Positron Annihilation for Materials Science & The intense Positron Source EPOS

R. Krause-Rehberg

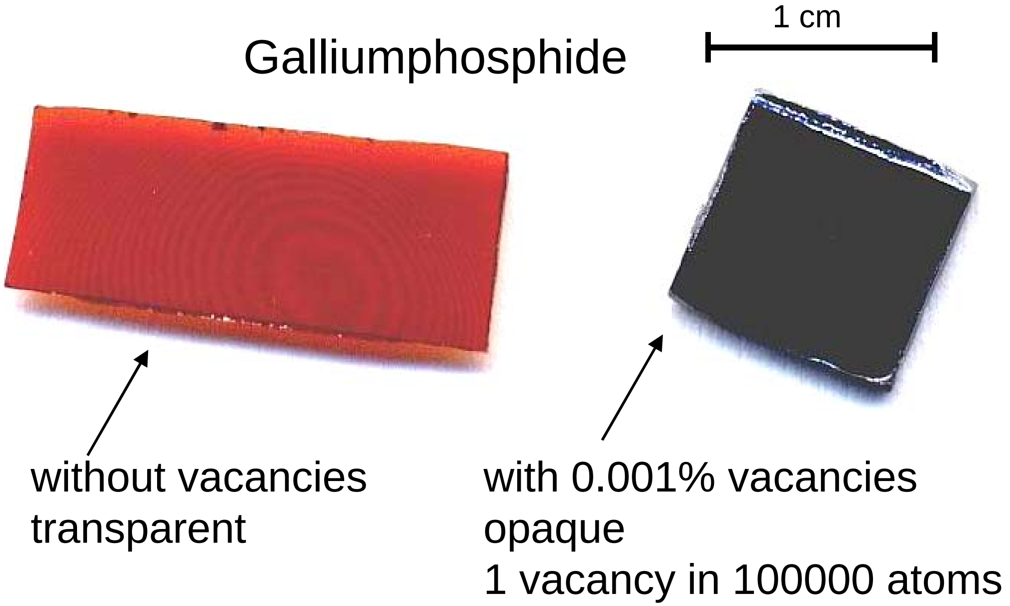
Univ. Halle

Martin-Luther-Universität
Halle-Wittenberg

- Why are nano-defects important at all?
- Positron trapping by defects
- Positronium to probe pores
- New positron facilities – the EPOS Project

Point defects determine properties of materials

- Point defects determine electronic and optical properties
- electric conductivity strongly influenced
- Doping of semiconductors (n-, p-Si)



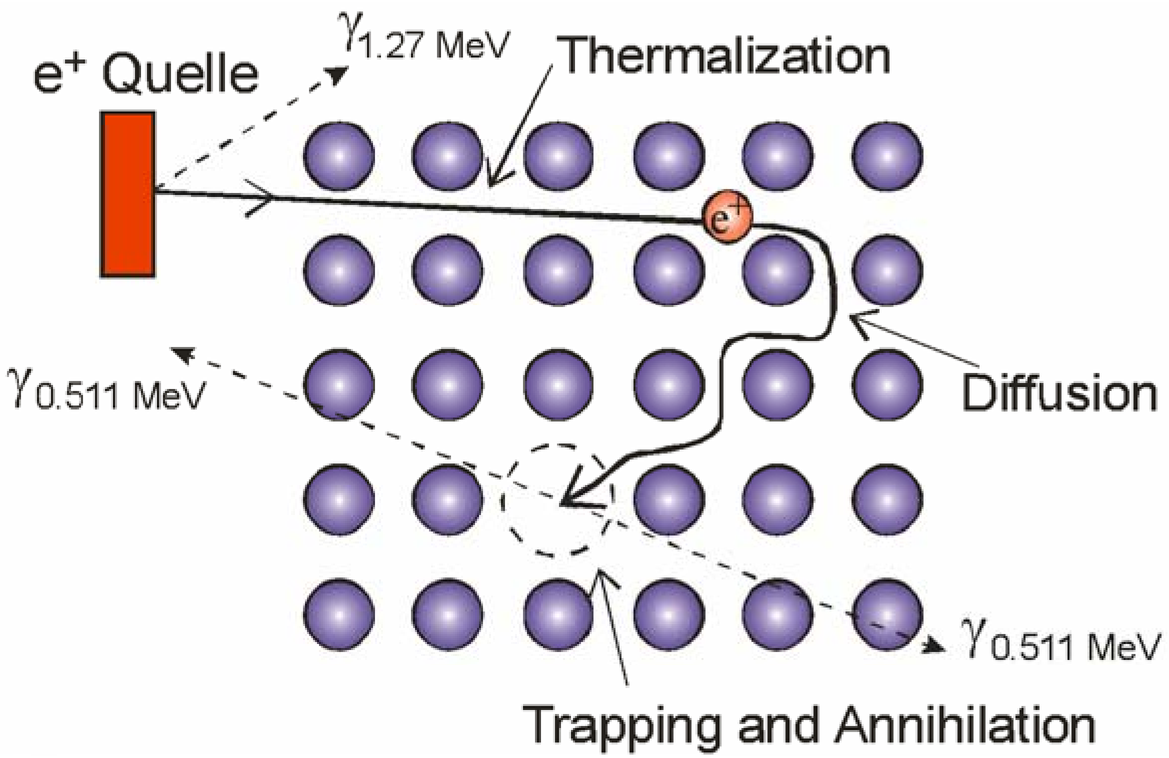
without vacancies
transparent

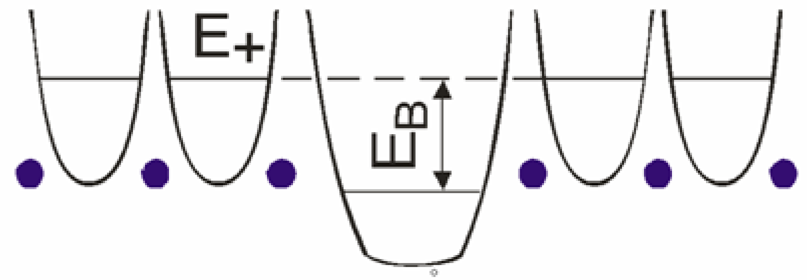
with 0.001% vacancies
opaque
1 vacancy in 100000 atoms

- Point defects are generated by irradiation (e.g. cosmic rays), by plastic deformation or by diffusion, …
- Metals in high radiation environment -> formation of voids -> embrittlement
- -> Properties of vacancies and other point defects must be known
- Analytical tools are needed to characterize point defects

The positron lifetime spectroscopy

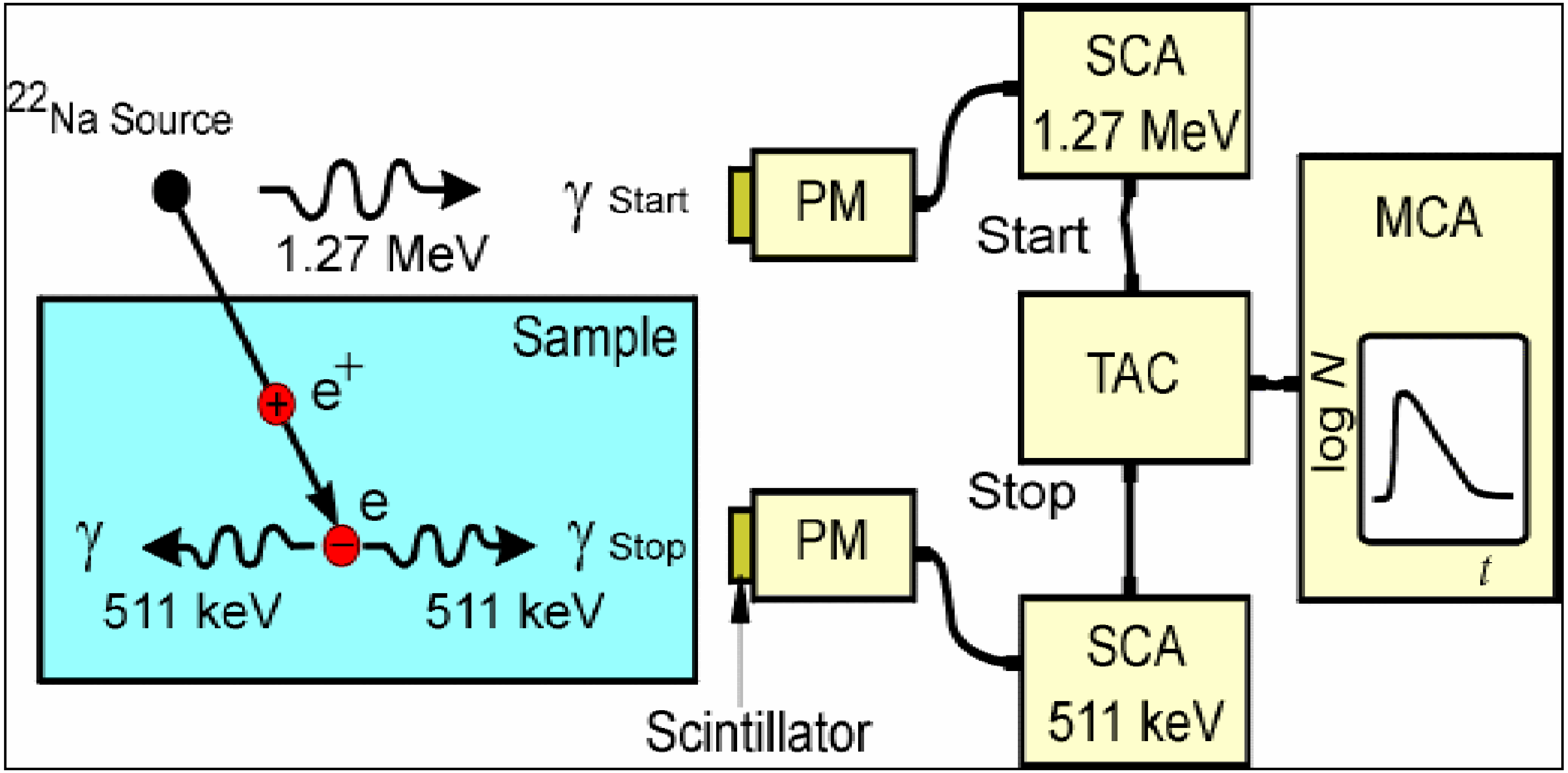
^{22}Na





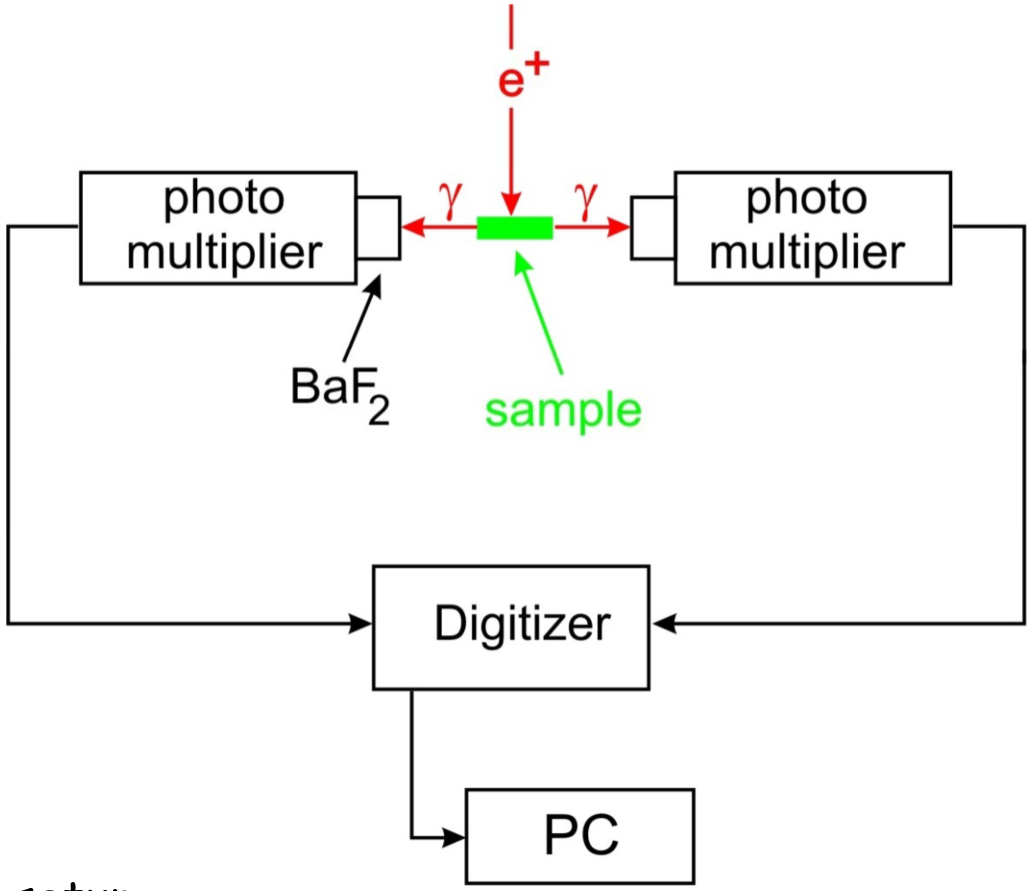
- positron wave-function can be localized in the attractive potential of a defect
- annihilation parameters change in the localized state
- e.g. positron lifetime increases in a vacancy
- lifetime is measured as time difference between appearance of 1.27 (start) and 0.51 MeV (stop) quanta
- defect identification and quantification possible

