Material Science by means of Positron Annihilation

NRF
National Research Foundation
iThemba LABS
Laboratory for Accelerator Based Sciences

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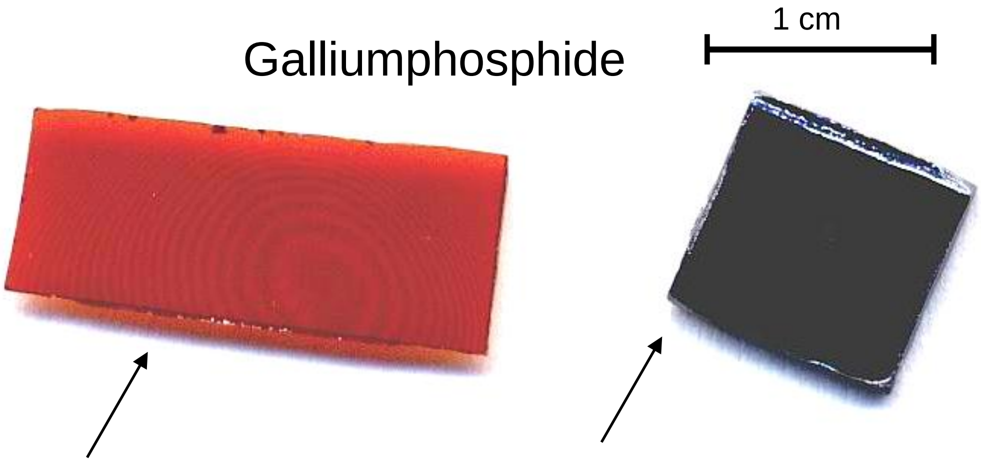
- Why are nano-defects important at all?
- Positron trapping by defects
- Positronium to probe pores
- other positron activities (ATHENA, ATRAP and …)

Point defects determine properties of materials

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

Galliumphosphide



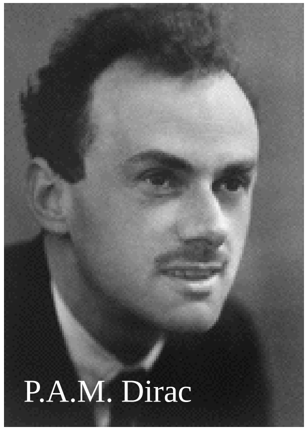
without vacancies
transparent

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

Discovery of the Positron

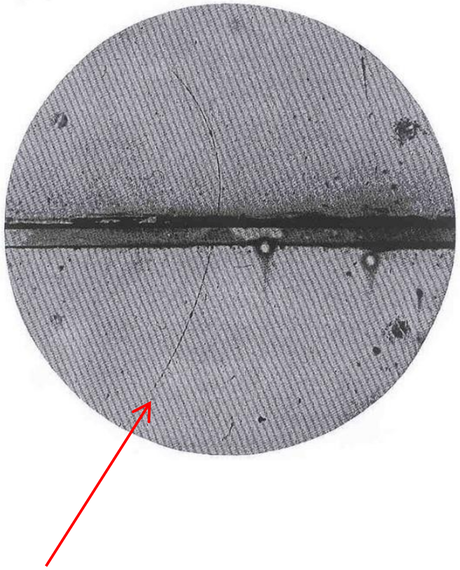
- Positron was predicted in 1928 by Paul A.M. Dirac
- Discovery in 1932 in cloud chamber pictures by C.D. Anderson



