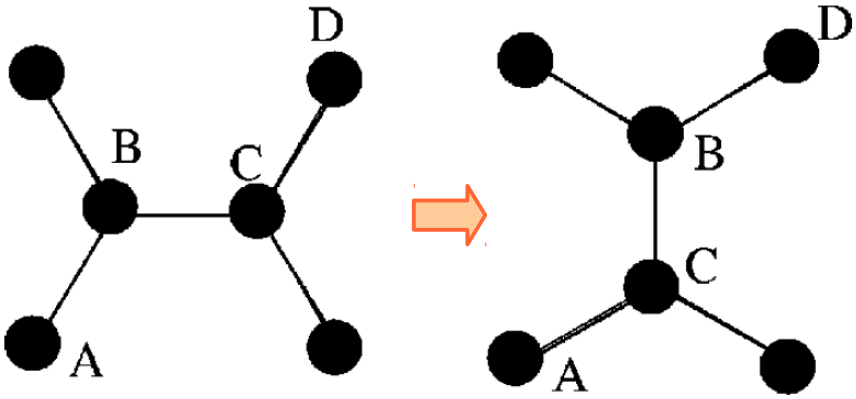
→ Based on an idea: the best a-Si model is a Continuous Random Network with no defects

→ CRN models are built by rules, and include only 4-fold coordinated Si atoms

The WWW procedure

Wooten, Winer and Weaire, PRL (1985)

c-Si ⇒ **a-Si (Sillium)**



Barkema and Mousseau

Barkema and Mousseau, PRB (2000)

Random ⇒ **a-Si**

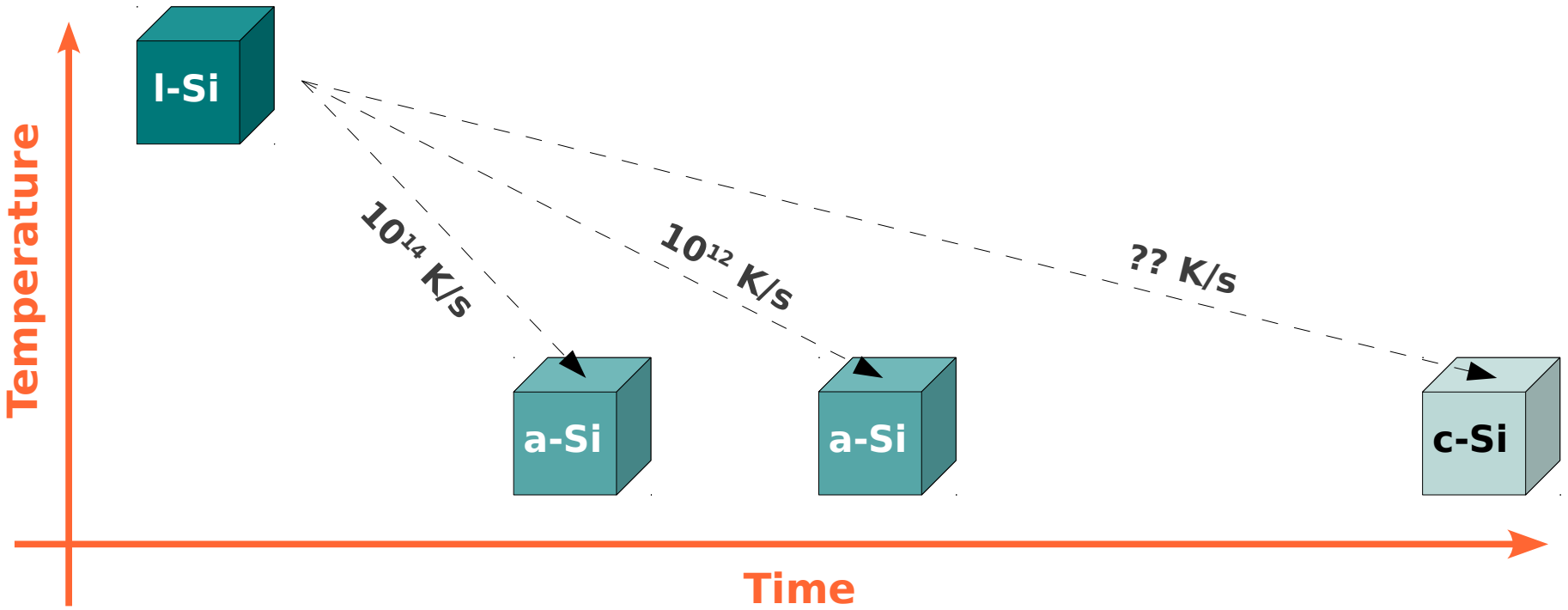
→ No defects in the final structure

→ Cooking recipes require a prior knowledge of the structure to obtain

a-Si model: the quenched liquid

→ Try to mimic quenching experiments

→ No preconceived notion of the final structure, use only atomic interactions



→ Presence of point defects in the final structure

→ Results depend on the classical potential used (and on the quench rate too)

Is there a winner?

CRN	Quenched liquid
- “Rules” dependence	- Potential dependence
- Requires potentials relaxation	- Ab initio not possible
+ No point defects	+ Point defects in final structure
+ Very good RDF, θ	+ Very good RDF, θ

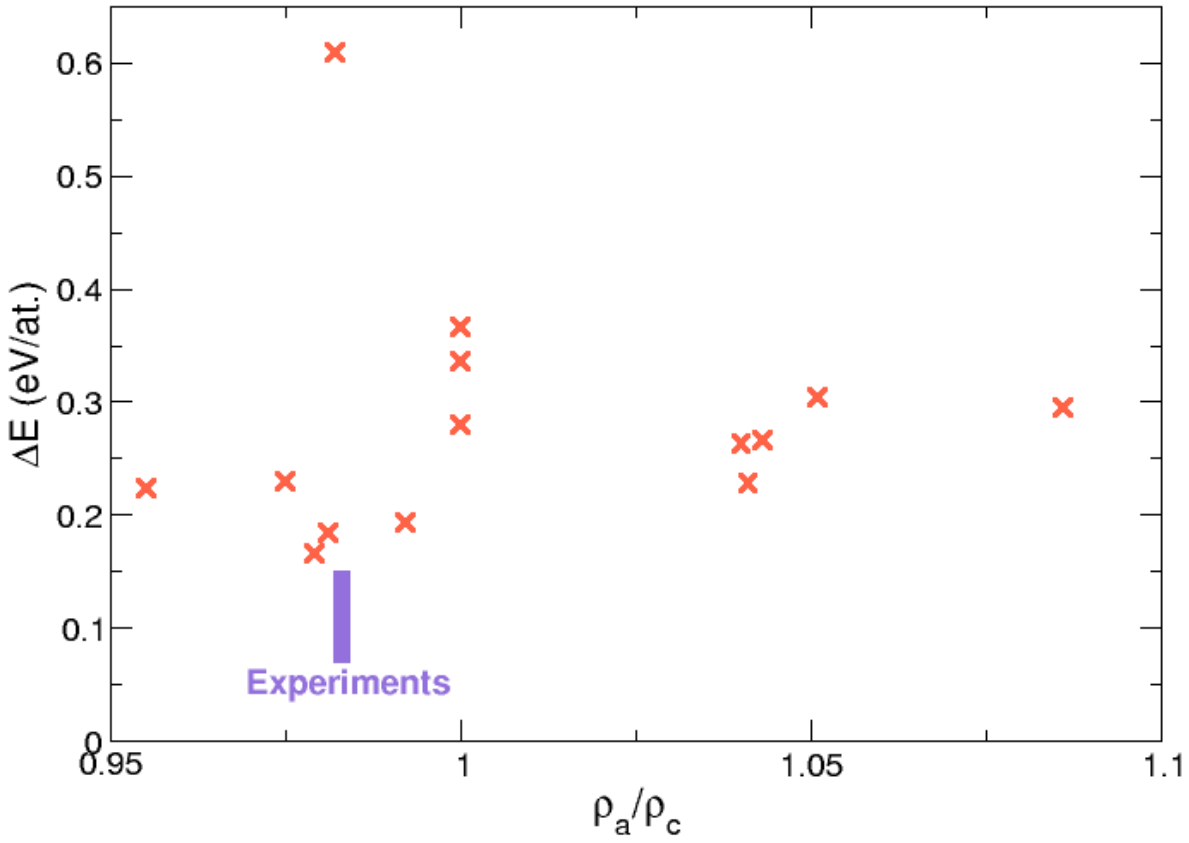
→ CRN typically considered as ideal a-Si

→ CRN used as starting point for investigating vacancies in a-Si

→ Averaged quantities (RDF, θ) cannot be used as a good quality criterion

Is it possible to push further the state of the art?