The positron lifetime spectroscopy - conventional setup



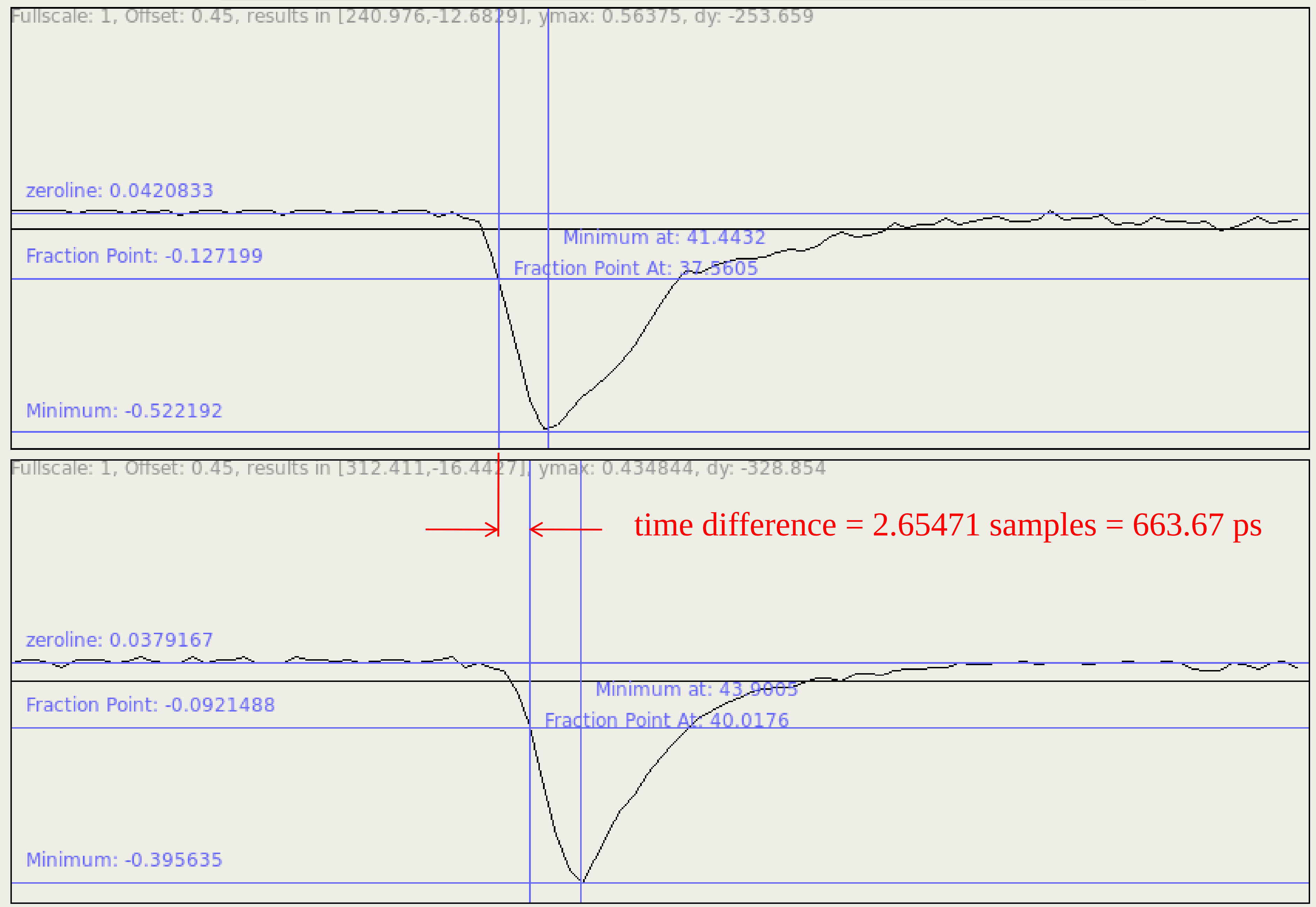
Positron lifetime: time between 1.27 MeV and 0.511 MeV quanta

Digital lifetime measurement



- much simpler setup
- timing very accurate (<10^{-6} instead of 5×10^{-3})
- pulse-shape discrimination (suppress “bad pulses”): better time resolution
- each detector for start & stop (double statistics)

Screenshot of two digitized anode pulses



Fullscale: 1, Offset: 0.45, results in [240.976,-12.6829], ymax: 0.56375, dy: -253.659

zeroline: 0.0420833

Fraction Point: -0.127199

Minimum at: 41.4432

Fraction Point At: 37.5605

Minimum: -0.522192

Fullscale: 1, Offset: 0.45, results in [312.411,-16.4427], ymax: 0.434844, dy: -328.854

time difference = 2.65471 samples = 663.67 ps

zeroline: 0.0379167

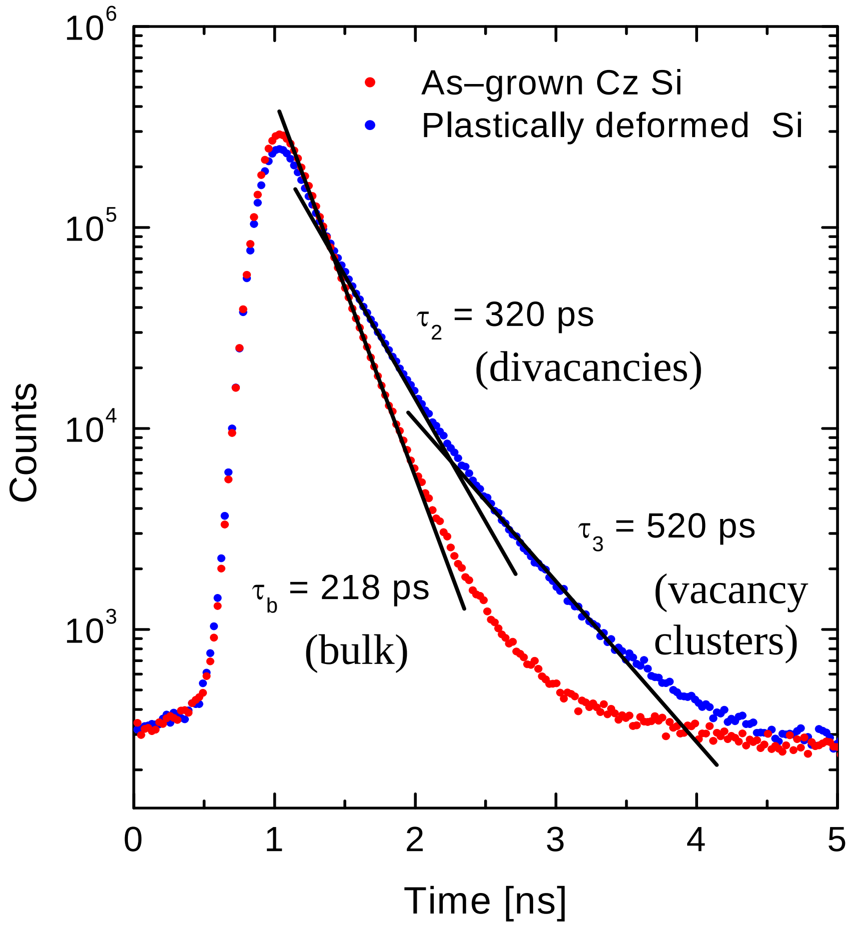
Fraction Point: -0.0921488

Minimum at: 43.9005

Fraction Point At: 40.0176

Minimum: -0.395635

Positron lifetime spectroscopy



- positron lifetime spectra consist of exponential decay components
- positron trapping in open-volume defects leads to long-lived components
- longer lifetime due to lower electron density
- analysis by non-linear fitting: lifetimes τ_i and intensities I_i

positron lifetime spectrum:

$$N(t) = \sum_{i=1}^{k+1} \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right)$$

trapping coefficient

$$\boxed{\kappa_\mathrm{d} = \mu C_\mathrm{d}} = \frac{I_2}{I_1}\left(\frac{1}{\tau_\mathrm{b}} - \frac{1}{\tau_\mathrm{d}}\right)$$

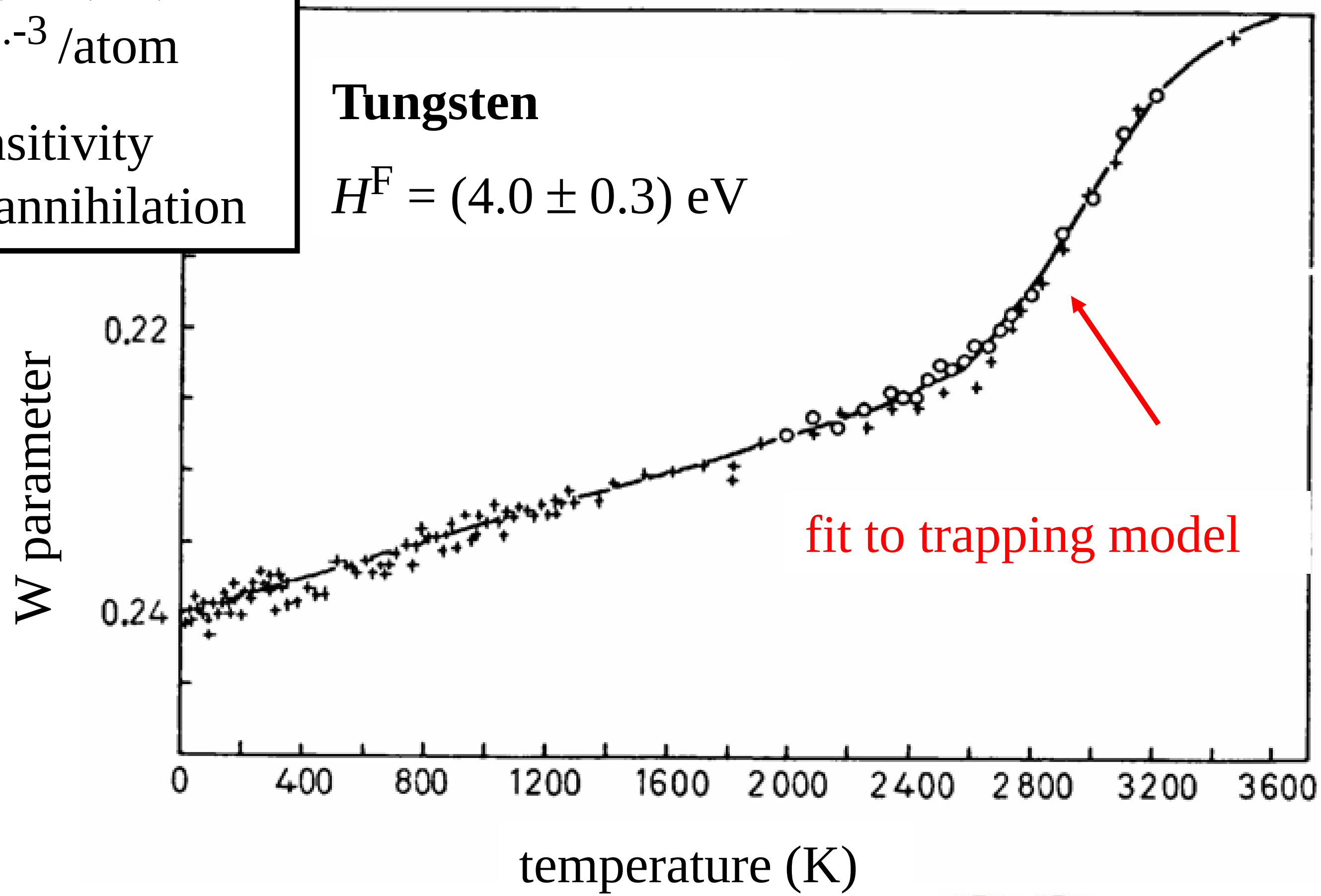
trapping rate

defect concentration

Vacancies in thermal Equilibrium

- Vacancy concentration in thermal equilibrium:
- in metals $H^{F} \approx 1 \ldots 4$ eV ⇒ at T_m [1v] $\approx 10^{-4 \ldots -3}$ /atom
- fits well to the sensitivity range of positron annihilation

$$C_{1v}(T) = \exp\left(\frac{S_{1v}^{F}}{k}\right)\exp\left(\frac{H_{1v}^{F}}{kT}\right)$$



Tungsten

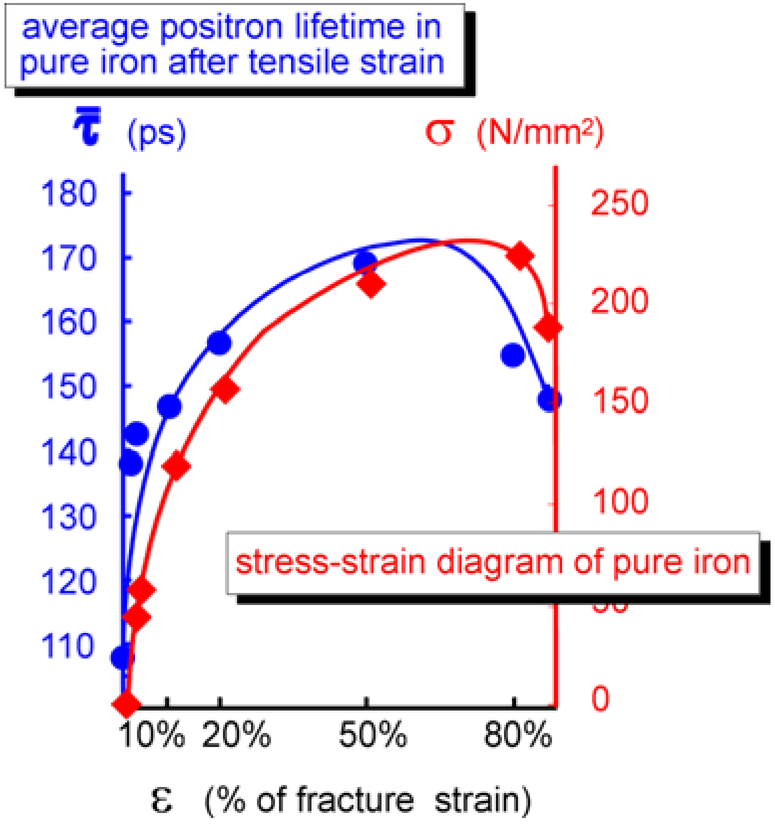
$H^{F} = (4.0 \pm 0.3)$ eV

fit to trapping model

(Ziegler, 1979)