P.A.M. Dirac

C.D. Anderson

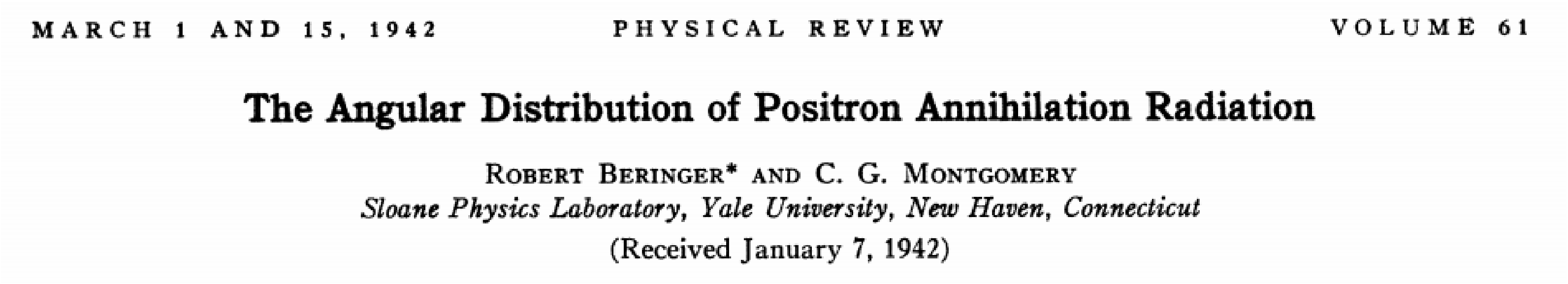
- Positronium as bound state of e^- and e^+ lightest atom was predicted (1934) and discovered (1951)
- Annihilation in matter was studied beginning in the 40^s
- Positrons can be obtained by
  - pair production from gamma radiation (E_γ > 1022 keV)
  - β^+ decay from isotopes (mostly ^{22}Na)



- first Identification of a positron in a cloud chamber
- 5 mm lead plate
- photo taken by C.D. Anderson

Electron structure of solids can be discovered

- during annihilation: conservation laws must be fulfilled (energy, momentum)
- positron cools down to thermal energies ->
- energy of annihilating electron-positron pair = energy of electron
- electron momentum distribution can directly be measured


MARCH 1 AND 15, 1942 PHYSICAL REVIEW VOLUME 61

The Angular Distribution of Positron Annihilation Radiation

ROBERT BERINGER* AND C. G. MONTGOMERY
Sloane Physics Laboratory, Yale University, New Haven, Connecticut
(Received January 7, 1942)

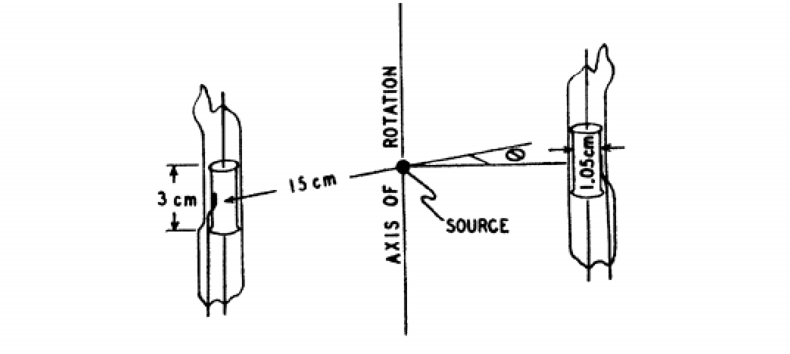
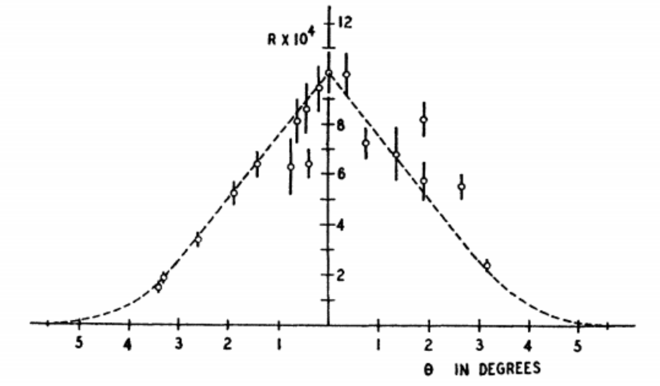
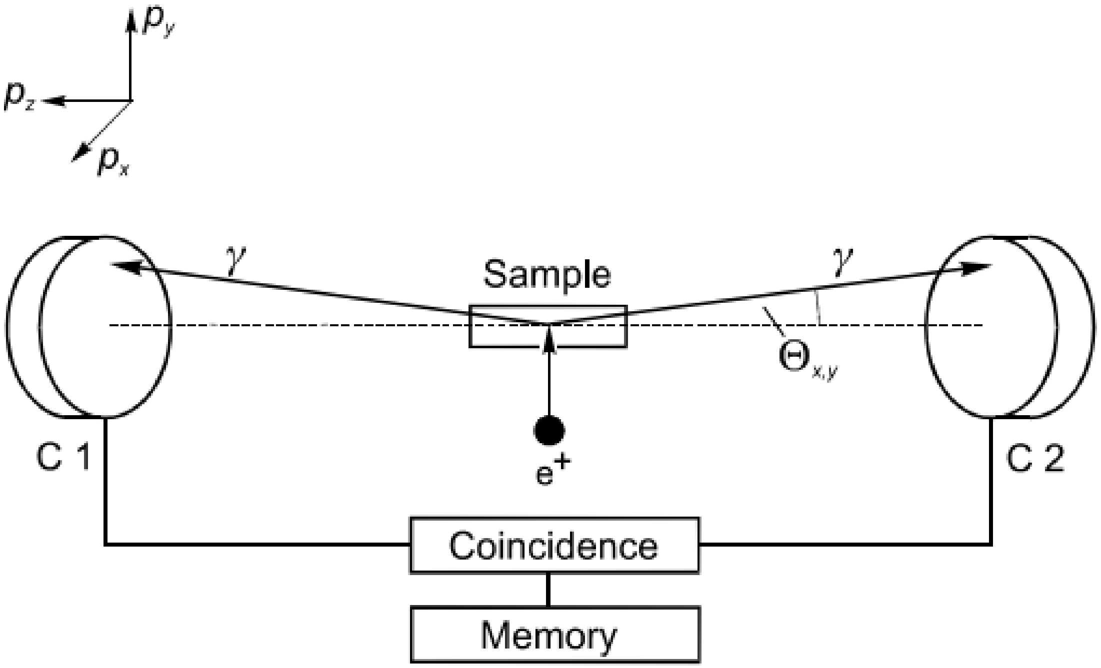