New direction: instead of examining averaged properties, focus on extensive quantities !

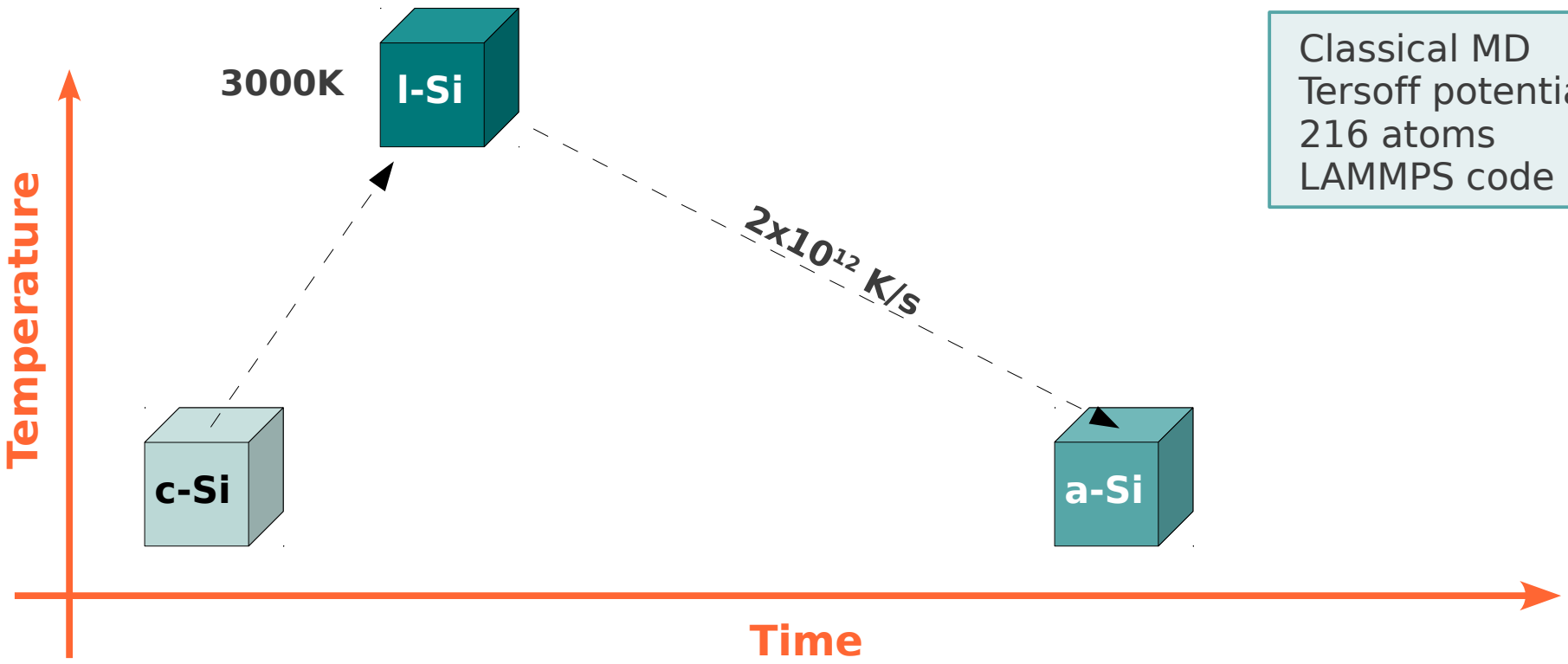


→ Final density is largely spread in simulated models

→ Few calculations are close (but still too high) in energy

Our goal: focus on energy and density

Starting point: slowly quenched liquid silicon



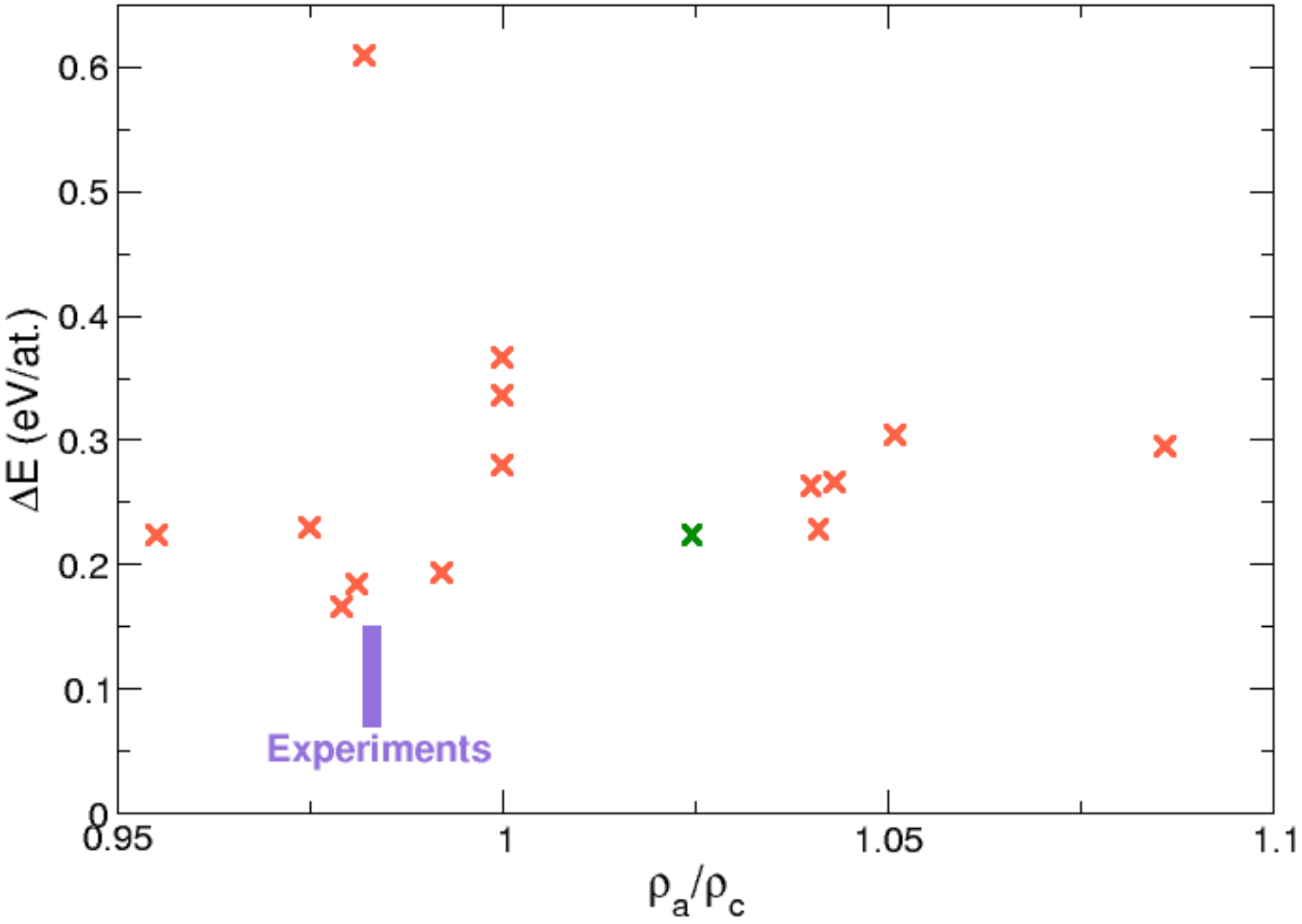
Classical MD
Tersoff potential
216 atoms
LAMMPS code

→ The structural parameters are in fair agreement with experiments

→ The final excess energy (rel. to c-Si) is 0.224 eV/at.