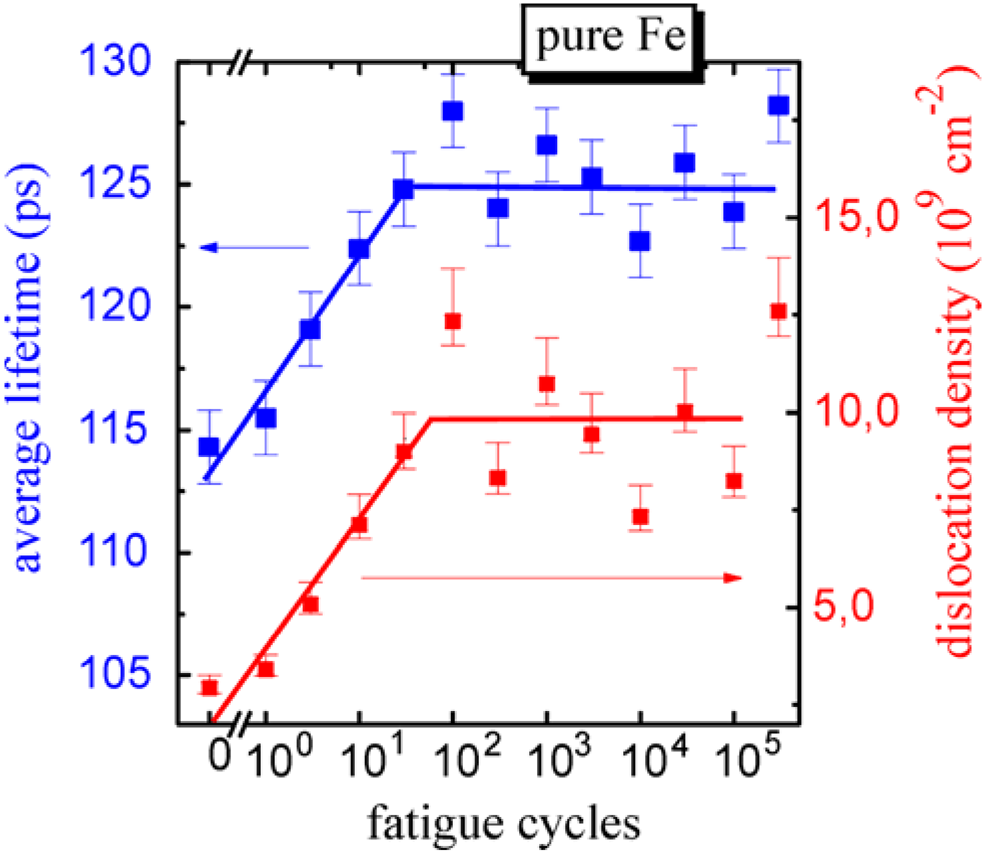
Defects in Iron after tensile strength and fatigue treatment

- We performed an extensive study of defects in mechanically damaged iron and steel
- Positrons are very sensitive: detection of defects already in the Hooks range of the stress-strain experiment
- Vacancy cluster and dislocations are detectable in both cases



average positron lifetime in pure iron after tensile strain

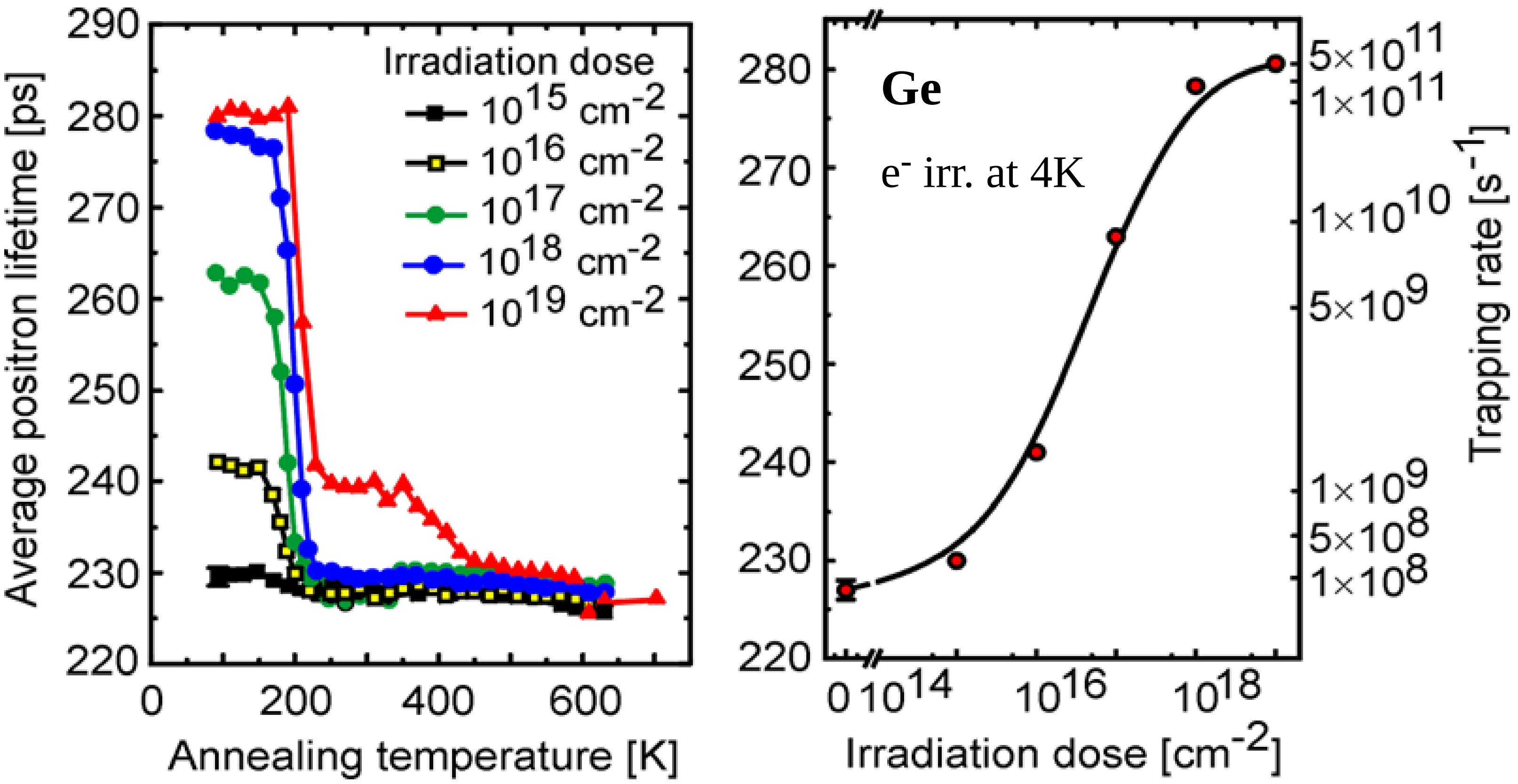
stress-strain diagram of pure iron



Somieski et al., J. Physique IV 5, C1/127-134 (1995)

Defects in electron-irradiated Ge

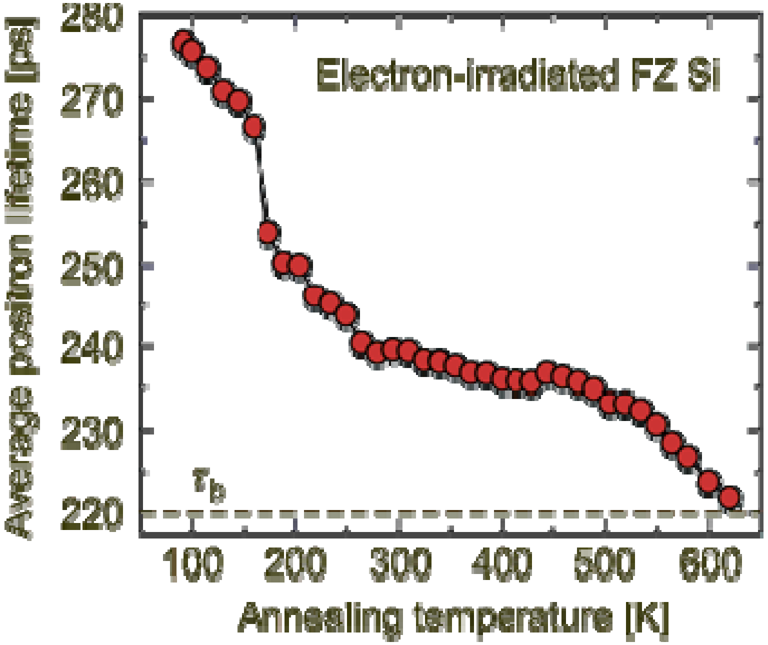
- Electron irradiation (2 MeV @ 4K) induces Frenkel pairs (vacancy - interstitial pairs)
- steep annealing stage at 200 K
- at high irradiation dose: divacancies are formed (thermally more stable)

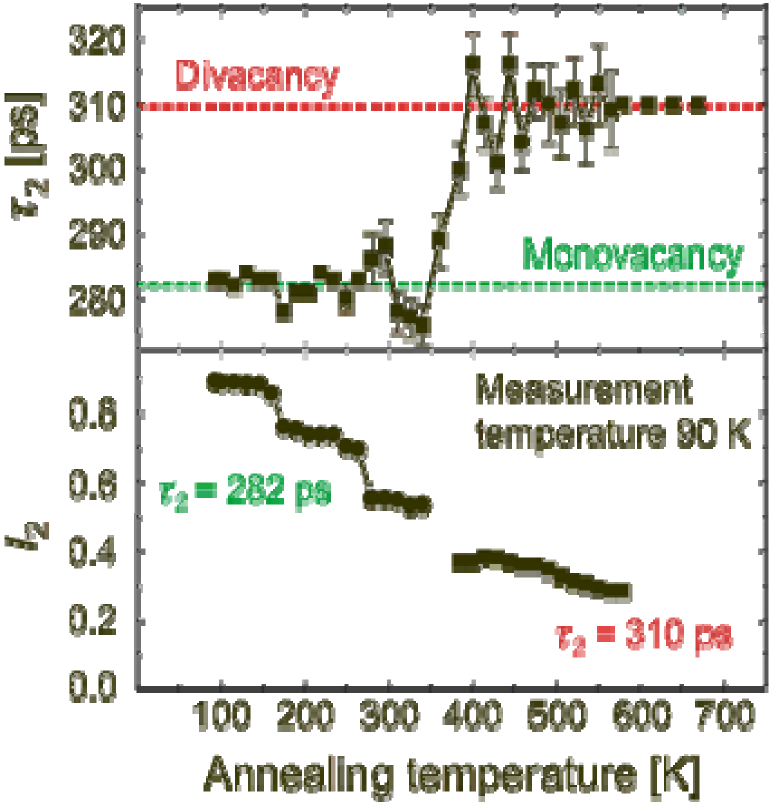


(Polity et al., 1997)