FIG. 1. Schematic arrangement of counters for observing coincidences from annihilation radiation.



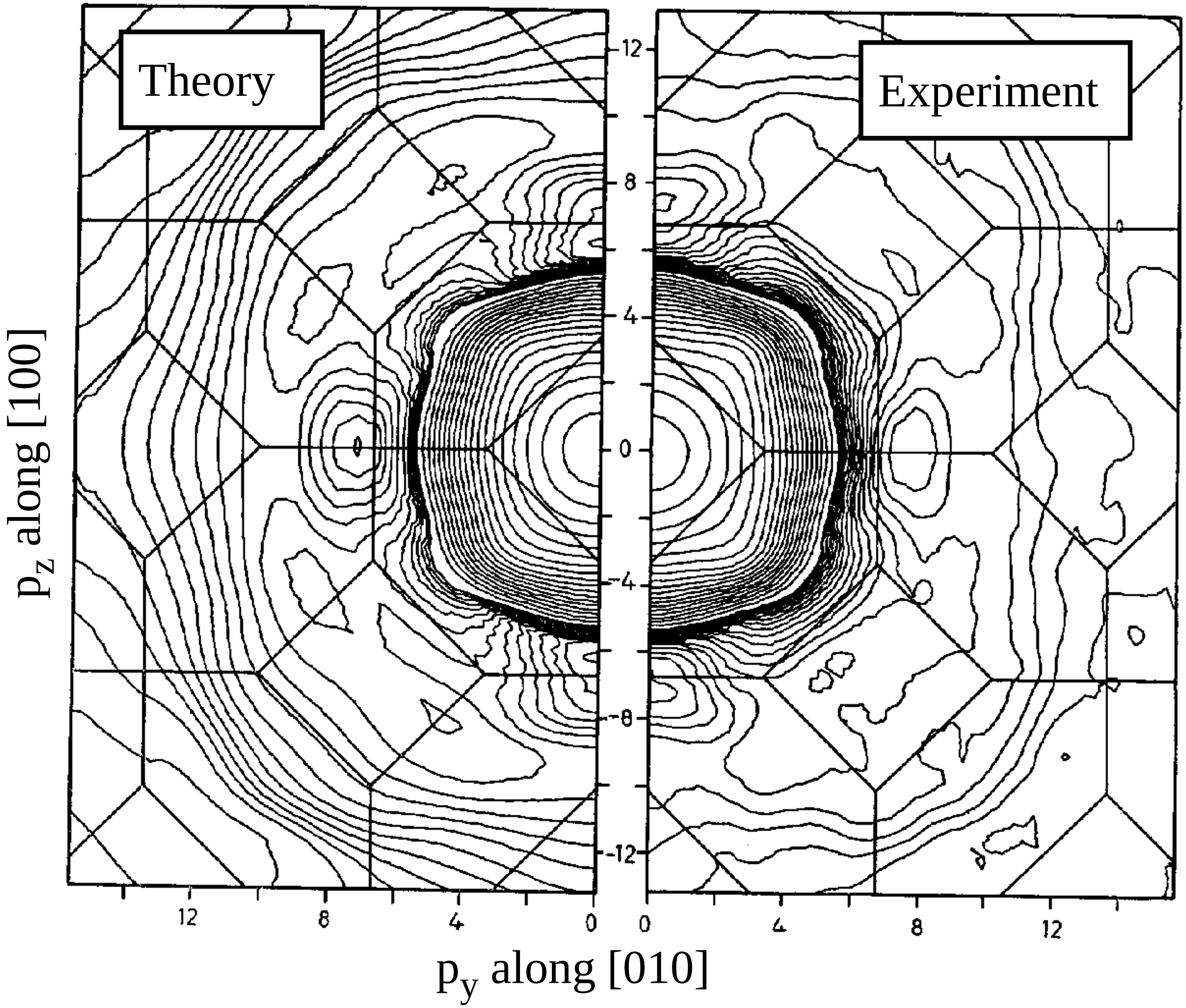
2D – ACAR (Angular Correlation of Annihilation Radiation)