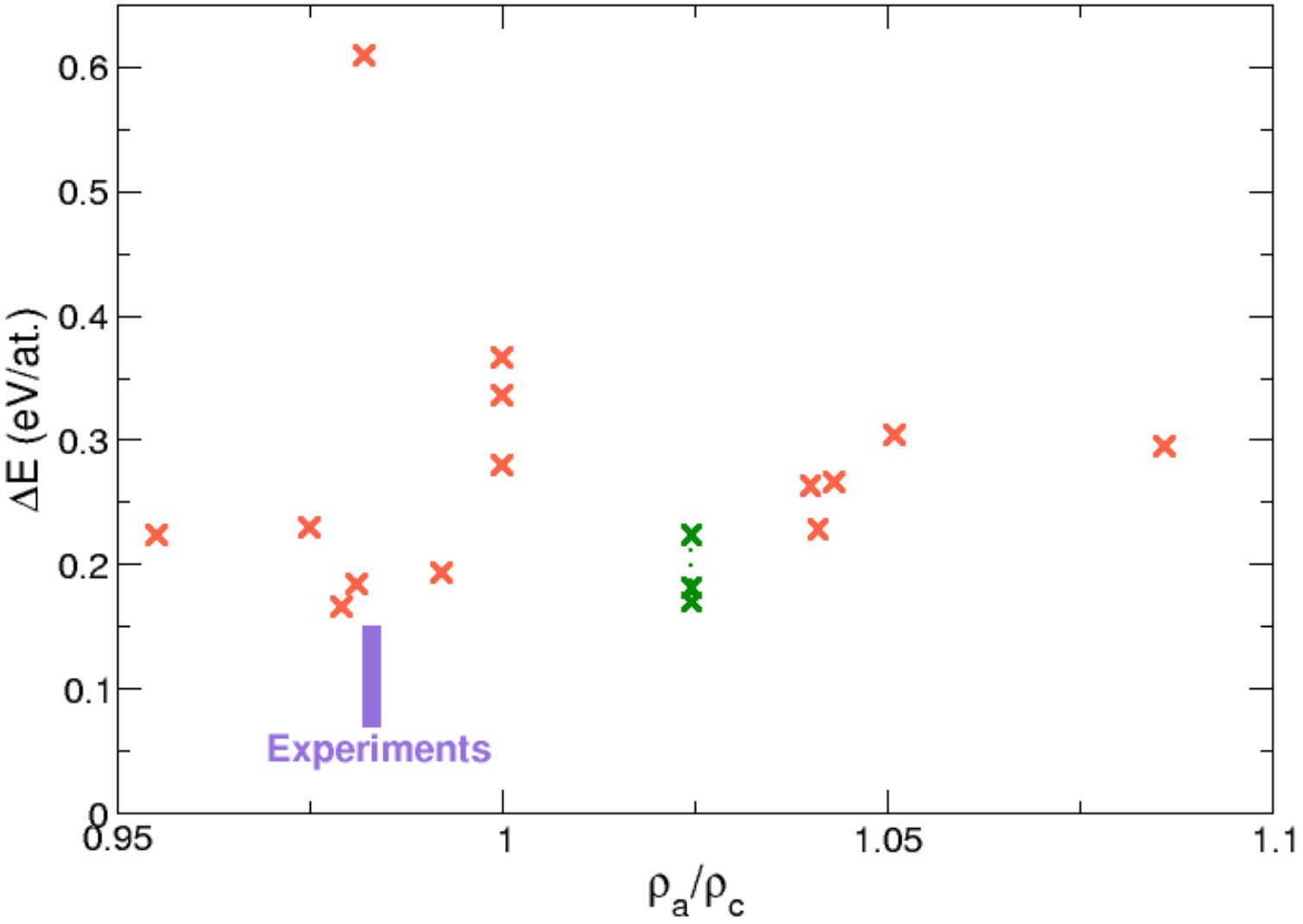
→ With a reference value of 0.1 eV/at., about 27 eV to gain !!!

The strength of ab initio annealing



0.224 eV/at.

The strength of ab initio annealing

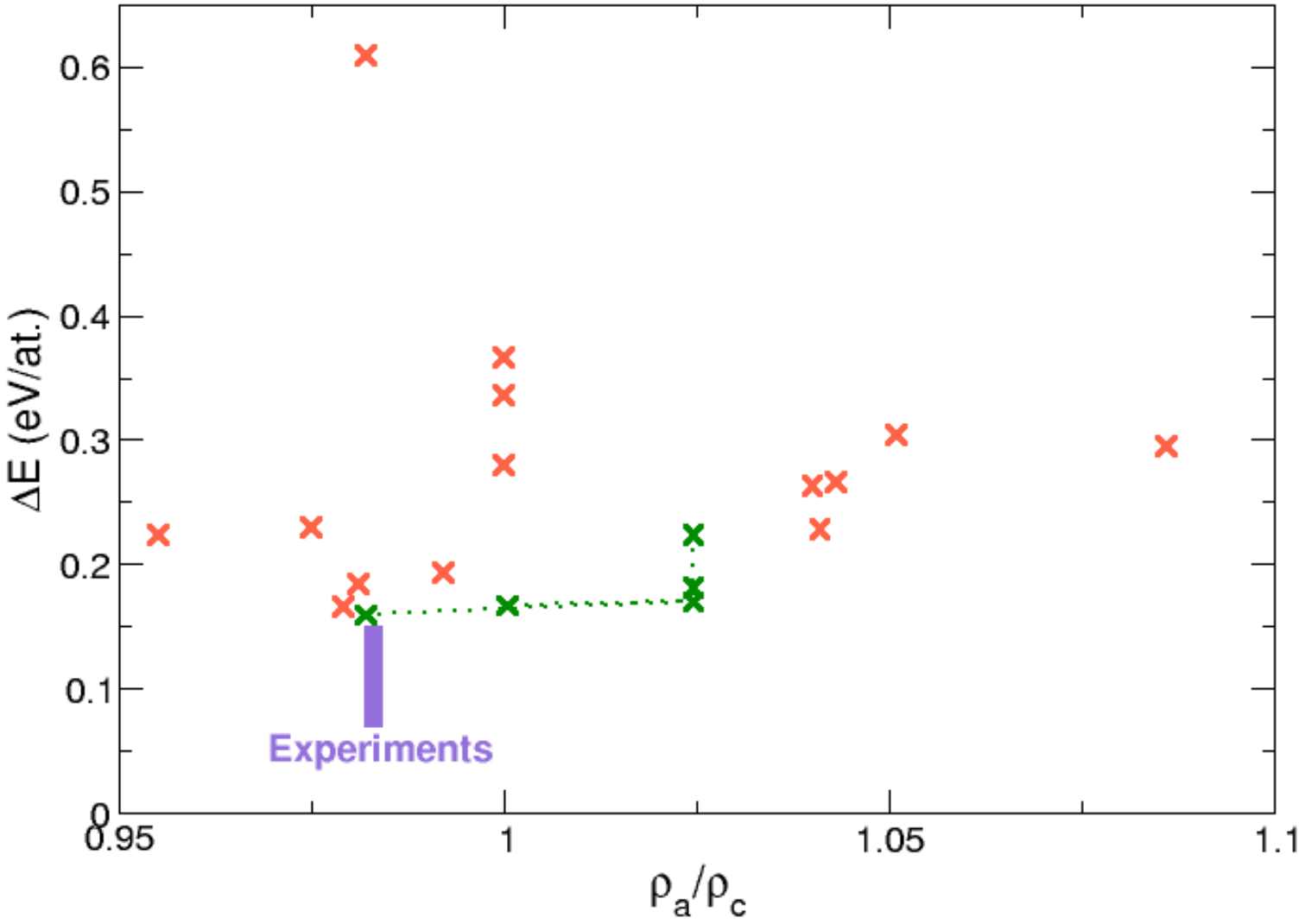


0.224 eV/at.

DFT-GGA
Annealing

0.170 eV/at.

The strength of ab initio annealing



0.224 eV/at.

DFT-GGA
Annealing

0.170 eV/at.

DFT-GGA
Scaling +
Annealing

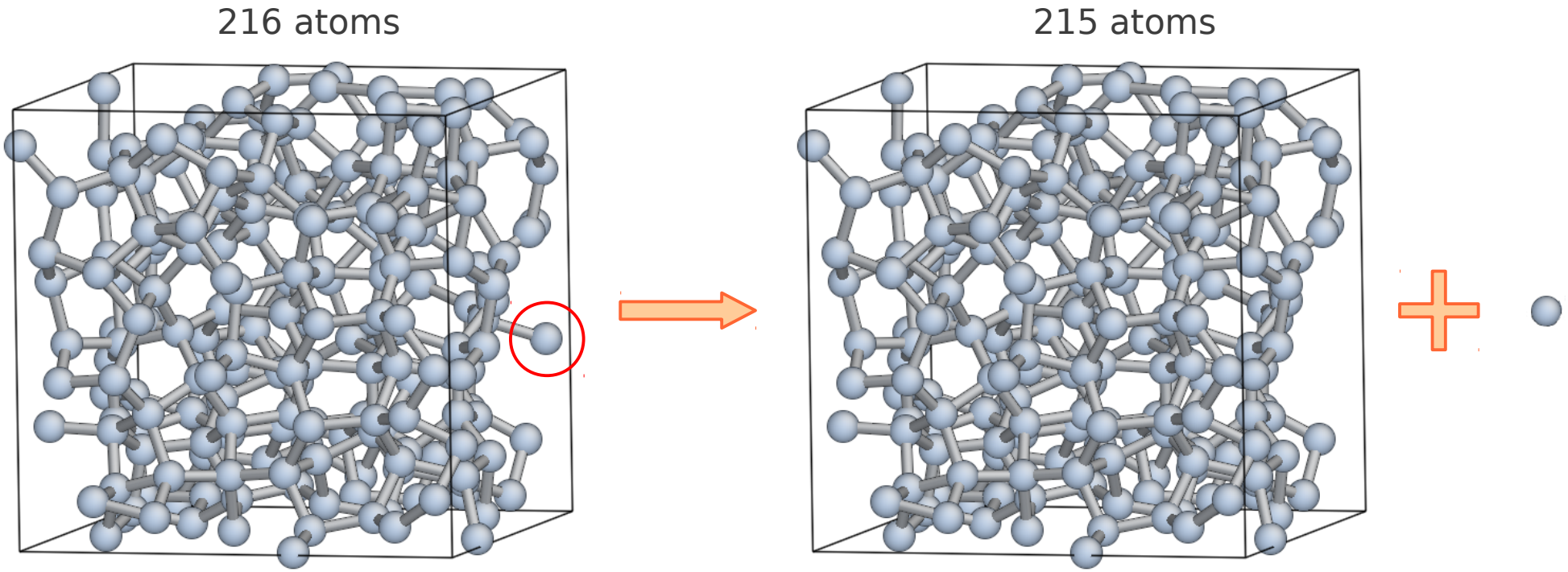
0.159 eV/at.