Electron irradiation of Si

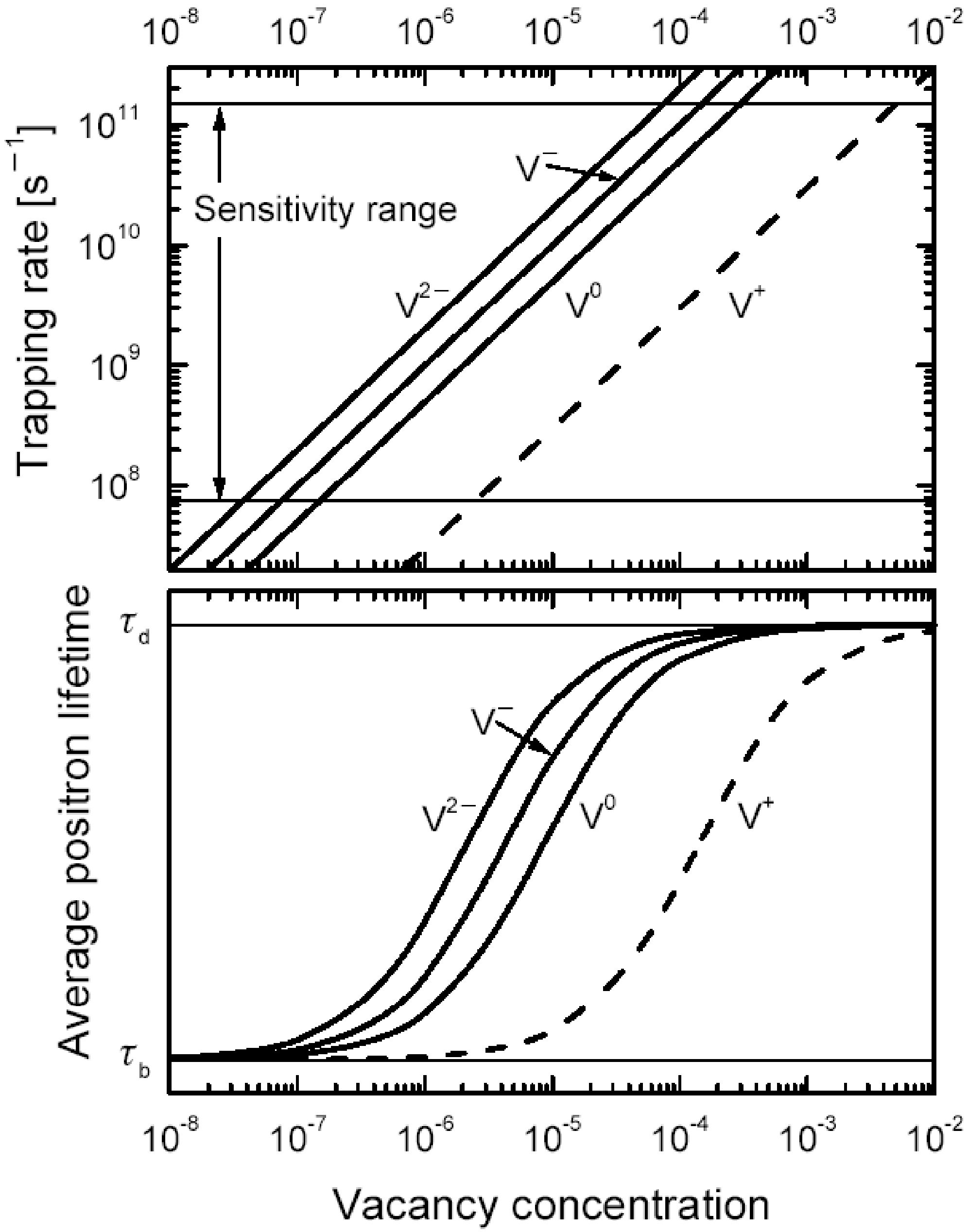
- low-temperature electron irradiation was performed at 4K (E_{e-}=2 MeV)
- annealing stage of monovacancies at about 170 K
- moving V_{Si} partly form divacancies
- divacancies anneal at about 550…650 K





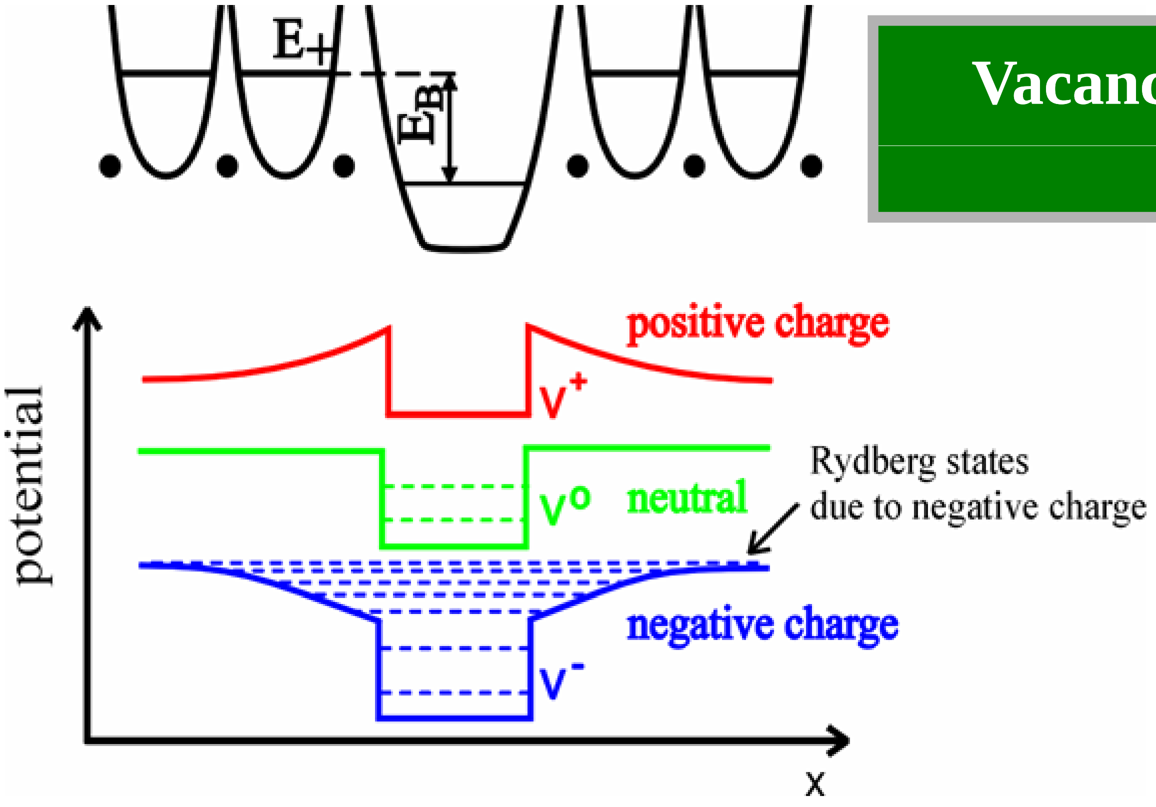
Polity et al., Phys. Rev. B **58** (1998) 10363

Sensitivity limits of PAS for vacancy detection



- **lower sensitivity limit** e.g. for negatively charged divacancies in Si starts at about 10^{15} cm^{-3}
- **upper limit**: saturated positron trapping
- defect identification still possible
- Then: only lower limit for defect density can be given

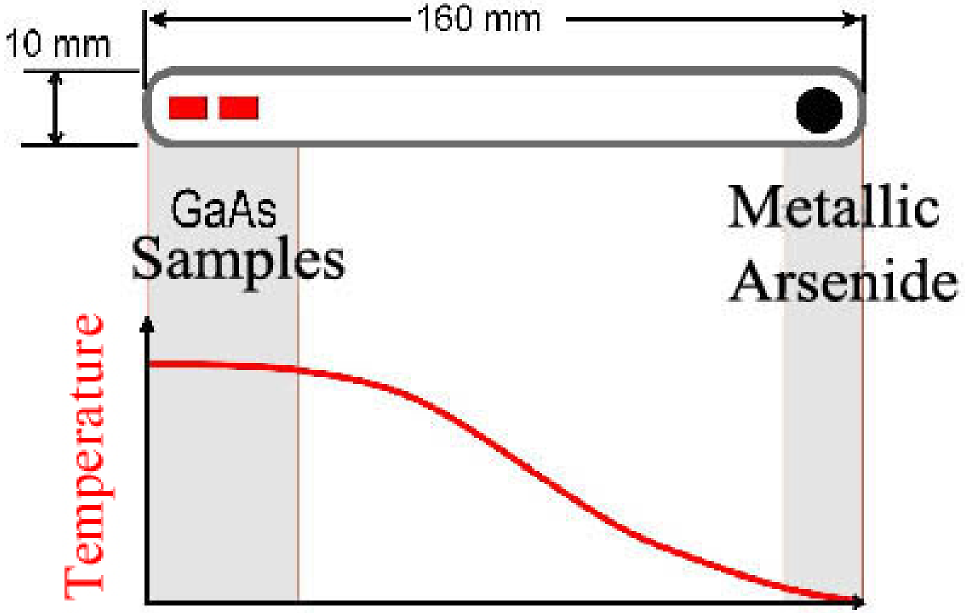
Vacancies in a semiconductor may be charged



- in a metal: charge of a vacancy is effectively screened by free electrons
- they are not available in semiconductors
- thus, long-range Coulomb potential added
- positrons may be attracted or repelled
- trapping coefficient μ is function of charge state

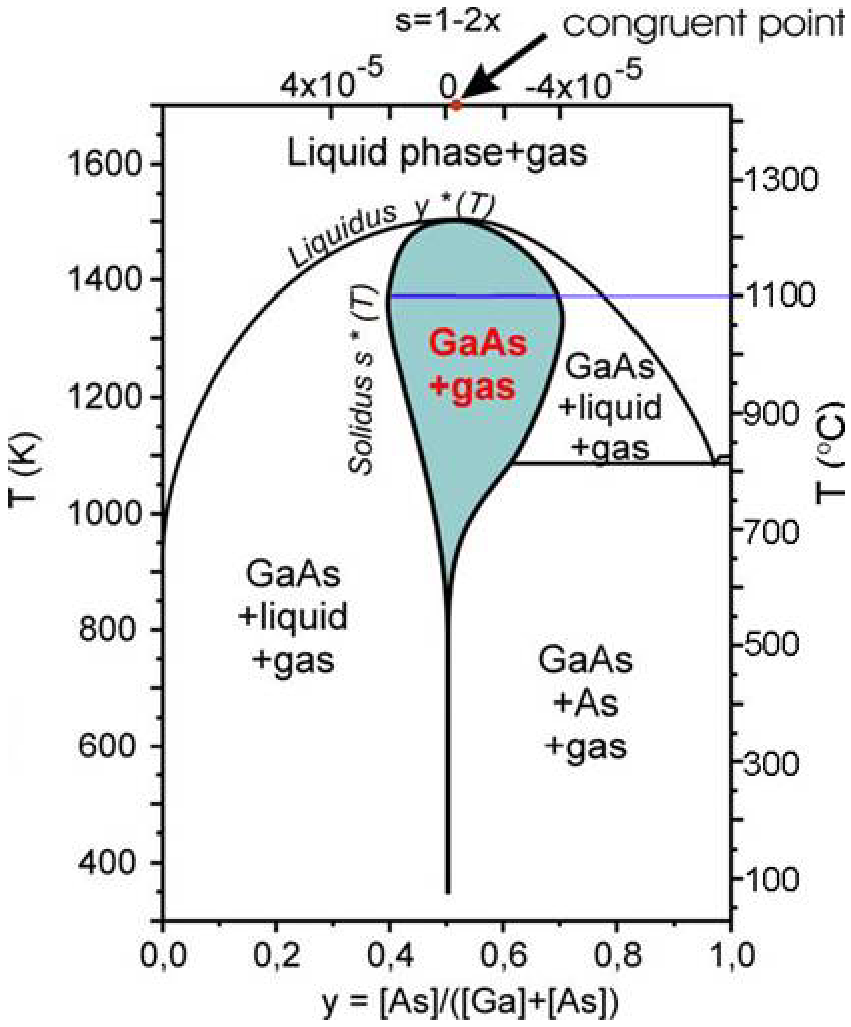
GaAs: annealing under defined As-partial pressure

- two-zone-furnace: Control of sample temperature **and** As partial pressure allows to navigate freely in phase diagram (existence area of compound)



T_{sample}: 1100° C

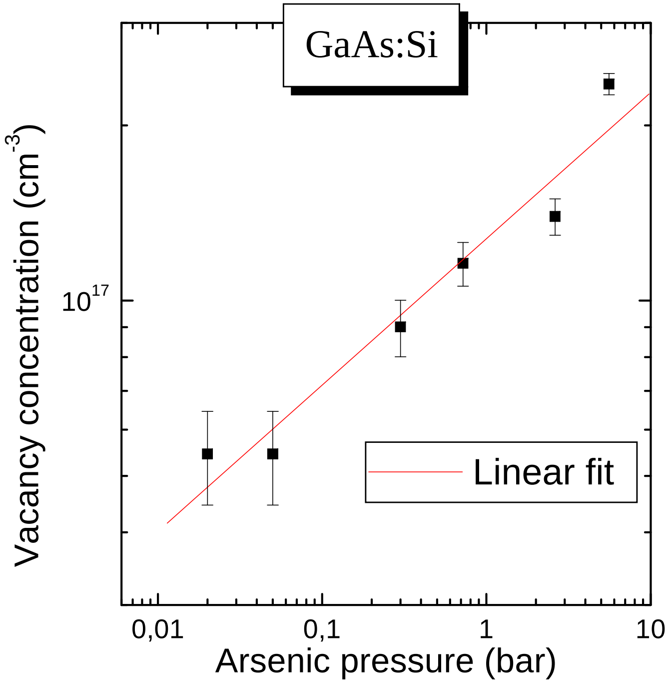
T_{As}: determines As-partial pressure



H. Wenzl et al., J. Cryst. Growth **109**, 191 (1991).

GaAs: Annealing under defined As pressure

Si_{Ga}-V_{Ga}



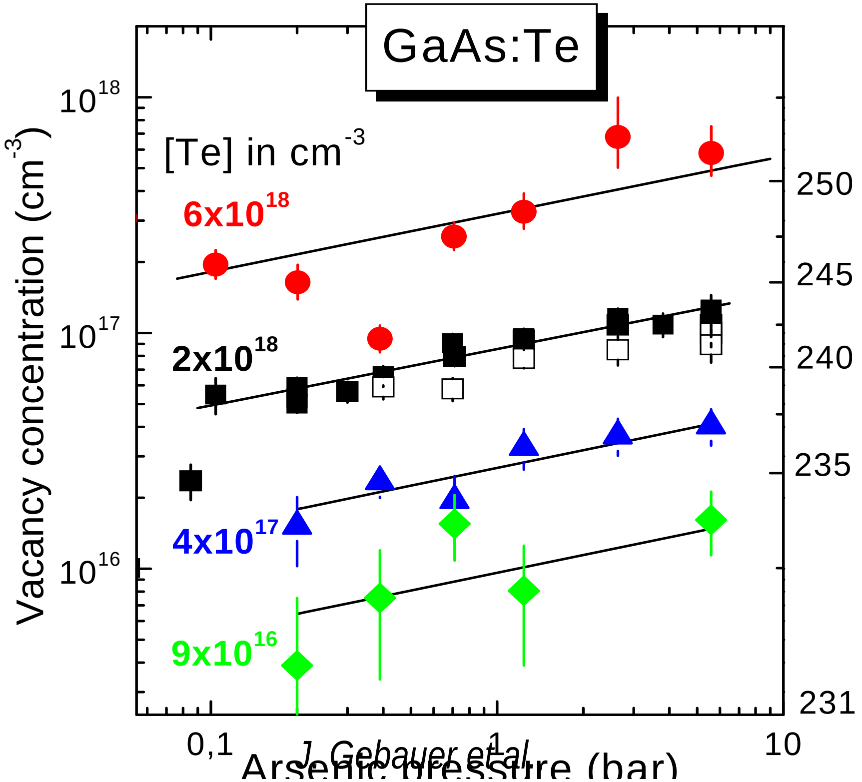
Thermodynamic reaction:

$1/4\ As_4^{gas} \leftrightarrow As_{As} + V_{Ga}$

Mass action law:

$[V_{Ga}] = K_{VG} \times p_{As}^{1/4}$

Te_{As}-V_{Ga}

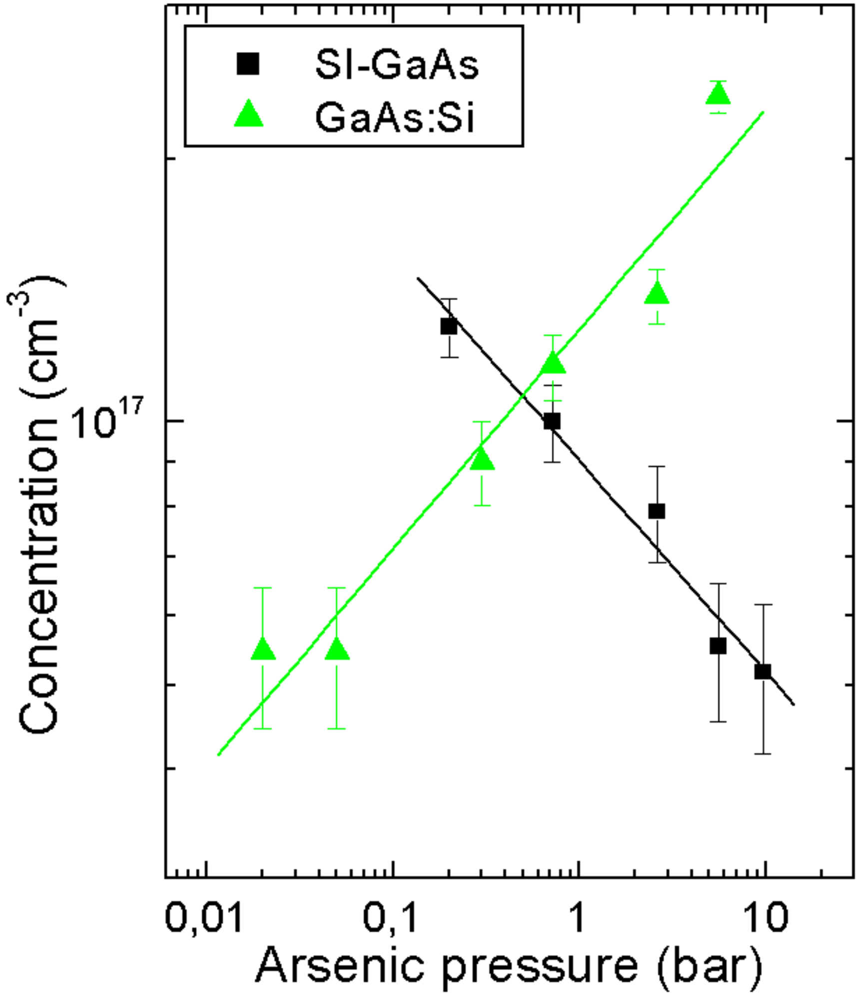


J. Gebauer et al.
Physica B 273-274, 705 (1999)

Fit: $[V_{Ga}\text{-Dopant}] \sim p_{As}^{n}$

$\rightarrow n = 1/4$

Comparison of doped and undoped GaAs



Thermodynamic reaction:

$$As_{As} \leftrightarrow V_{As} + 1/4As_4^{gas}$$

Mass action law:

$$[V_{As}] = K_{VAs} \times p_{As}^{-1/4}$$

Fit: $[V\text{-complex}] \sim p_{As}^{n}$

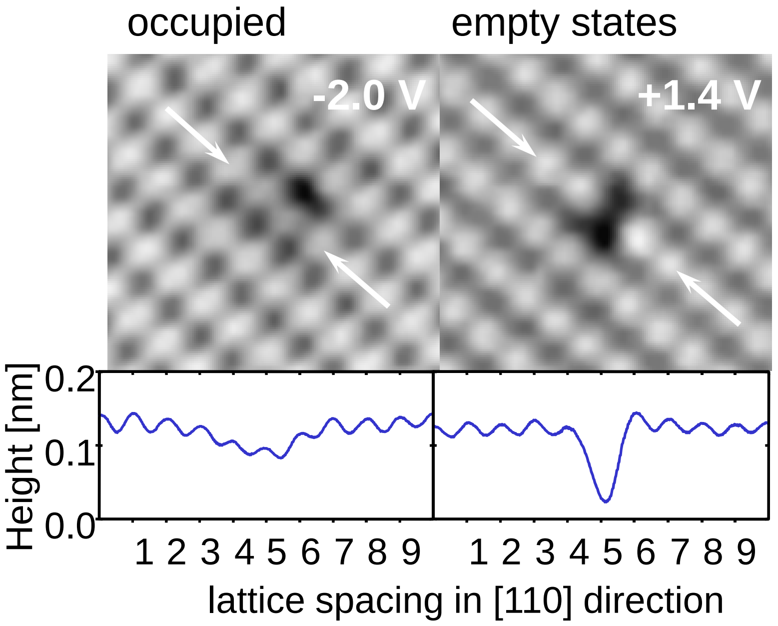
$\rightarrow n = -1/4$

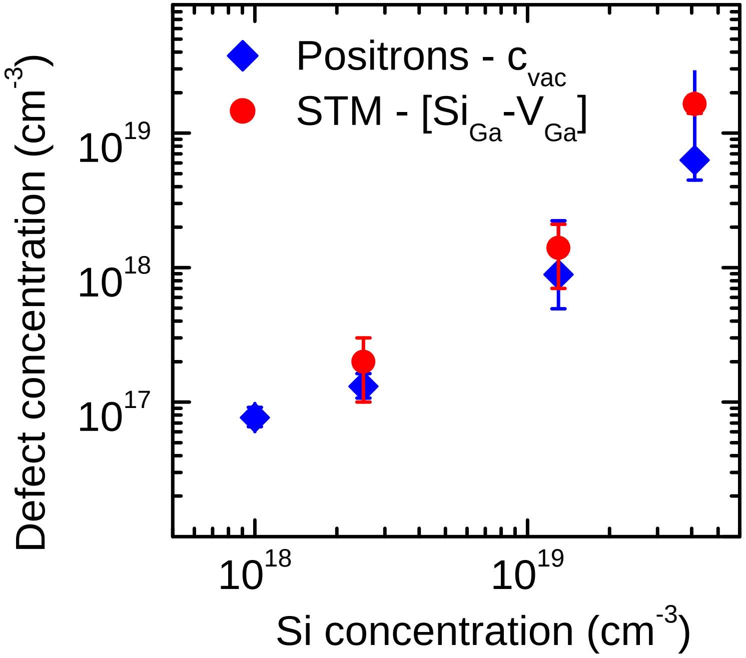
↓

undoped GaAs: As vacancy

Bondarenko et al., 2003

Identification of V_{Ga}-Si_{Ga}-Complexes in GaAs:Si





- Scanning tunneling microscopy at GaAs (110)-cleavages planes (by Ph. Ebert, Jülich)
- Defect complex identified as **V_{Ga}-Si_{Ga}**

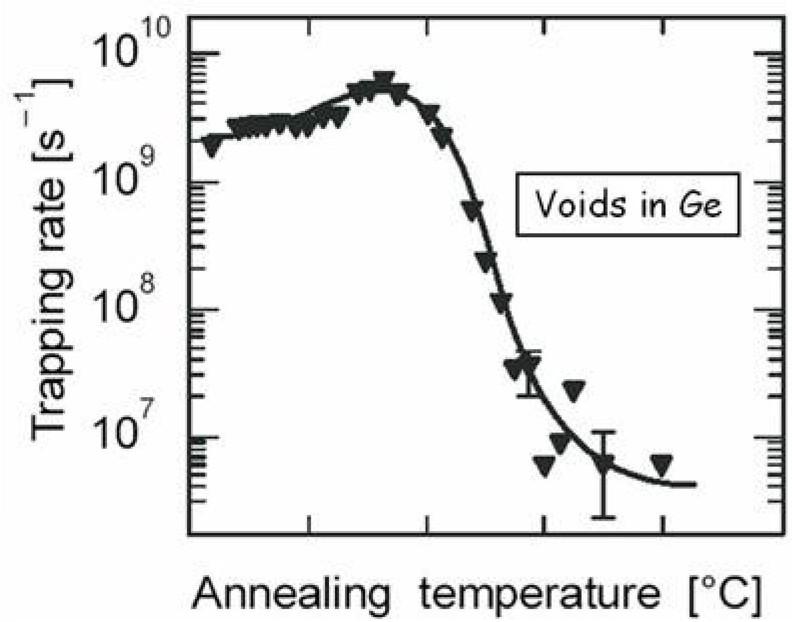
- Quantification → Agreement

Mono-Vacancies in GaAs:Si are V_{Ga}- Si_{Ga}-complexes

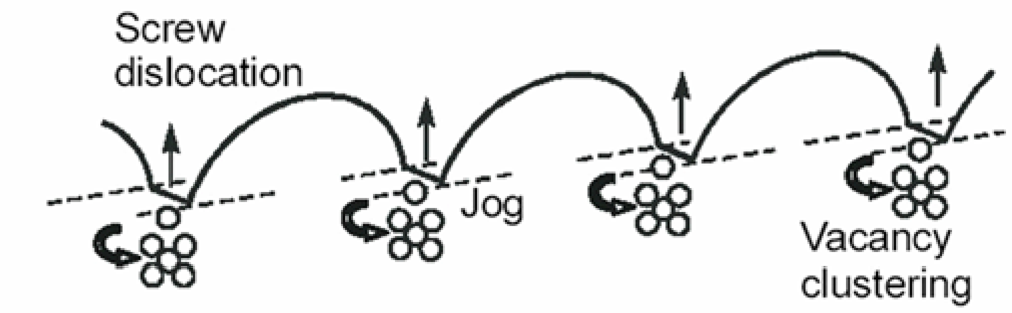
Gebauer et al., Phys. Rev. Lett. **78** (1997) 3334

Vacancy clusters in semiconductors

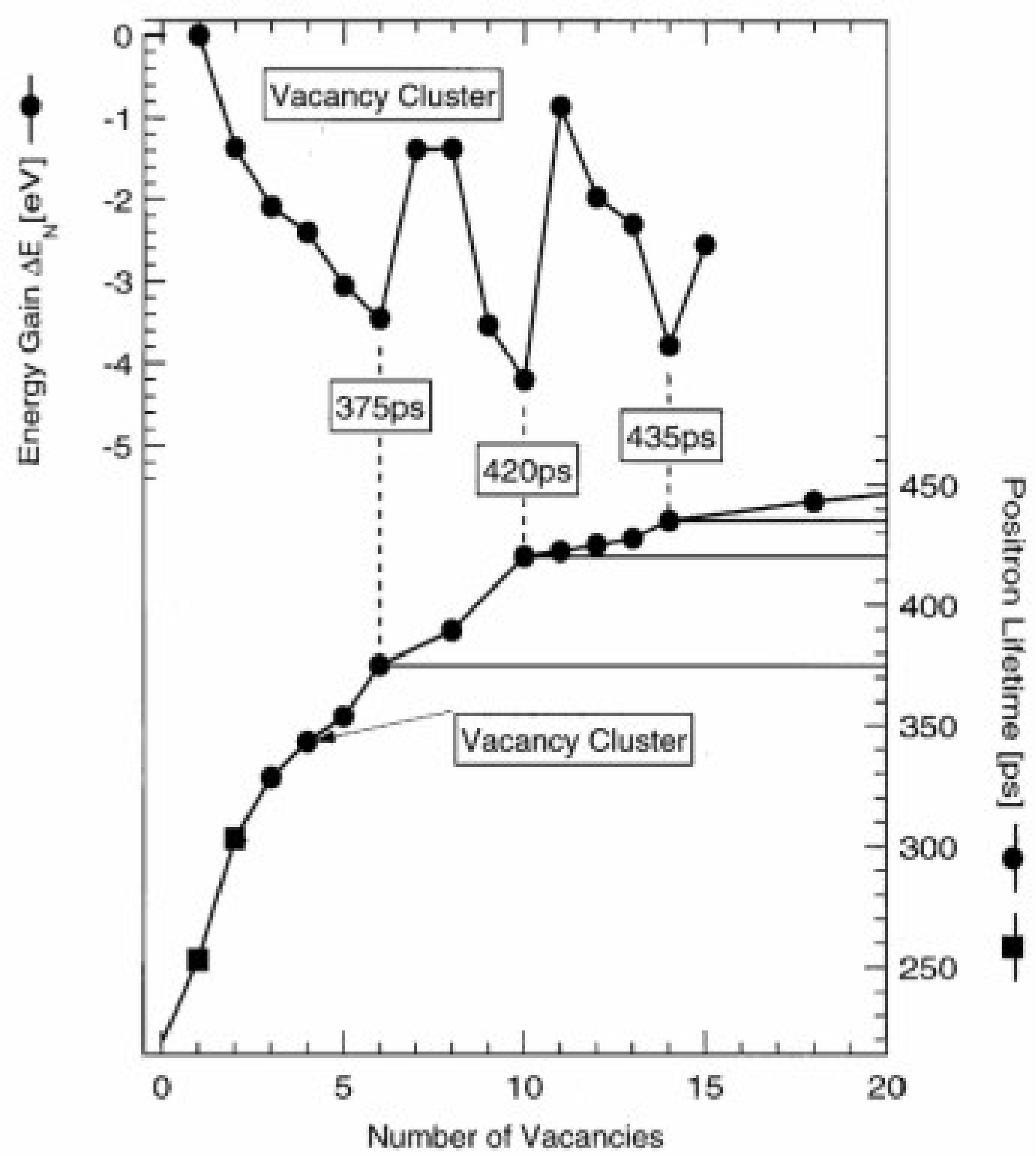
- vacancy clusters were observed after neutron irradiation, ion implantation and plastic deformation
- due to large open volume (low electron density) -> positron lifetime increases distinctly
- example: plastically deformed Ge
- defect lifetime: τ = 525 ps
- reason for void formation: jog dragging mechanism
- trapping rate of voids disappears during annealing experiment