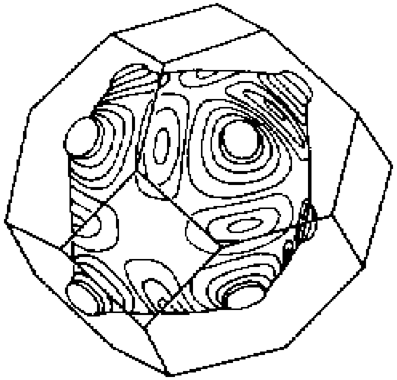
- now: two-dimensional (position-sensitive) detectors
- measurement of single crystals in different directions:
- reconstruction of Fermi surface possible



$$N_c(\Theta_x,\Theta_y) = A_c \int_{-\infty}^{\infty} \sigma(\Theta_x m_0 c, \Theta_y m_0 c, p_z)\, \mathrm{d}p_z$$

2D-ACAR of Copper





Fermi surface
of copper

(Berko, 1979)

Positrons are sensitive for Crystal Lattice Defects

- 1950…1960: in addition to ACAR -> different experimental techniques were developed
- Positron lifetime spectroscopy and Doppler broadening spectroscopy
- end of 60s: lifetime is sensitive to lattice imperfections
  - Brandt et al. (1968): **vacancies in ionic crystals**
  - Dekhtyar et al. (1969): **plastically deformed semiconductors**
  - MacKenzie et al. (1967): **vacancies in thermal equilibrium** in metals
- Positrons are localized (trapped) by open-volume defects