→ Ab initio greatly lowers the energy (relaxation or electronic effect ?)

→ Density cannot be optimized during annealing (→ scaling)

→ Final energy/density close to experiments

Formation energy of vacancy in imperfectly relaxed a-Si



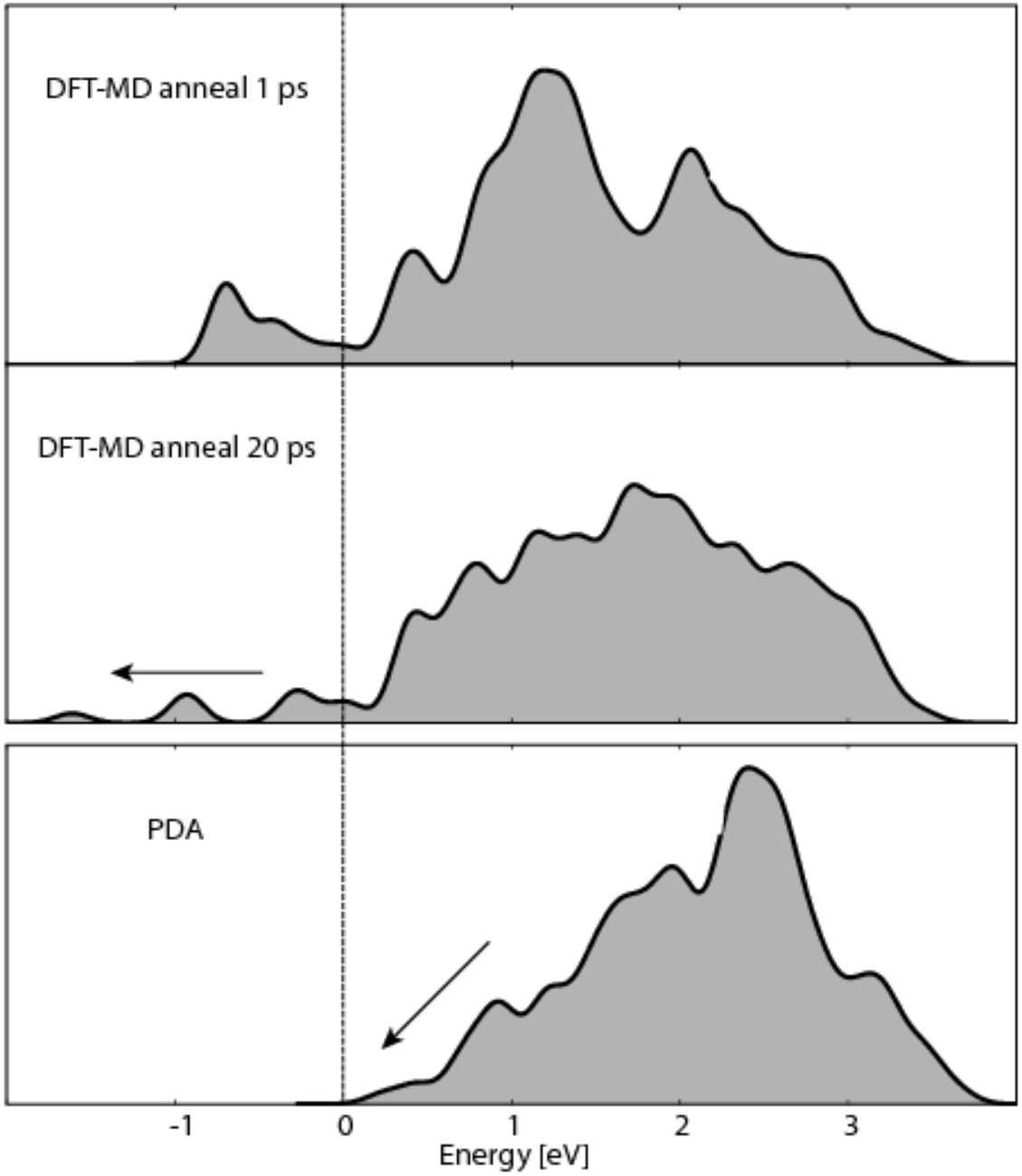
$$E_f = E(215) + E(1) - E(216)$$

→ If the amorphous network is not well relaxed, Ef can be negative !

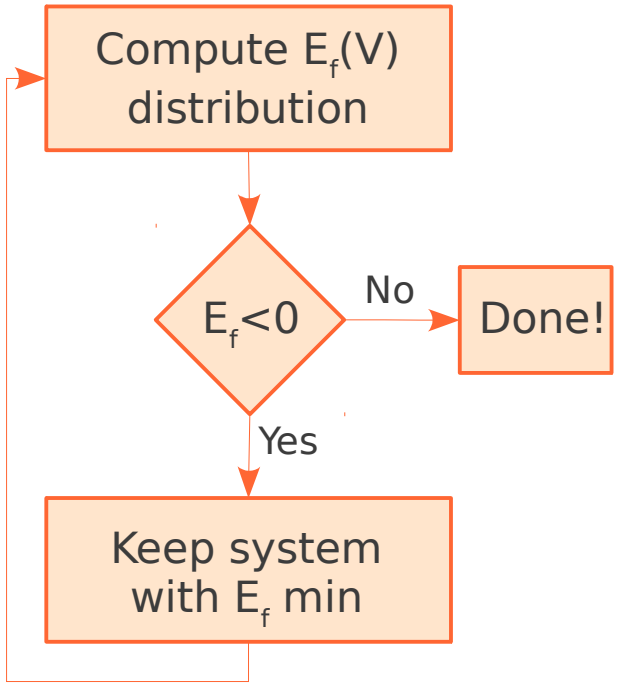
Miranda et al., J. Non. Cryst. Solids (2004)