Krause-Rehberg et al., 1993



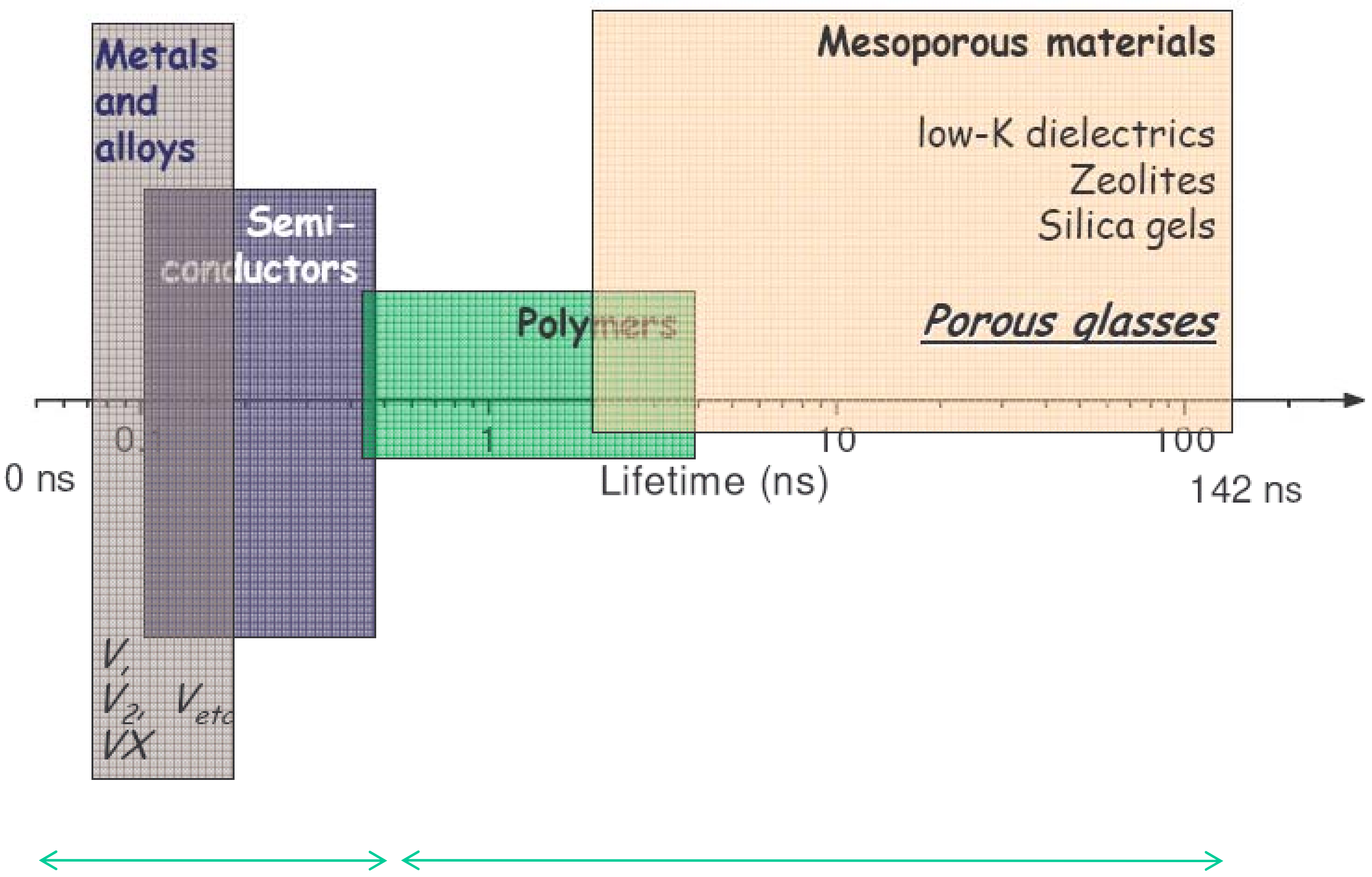
Theoretical calculation of vacancy clusters in Si



- there are cluster configurations with a large energy gain
- „Magic Numbers" with 6, 10 und 14 vacancies
- positron lifetime increases distinctly with cluster size
- for n > 10 saturation effect, i.e. size cannot be determined

T.E.M. Staab et al.,
Physica B 273-274 (1999) 501-504

Typical Lifetimes

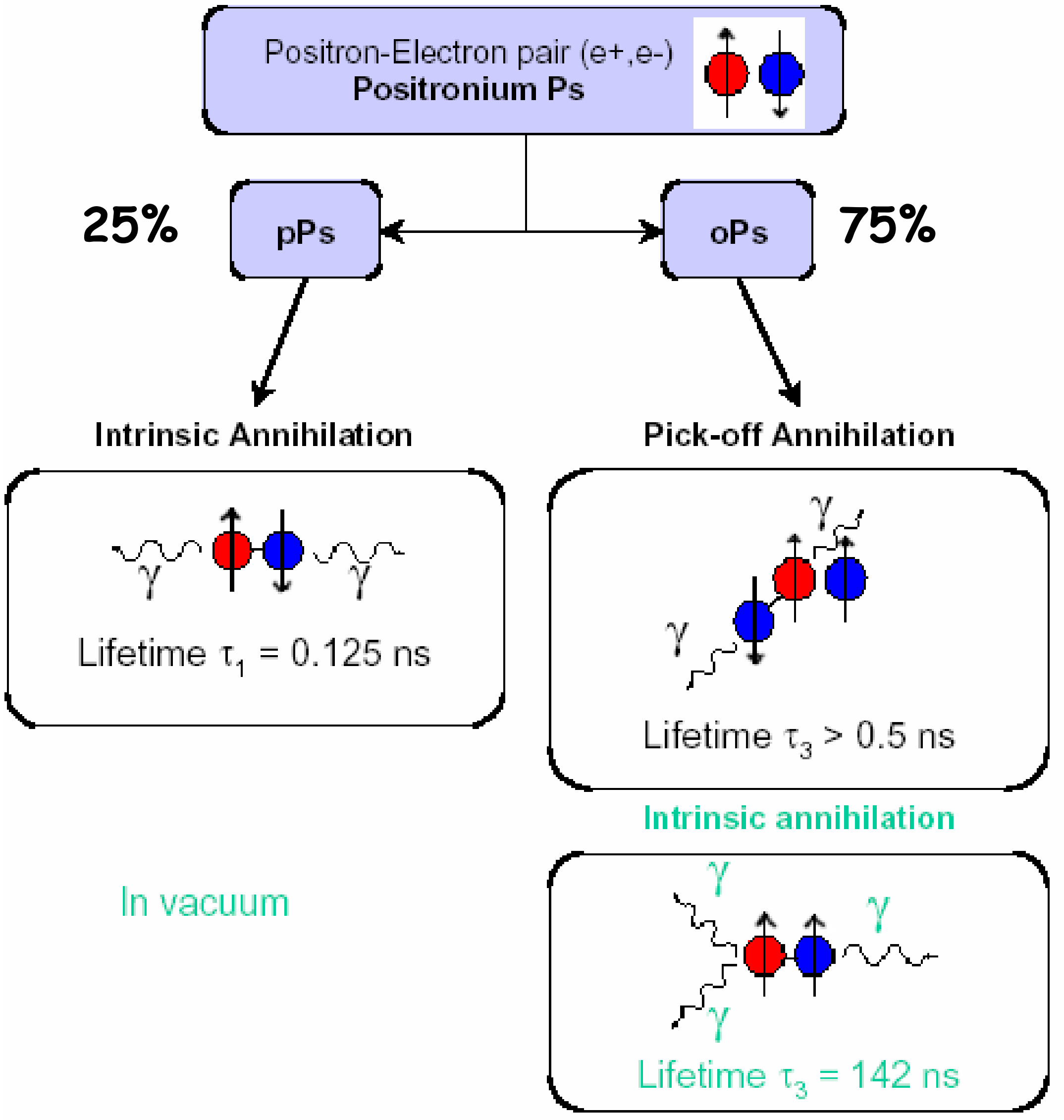


Positron

Positronium

Principles of PALS: ortho-Positronium

In materials without free electrons Positronium may be formed (Polymers, glass, liquids, gases).