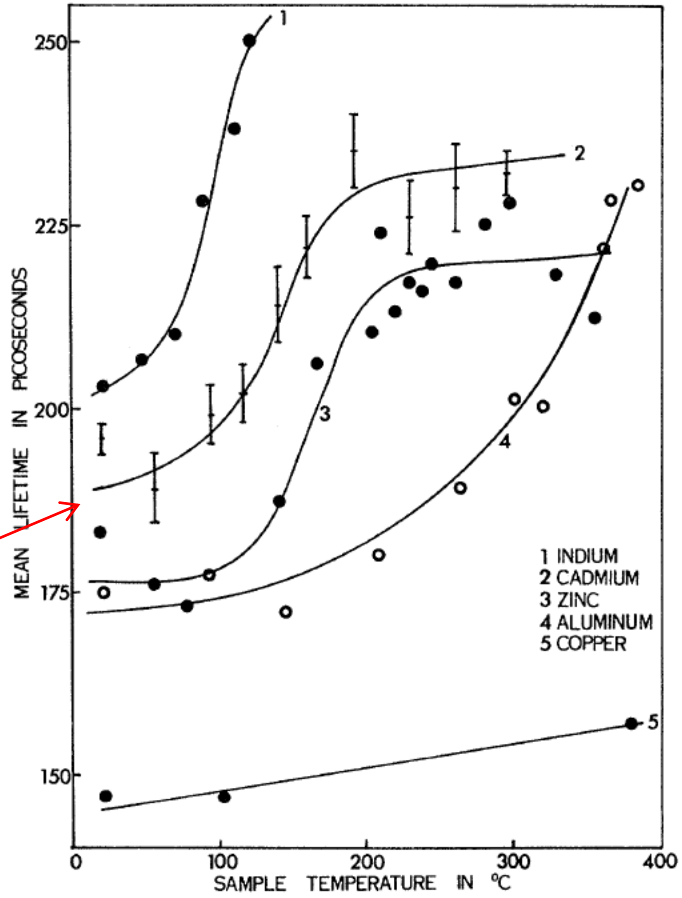
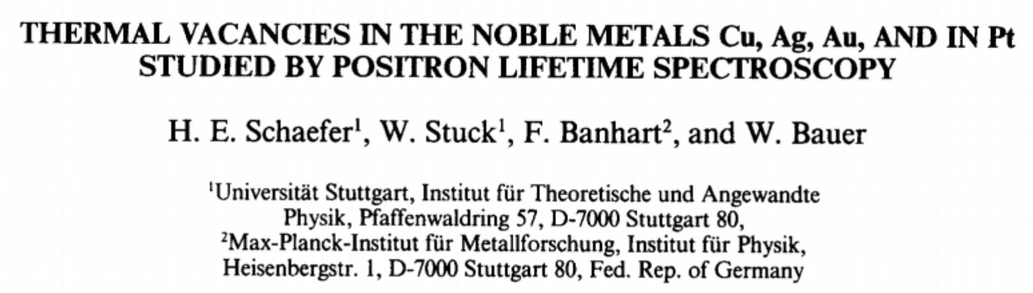


FIG. 1. Positron mean lifetimes in several metals as a function of temperature.

Determination of Vacancy Formation Enthalphy



THERMAL VACANCIES IN THE NOBLE METALS Cu, Ag, Au, AND IN Pt
STUDIED BY POSITRON LIFETIME SPECTROSCOPY

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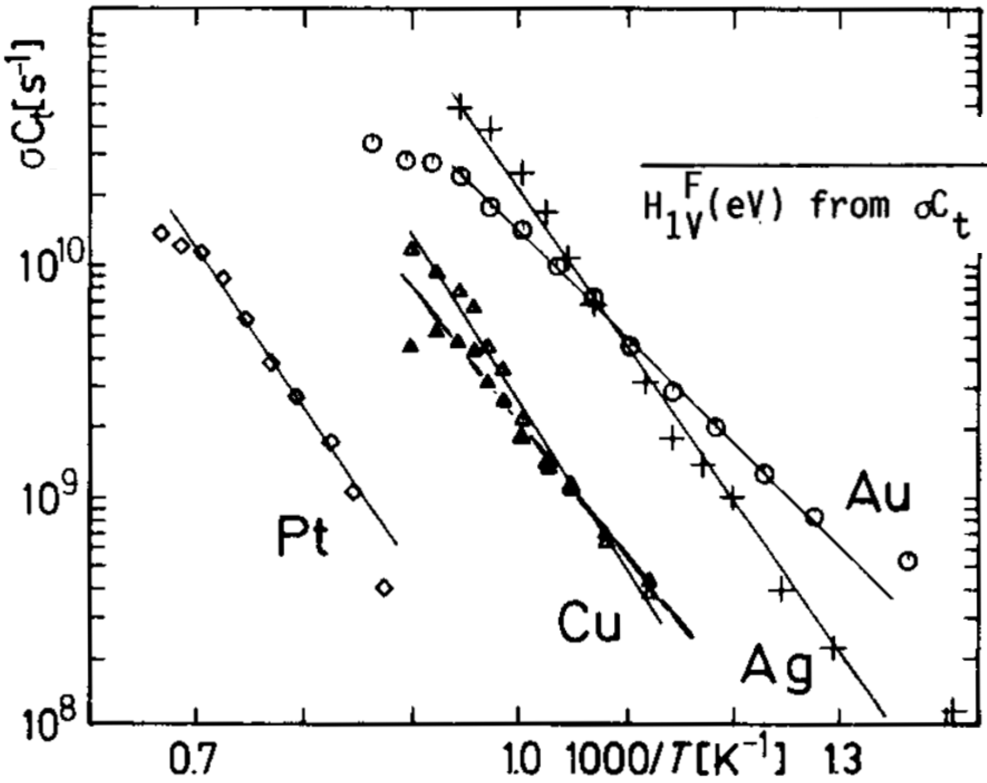
Heisenbergstr. 1, D-7000 Stuttgart 80, Fed. Rep. of Germany