The ultimate refining: the PDA procedure

Vacancy formation energy distribution



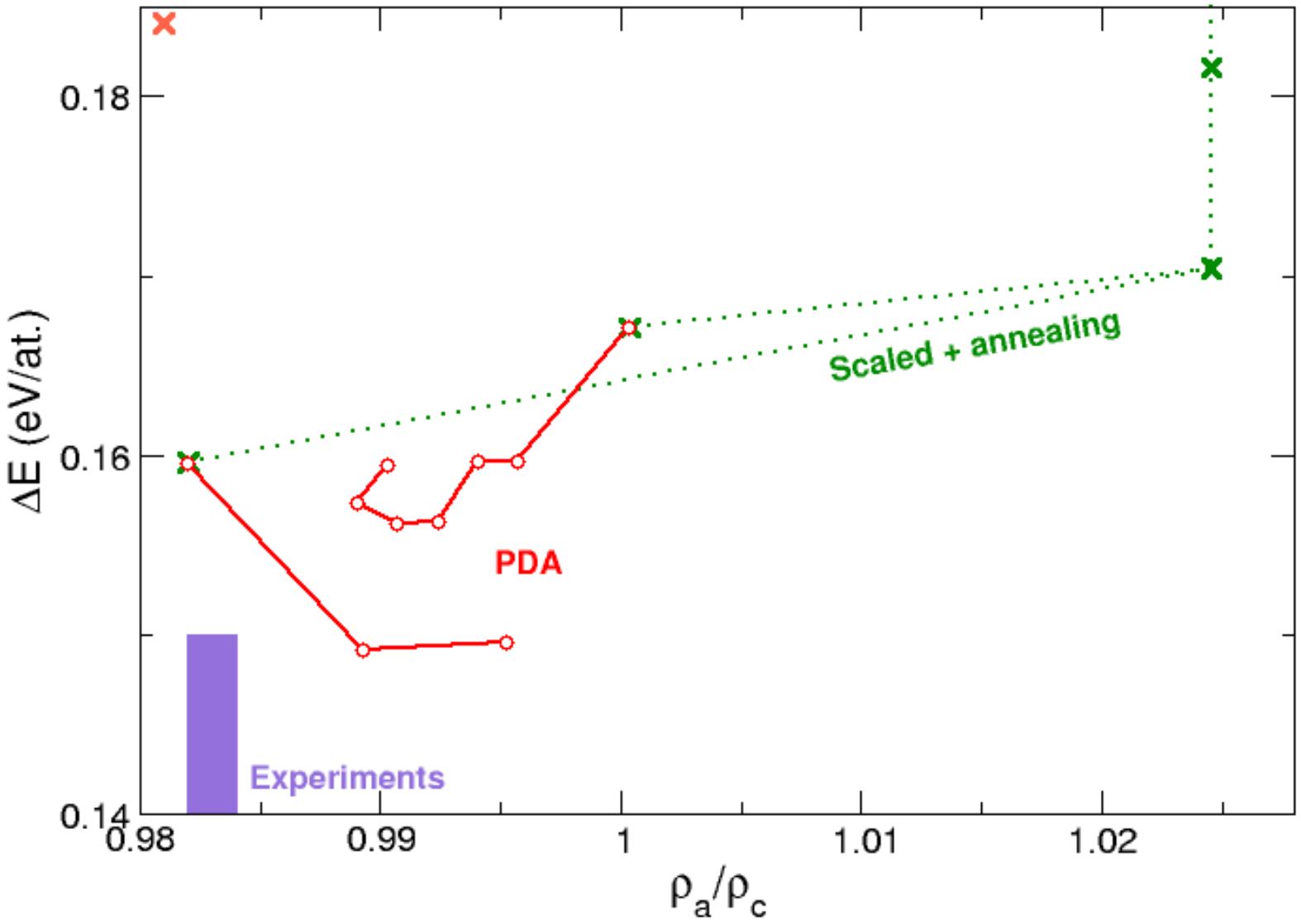
PDA procedure



→ Simultaneous optimization of energy and density

→ less time-consuming than annealing

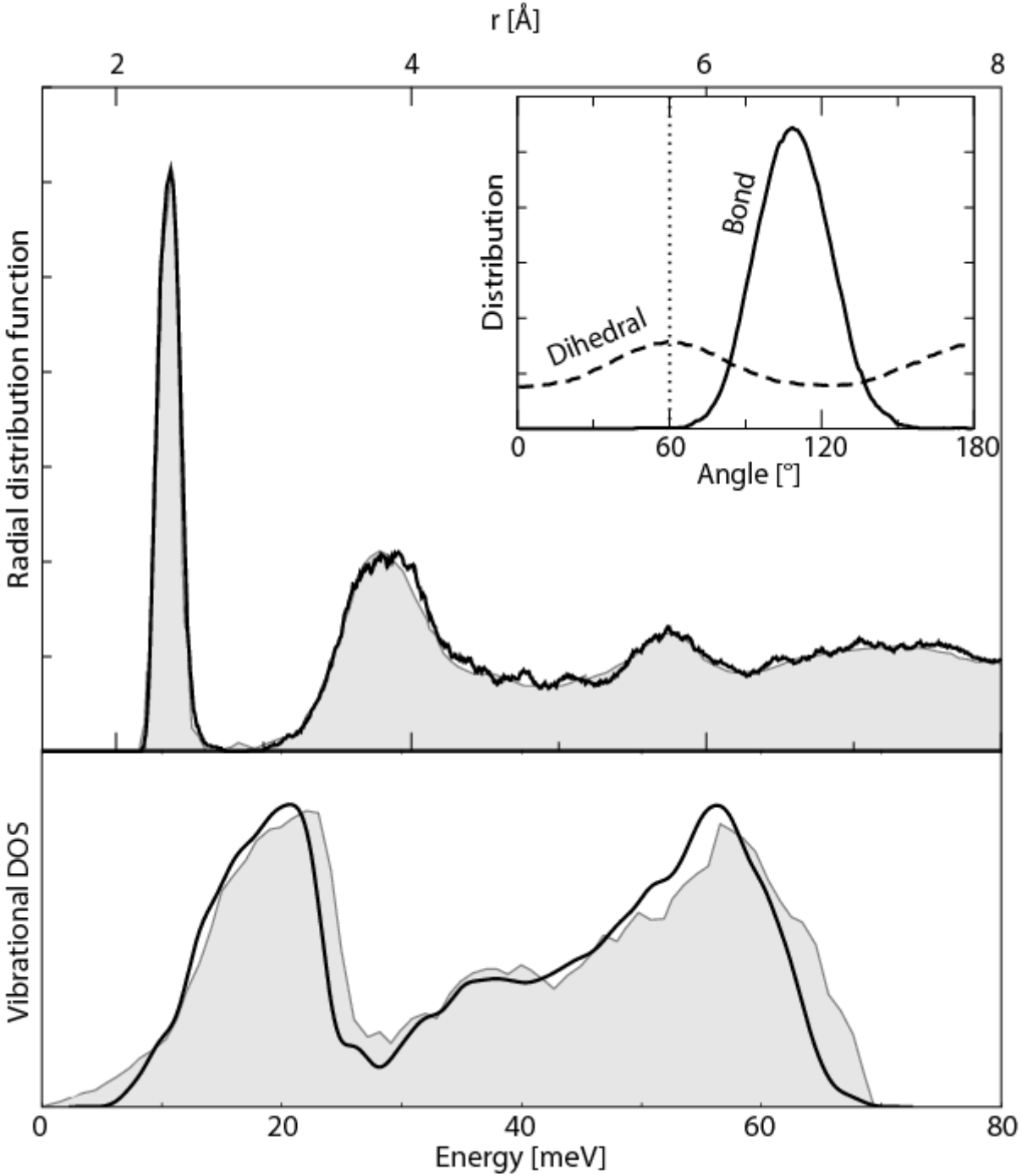
The ultimate refining: the PDA procedure



→ The best optimized sample reaches the upper range of experiments

→ Density is slightly too high

Final model: structural properties



	Exp.	Calc.
<r>	2.351	2.351
<θ>	107.8°-108.5°	108.2°
Δθ	9°-11°	10.5°

RDF and vibrational DOS in excellent agreement with exp.

→ Averaged structural properties better than in previous models

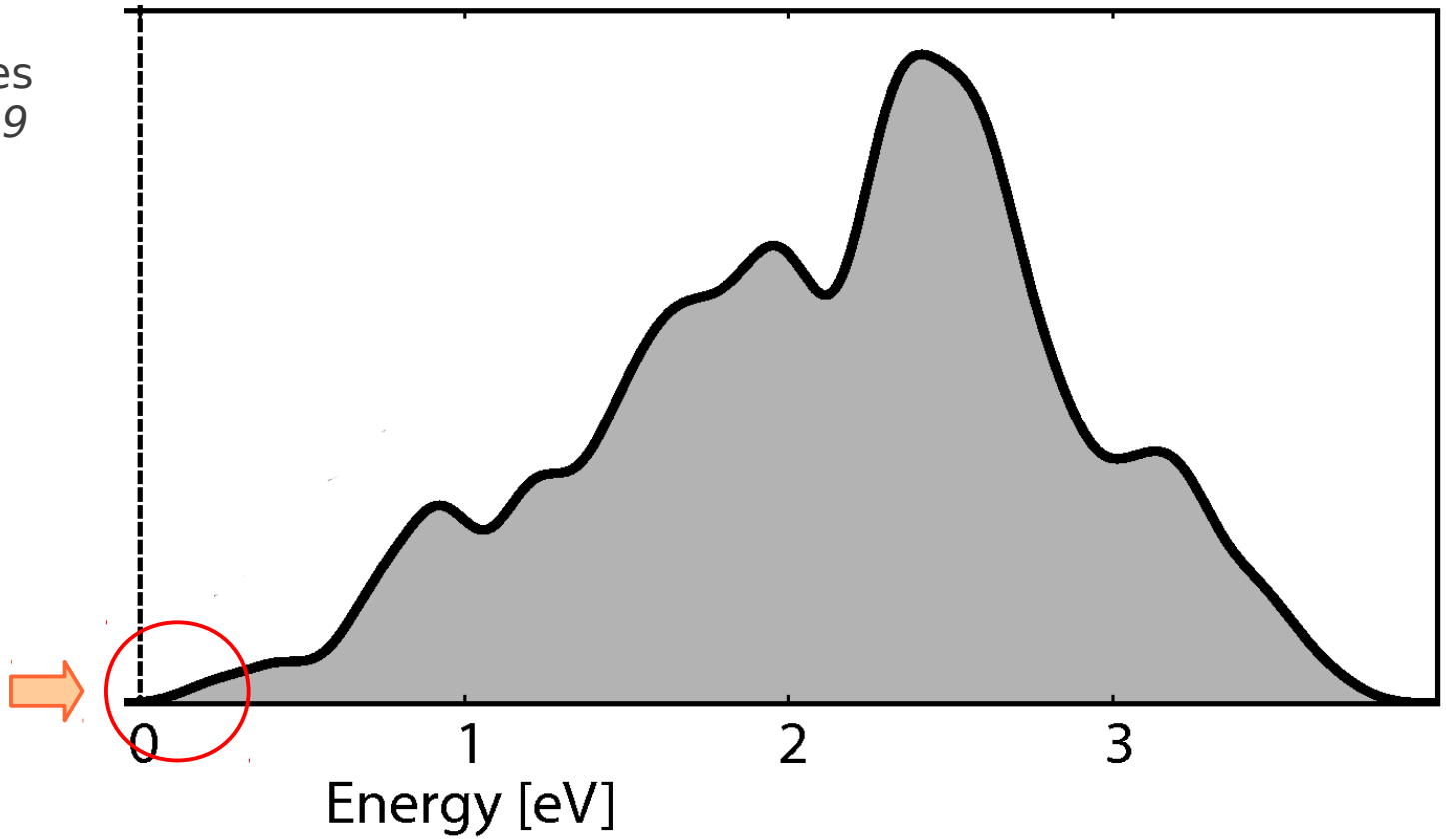
→ Vibrational properties well reproduced