Positron-Electron pair (e+,e-)
Positronium Ps

25% **pPs**

oPs **75%**

Intrinsic Annihilation

Lifetime τ_1 = 0.125 ns

Pick-off Annihilation

Lifetime τ_3 > 0.5 ns

Intrinsic annihilation

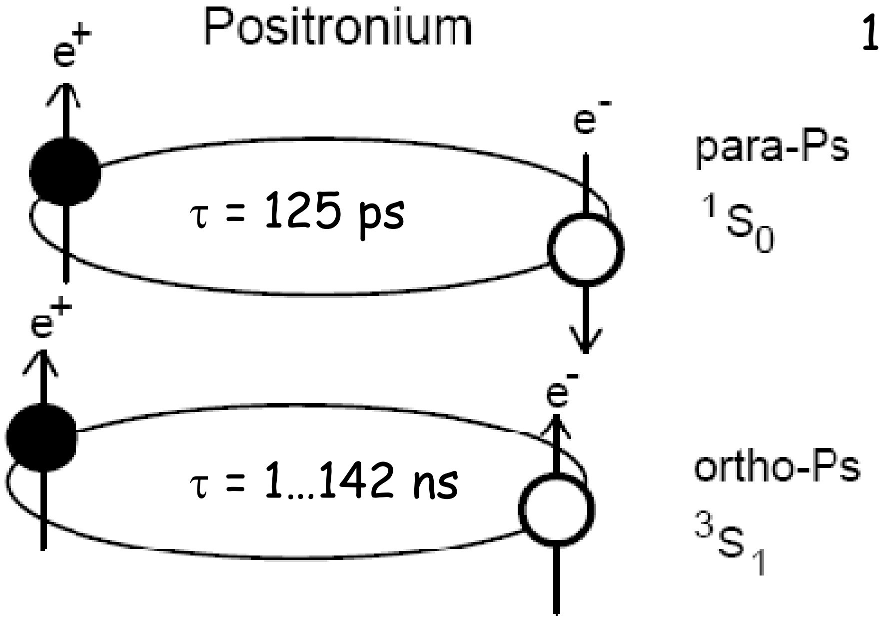
In vacuum

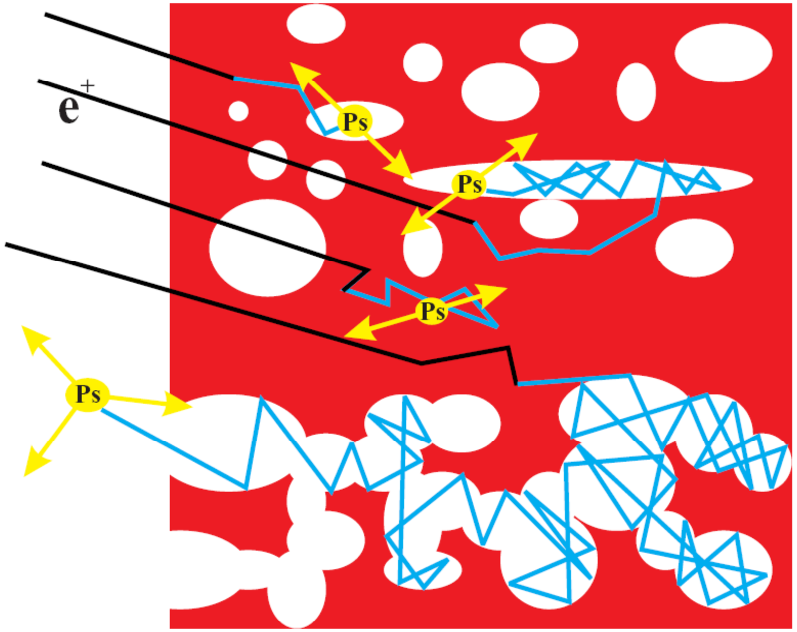
Lifetime τ_3 = 142 ns

Pick-off annihilation

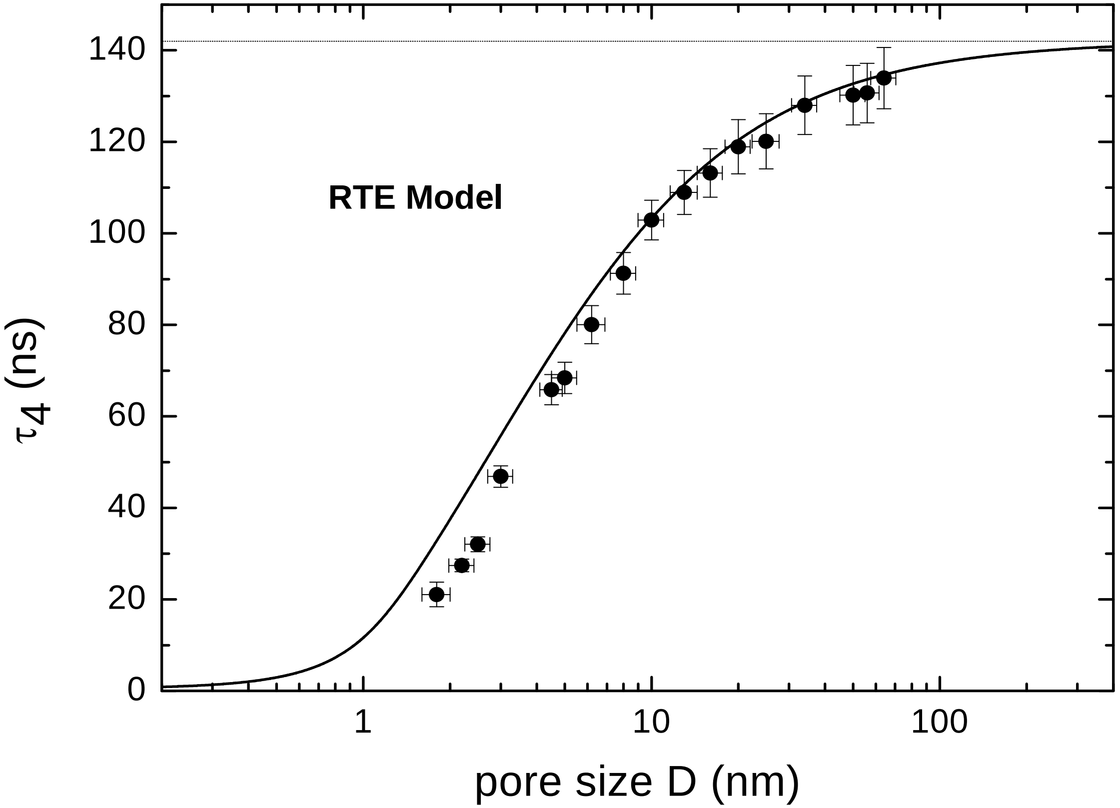
pick-off annihilation:

- o-Ps is converted to p-Ps by capturing an electron with anti-parallel spin
- happens during collisions at walls of pore
- lifetime decreases rapidly
- lifetime is function of pore size 1.5 ns to 142 ns

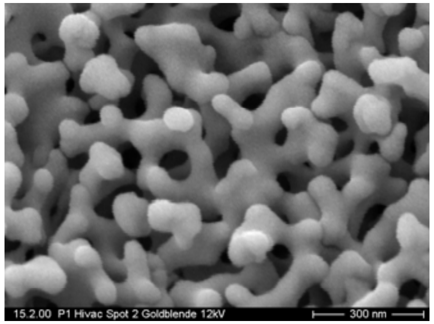




o-Ps lifetime τ_4 versus pore size



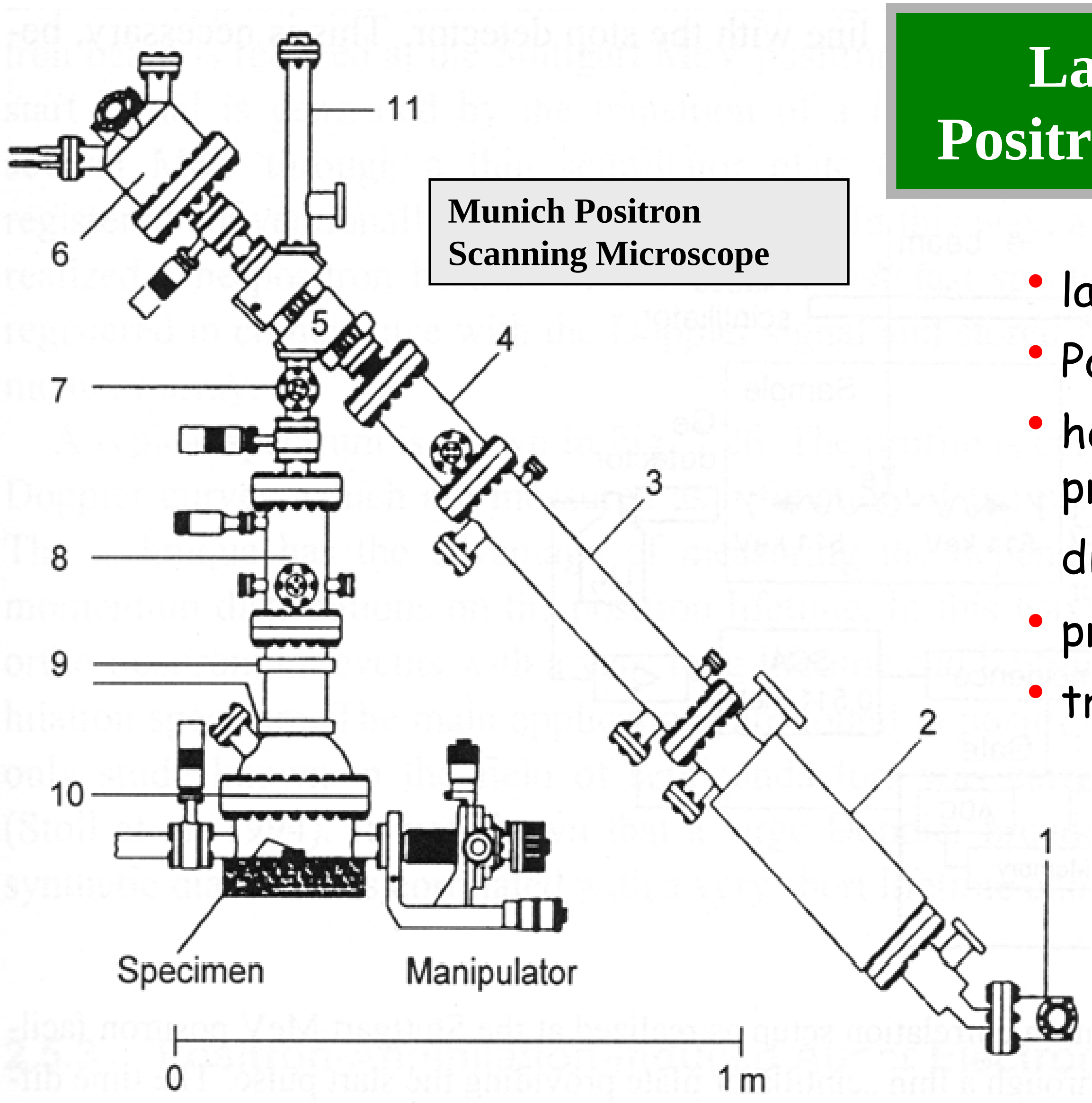
- we measured porous CPG glass in a broad pore size range



- given pore size obtained by N_2-adsorption and/or mercury intrusion technique
- for T=300 K fair agreement to the RTE model for large pores

RTE model: D. W. Gidley, T. L. Dull, W. E. Frieze, J. N. Sun, A. F. Yee, *J. Phys. Chem. B* **2001**, *105,* 4657.

Lateral Resolution with Positron-Scanning-Microscope



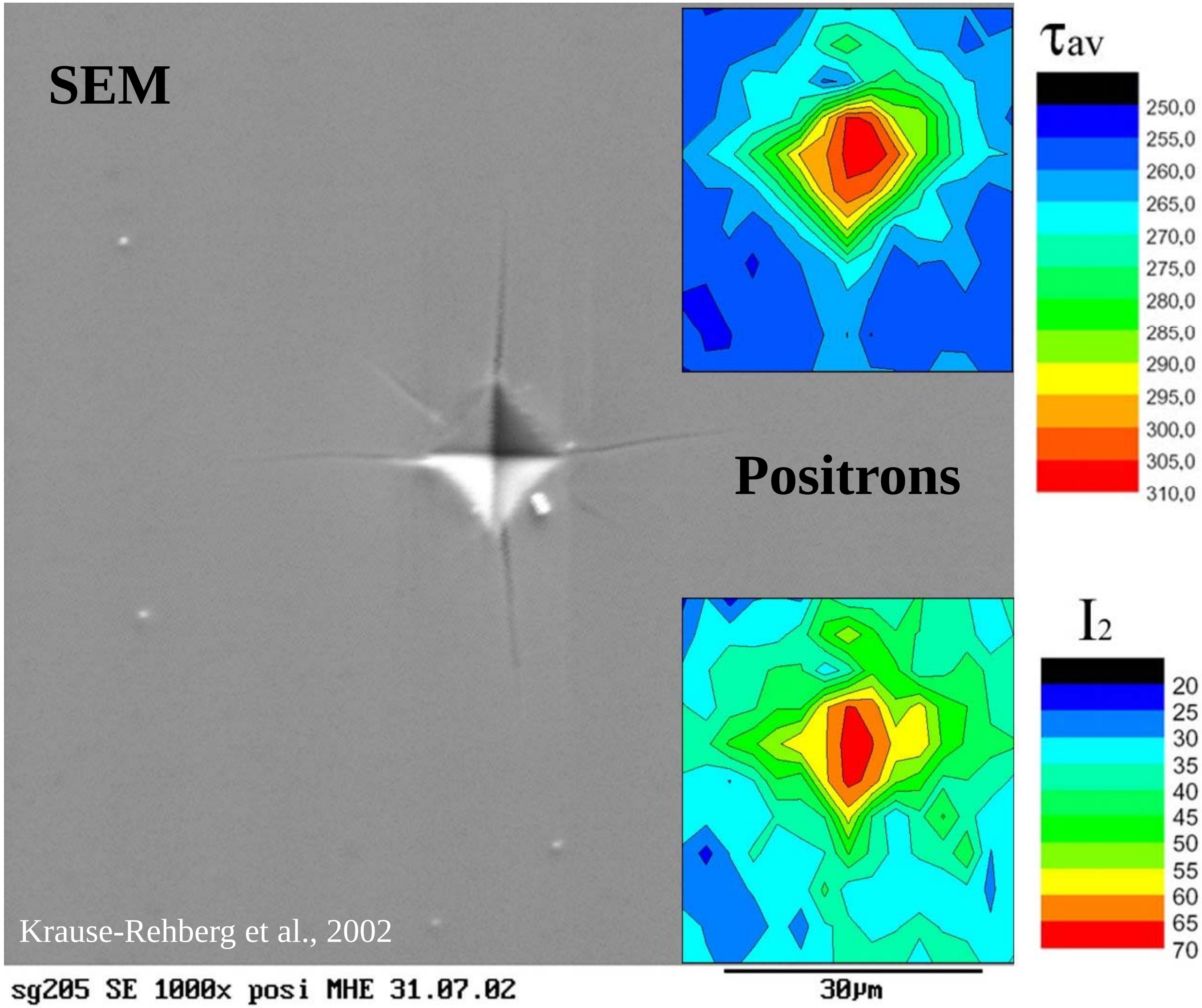
Munich Positron Scanning Microscope

- lateral resolution 2 µm
- Positron lifetime spectroscopy
- however lateral resolution principally limited by positron diffusion ($L_+ \approx$ 100nm)
- problem: low count rate
- transfer to FRM-II

W. Triftshäuser et al., NIM B **130** (1997) 265

Microhardness indentation in GaAs

- Comparison of SEM and Munich Positron Scanning Microscope
- problem here at the moment: intensity
- hope: strong positron source at FRM-II Garching or EPOS project in Rossendorf