Coordination issue

C=3.88, i.e. 12% DB
or about 2% vacancies
Laaziri et al, PRB 1999

All our models:
C = 3.99 - 4.02

Very low energy
vacancies



→ Considering E_f = 0.1 eV, the amount of thermal vacancy at RT is about 2%

Is the exp/model energy comparison complete?

$$\Delta H = \Delta U + P\Delta V$$
$$= \Delta U(\text{ions}+e^-) + \Delta U(ZPE) + \Delta U(T\neq 0) + P\Delta V$$

- Electronic structure effects: beyond standard DFT-GGA/LDA ? (hybrid functional, QMC)

  LDA model: ΔU=0.148 eV/at. / ρ_a/ρ_c = 1.009
  Hybrid calc. : ΔU=0.18 eV/at. (PBE0) ; E=0.20 eV/at. (HSE06)

- Zero-point energy: calculated using classical potentials and harmonic approximation

  ΔZPE = -0.005 eV/at.

- T≠0: Harmonic approximation

  $\Delta U(T = 938K)$ = +0.005 eV/at.

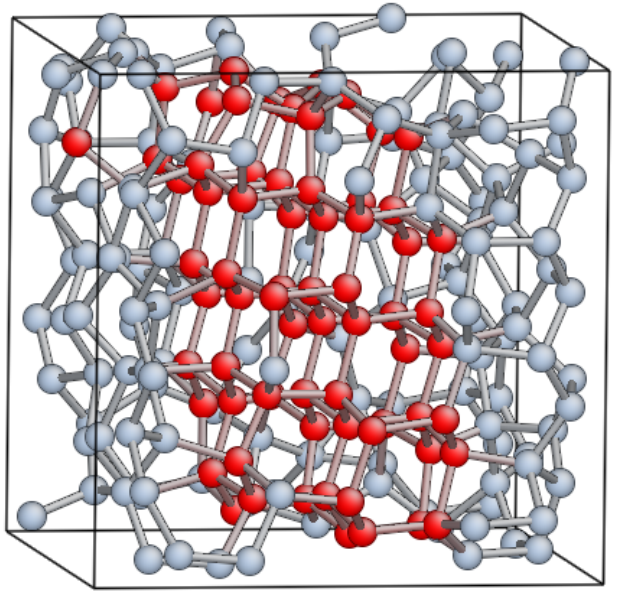
- PΔV: Considering a 2% expansion of a-Si/c-Si, and atmospheric pressure

  PΔV = 0.00000025 eV/at.

→ Should we consider anharmonic effects (thermal expansion, e^--ph coupling)?

Final model: Do a fully disordered network really exist?

Our model energy is in the upper range of measurements !



➡ Effect of remaining defects ?

CRN model: E=0.149 eV/at. / ρ_a/ρ_c = 0.967

➡ The paracrystalline assumption

PC model: E=0.115 eV/at. / ρ_a/ρ_c = 0.994

➡ The only (?) way to decrease energy is by introducing “crystallinity” into the system

→ Several experimental a-Si states possible (depending on H presence) ?

→ Can a perfectly continuous random network exist in the real world ?

Conclusions

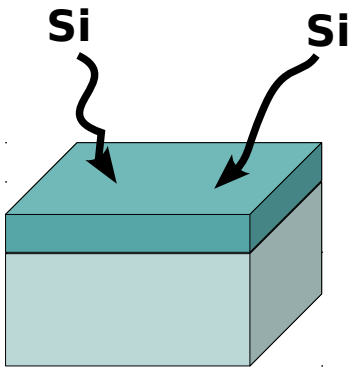
- New procedure for obtaining high quality optimized Si amorphous models based on an energy criterion, combining first-principles annealing and a point defect removal procedure
- The energy is a critical quantity ... the density is not one
- Our investigations may hint that a fully continuous random network can not be obtained in experiments

And now ???

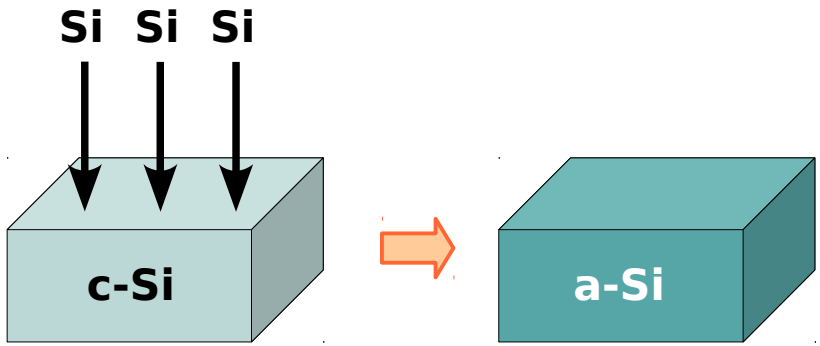
- Explore the energy landscape for vacancy migration using saddle-point search techniques

Fabrication of amorphous silicon

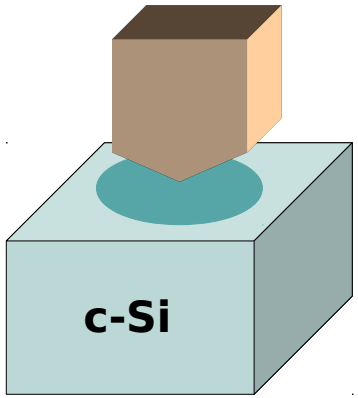
Various deposition techniques
(PECVD, HWCVD, EBE)



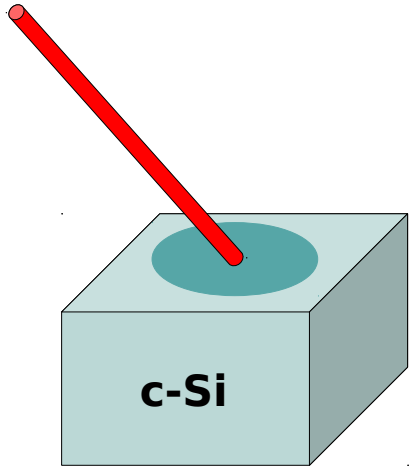
Irradiation of c-Si (by Si
ions or other particles)



Indentation



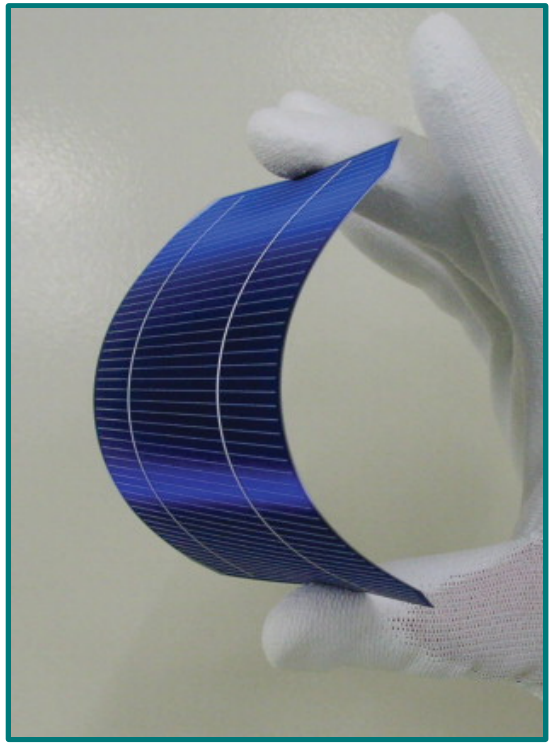
Laser quenching



Applications of a-Si

→ Lower efficiency than crystalline or polycrystalline silicon

→ But much lower production cost, and deposition easier in all aspects

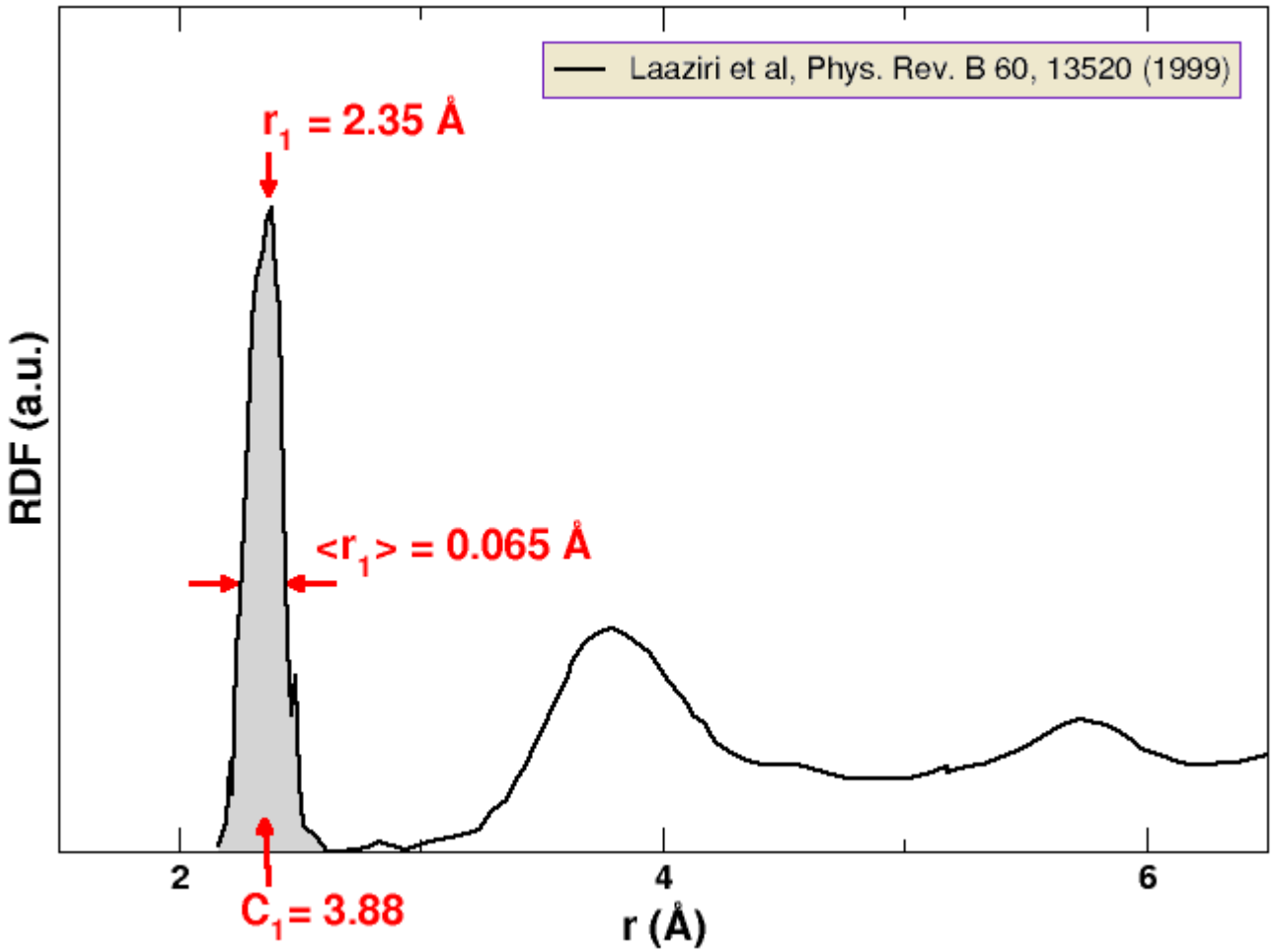


→ Light photovoltaic applications

→ Liquid crystal displays

→ Printed electronics

Structural properties of a-Si: RDF



→ Well-resolved 1st neighbor peak (same distance than in crystal)

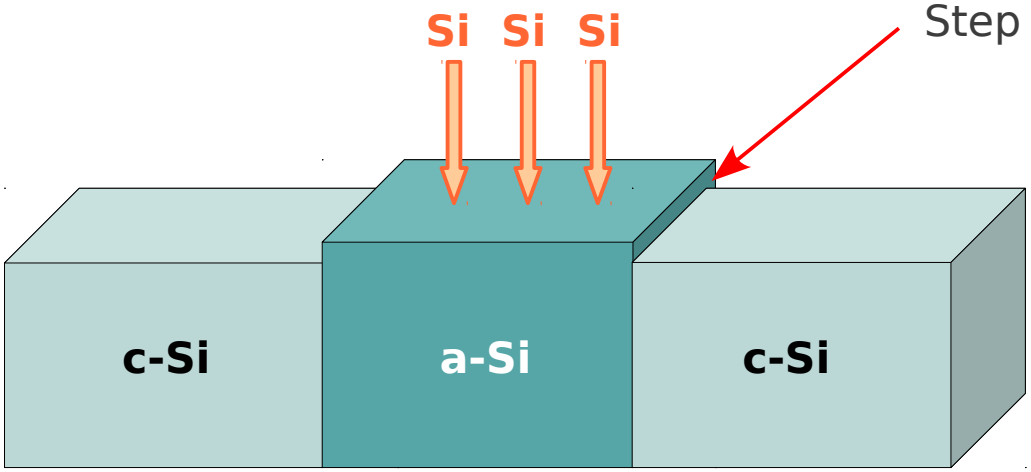
→ The disorder is more pronounced for distant neighbors

→ A dangling bond density of 12% ????

Structural properties of a-Si: angular dispersion and density

Raman scattering
Neutron diffusion

$8° < \Delta\theta < 11°$



Step height → a-Si 1.8% less dense than c-Si
Custer et al, APL 64, 437 (1994)