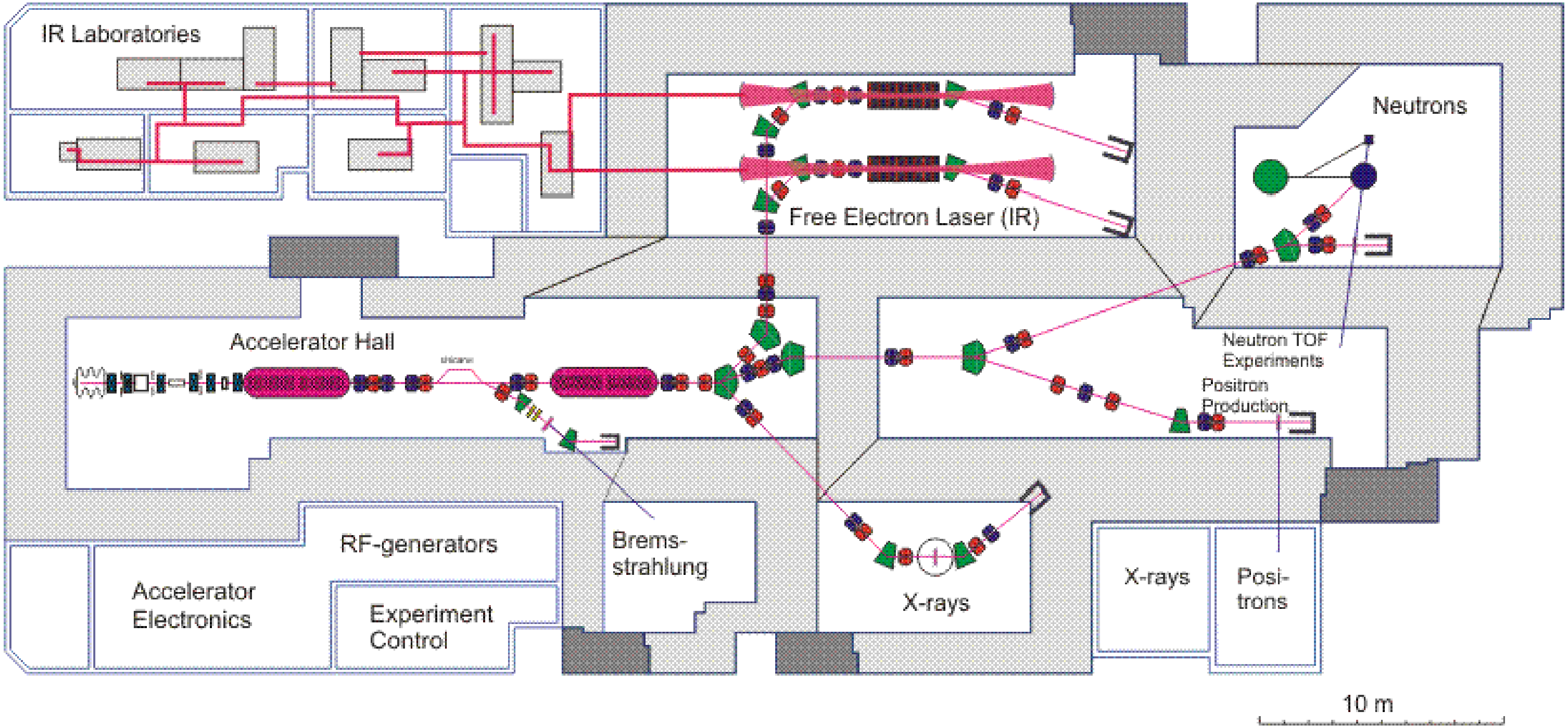


Krause-Rehberg et al., 2002

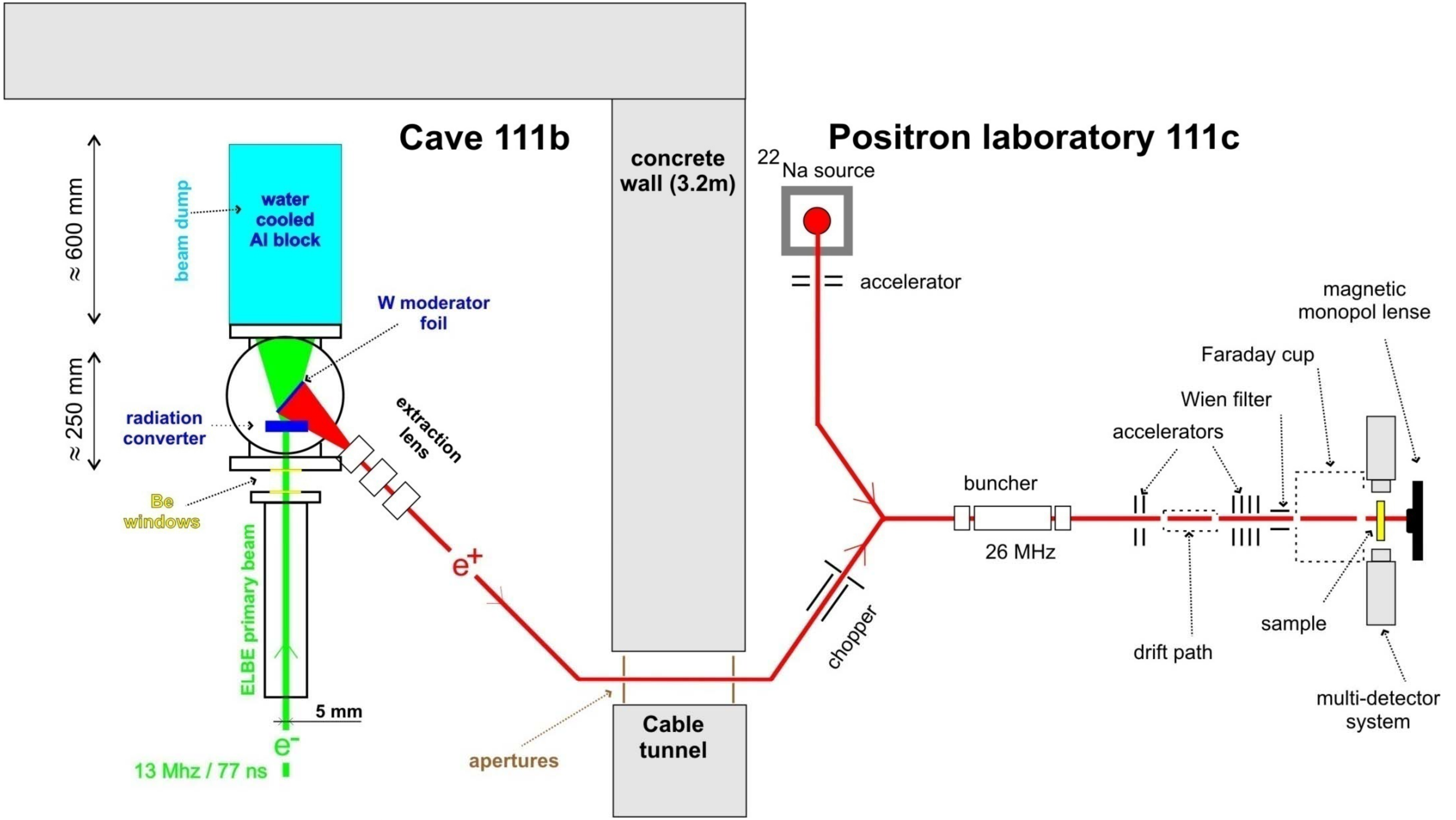
EPOS = ELBE Positron Source

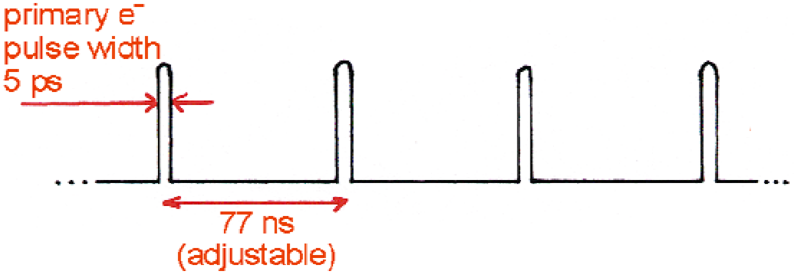
- ELBE -> electron LINAC (40 MeV and up to 40 kW) in Research Center Dresden-Rossendorf
- EPOS will be the combination of a positron lifetime spectrometer, Doppler coincidence, and AMOC
- user-dedicated facility
- main features:
  - high-intensity bunched positron beam (E_+ = 0.5…30 keV)
  - very good time resolution by using the unique primary time structure of ELBE
  - high quality spectra by lifetime and Doppler spectroscopy in coincidence mode
  - very high count rate by multi-detector array
  - all spectrometers digital
  - conventional source included for Doppler measurements (when primary beam is not available)
  - fully remote control via internet by user

Ground plan of the ELBE hall

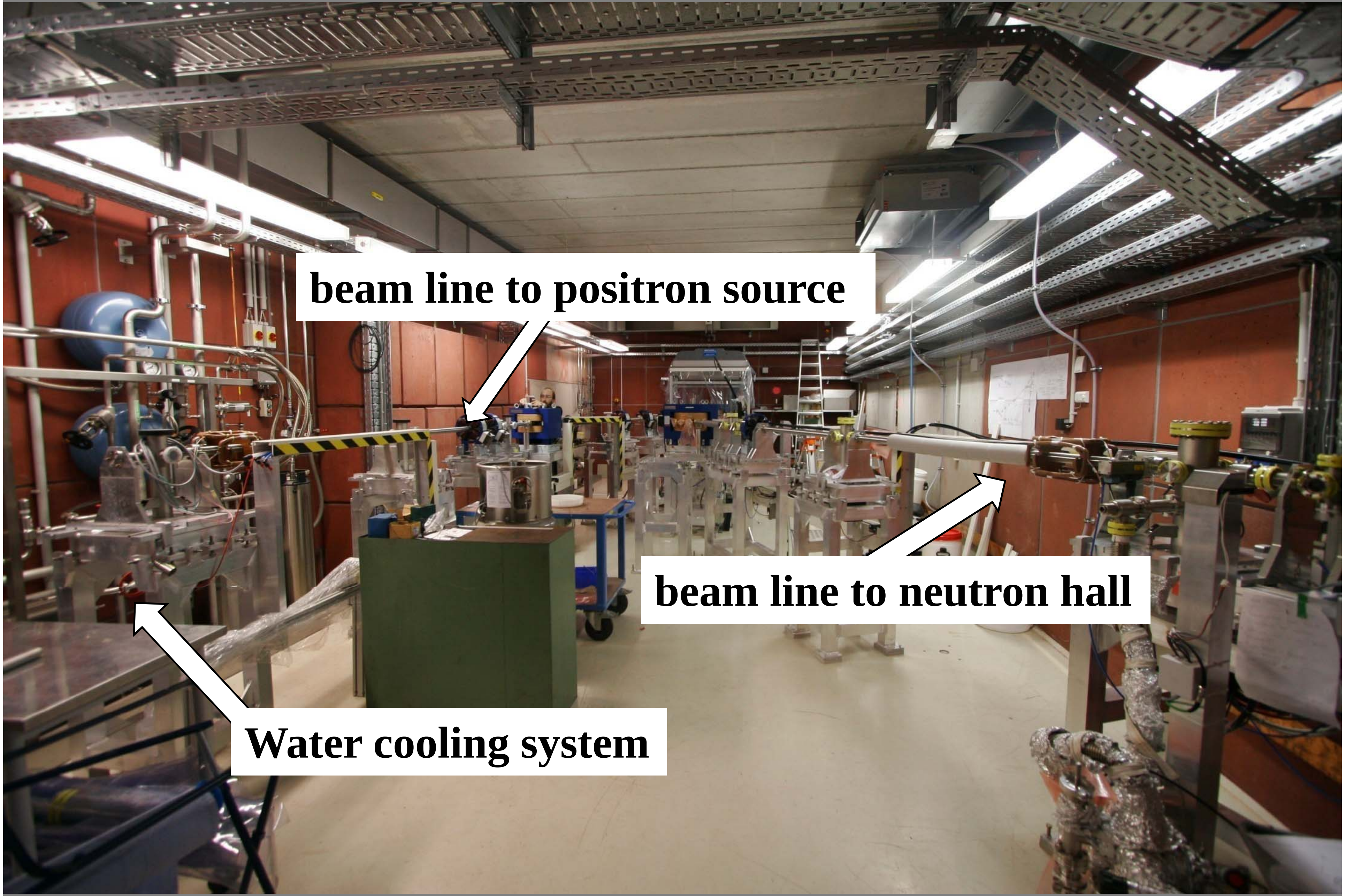


EPOS scheme


Cave 111b
Positron laboratory 111c
concrete wall (3.2m)
^{22}Na source
accelerator
≈ 600 mm
≈ 250 mm
beam dump
water cooled Al block
W moderator foil
radiation converter
extraction lens
Be windows
ELBE primary beam
e+
5 mm
e-
13 Mhz / 77 ns
apertures
Cable tunnel
chopper
buncher
26 MHz
accelerators
Wien filter
Faraday cup
magnetic monopol lense
drift path
sample
multi-detector system


primary e-
pulse width
5 ps
77 ns
(adjustable)

Cave 111b



beam line to positron source

beam line to neutron hall

Water cooling system

EPOS - Applications

Variety of applications in all field of materials science:

- defect-depth profiles due to surface modifications and ion implantation
- tribology (mechanical damage of surfaces)
- polymer physics (pores; interdiffusion; …)
- low-k materials (thin high porous layers)
- defects in semiconductors, ceramics and metals
- epitaxial layers (growth defects, misfit defects at interface, …)
- fast kinetics (e.g. precipitation processes in Al alloys; defect annealing; diffusion; …)
- radiation resistance (e.g. space materials)
- many more …

Conclusions

- Positrons are a unique tool
  - for characterization of vacancy-type defects in crystalline solids
  - for embedded nano-particles (e.g. small precipitates)
  - for nano-porosimetry
- New facilities become available for user-dedicated operation having
  - better time resolution and spectra quality
  - lateral resolution 1 μm
  - much higher intensity

This presentation can be found as pdf-file on our Website:
http://positron.physik.uni-halle.de

contact: mail@KrauseRehberg.de