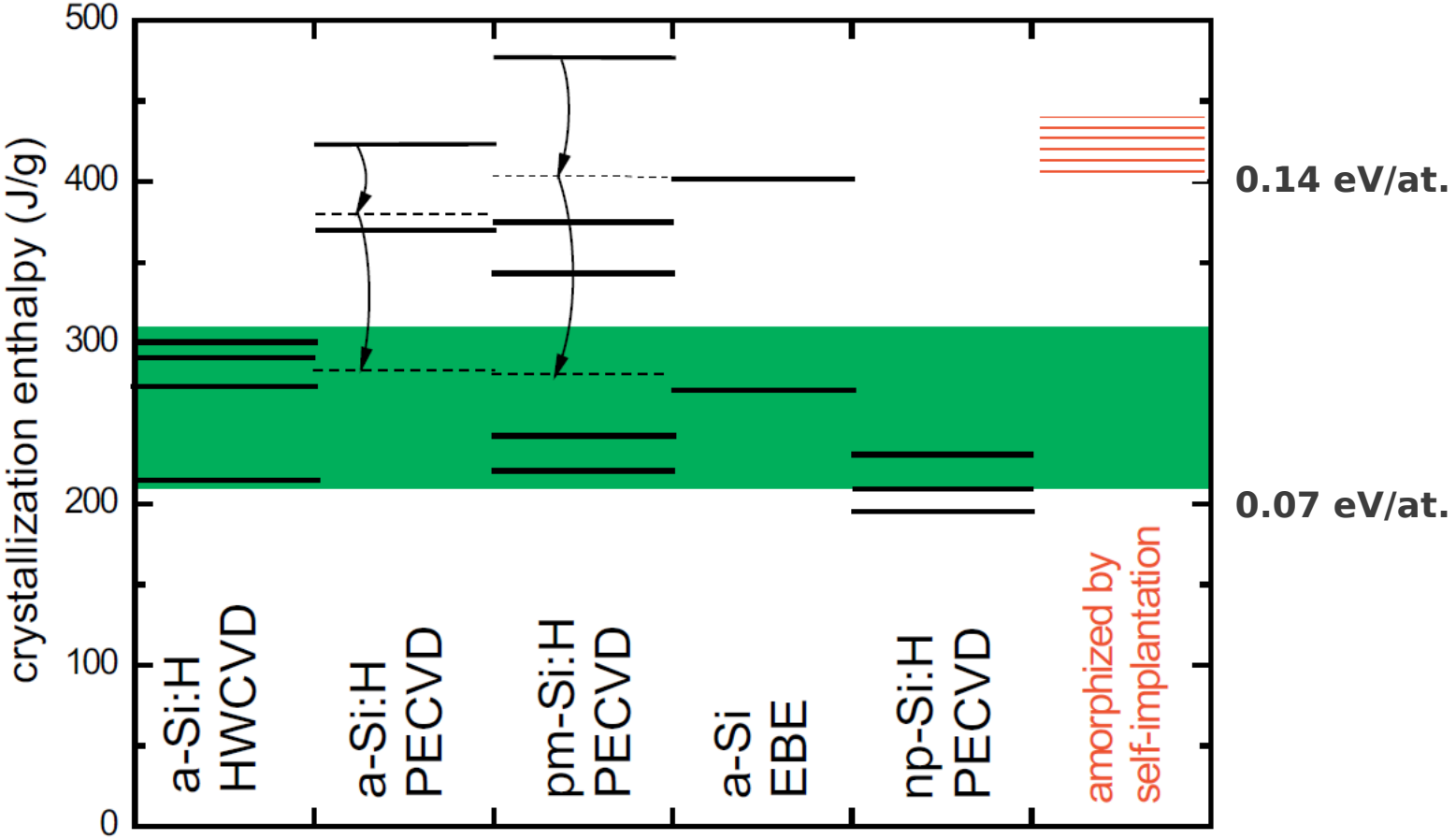
Confirmed by X-ray diffraction

→ The angular disorder is small in all investigations

→ a-Si is less dense than c-Si by 1.8%

Energy properties of a-Si: calorimetry

Kail et al, Phys. Stat. Sol. 5, 361 (2011)

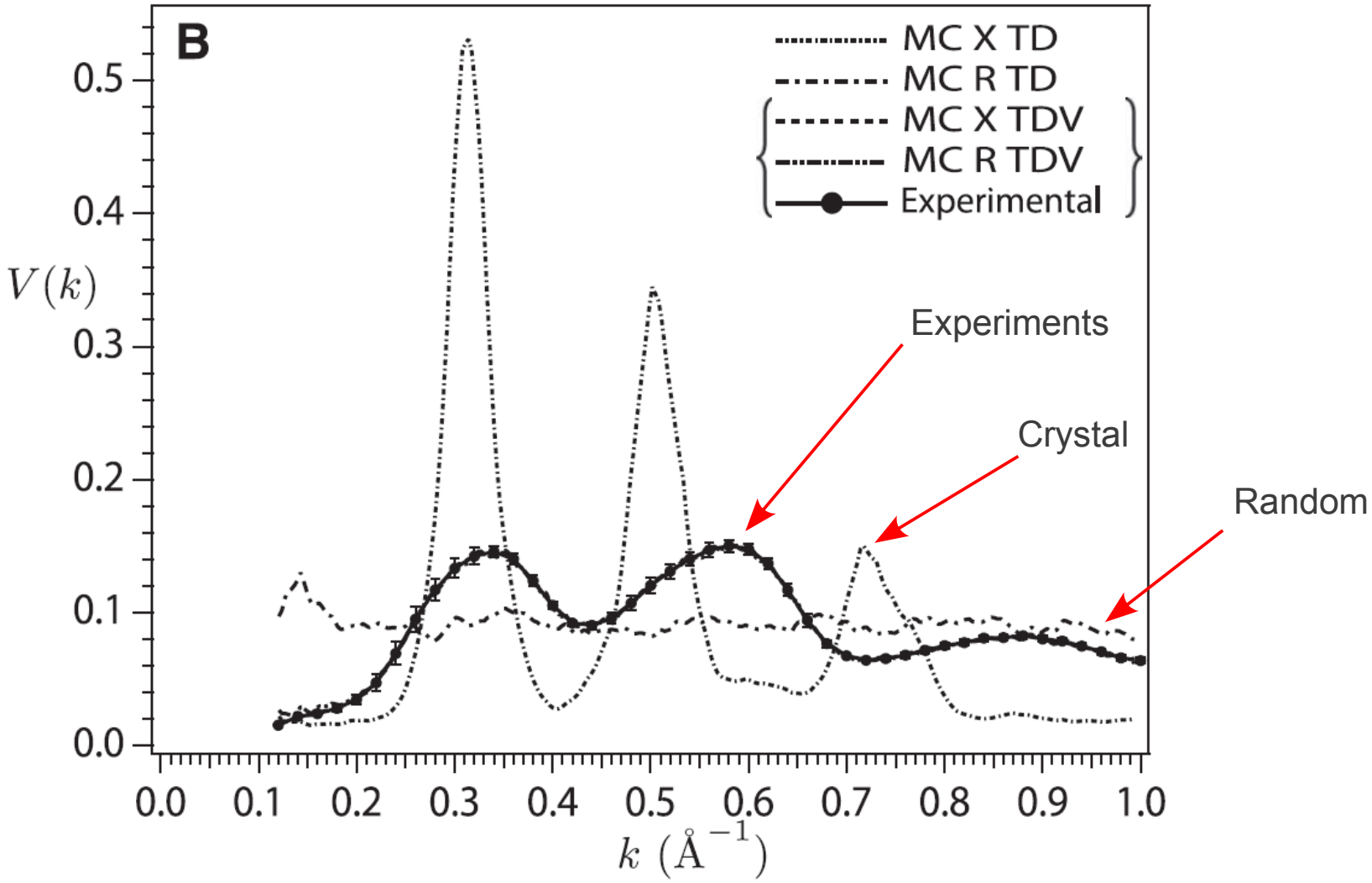


→ The relative enthapy of a-Si ranges from 0.07 to 0.15 eV/at

→ The relaxation state is very dependent on the history

Presence of a medium range order in a-Si?

Treacy et al, Science 335, 950 (2012)



→ Fluctuation Electron Microscopy exp. lead to a structured signal for correlation beyond the 1st neighbors.

What is an amorphous material? a-Si?

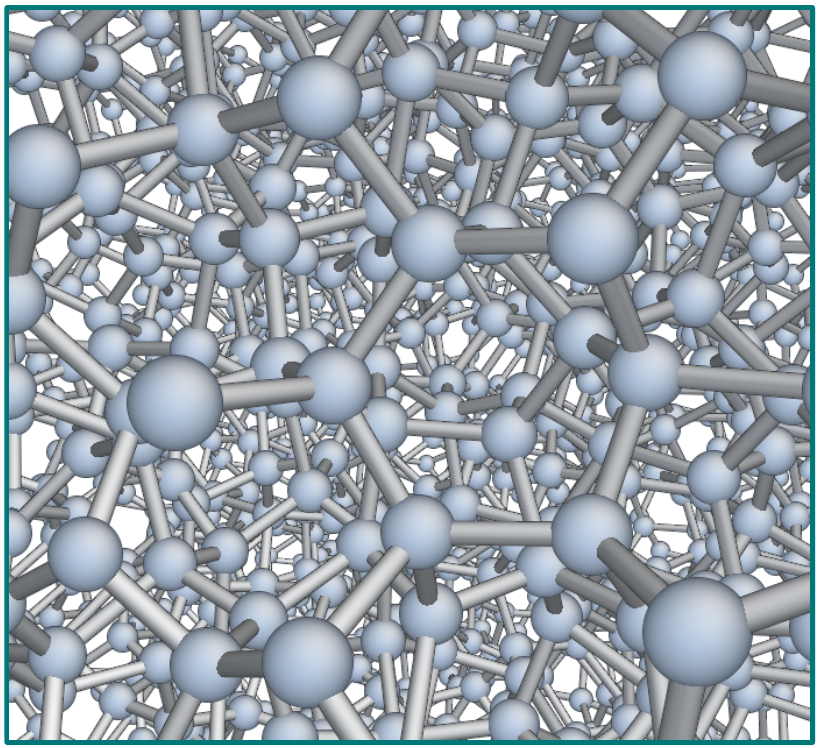
Le petit Larousse

“Dans la matière solide, l'état amorphe est un état rigide désordonné. Il se différencie de l'état cristallin par l'absence d'ordre à longue distance. Les verres en constituent l'exemple type.”

Wikipedia

“In condensed matter physics, an amorphous or non-crystalline solid is a solid that lacks the long-range order characteristic of a crystal”

“A glass is an amorphous solid that transforms into a liquid upon heating through the glass transition.”



→ a-Si is a solid lacking long-range order, BUT with short-range order. It is then an amorphous material

→ Whether a-Si can be called a glass is still a matter of debate