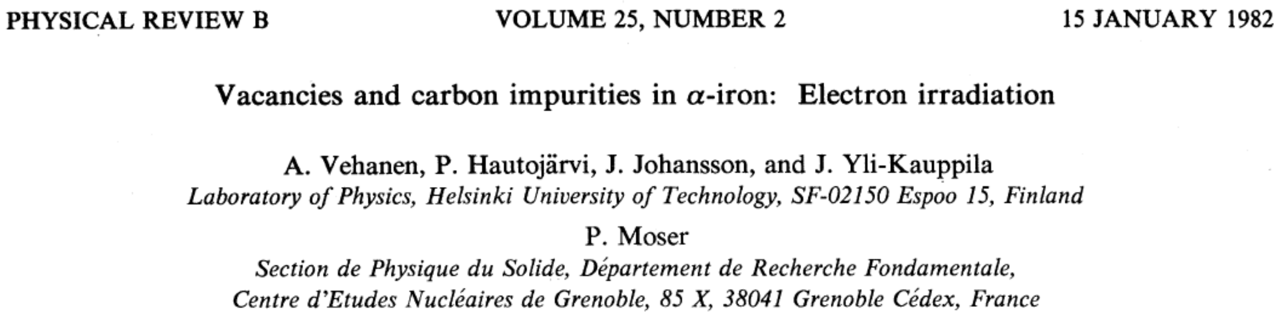


	Cu	Ag	Au	Pt
H_{1V}^F(eV) from σC_t	1.13±.04*	1.31±.07	.89±.02	1.35±.09

- Arrhenius-Plot delivers H_{1V}
- was performed for many alloys

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

Study of non-equilibrium Defects



PHYSICAL REVIEW B VOLUME 25, NUMBER 2 15 JANUARY 1982

Vacancies and carbon impurities in α-iron: Electron irradiation

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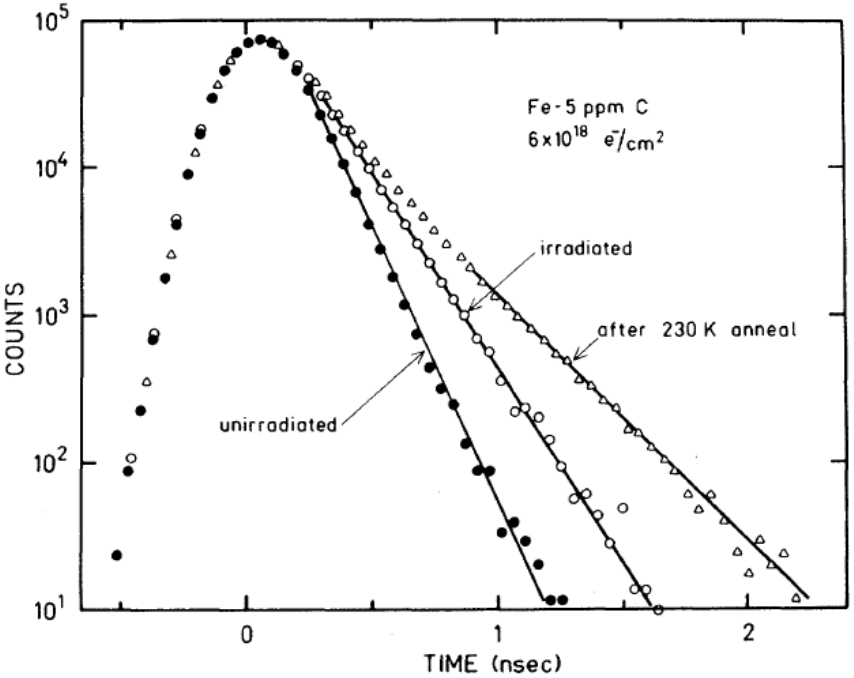
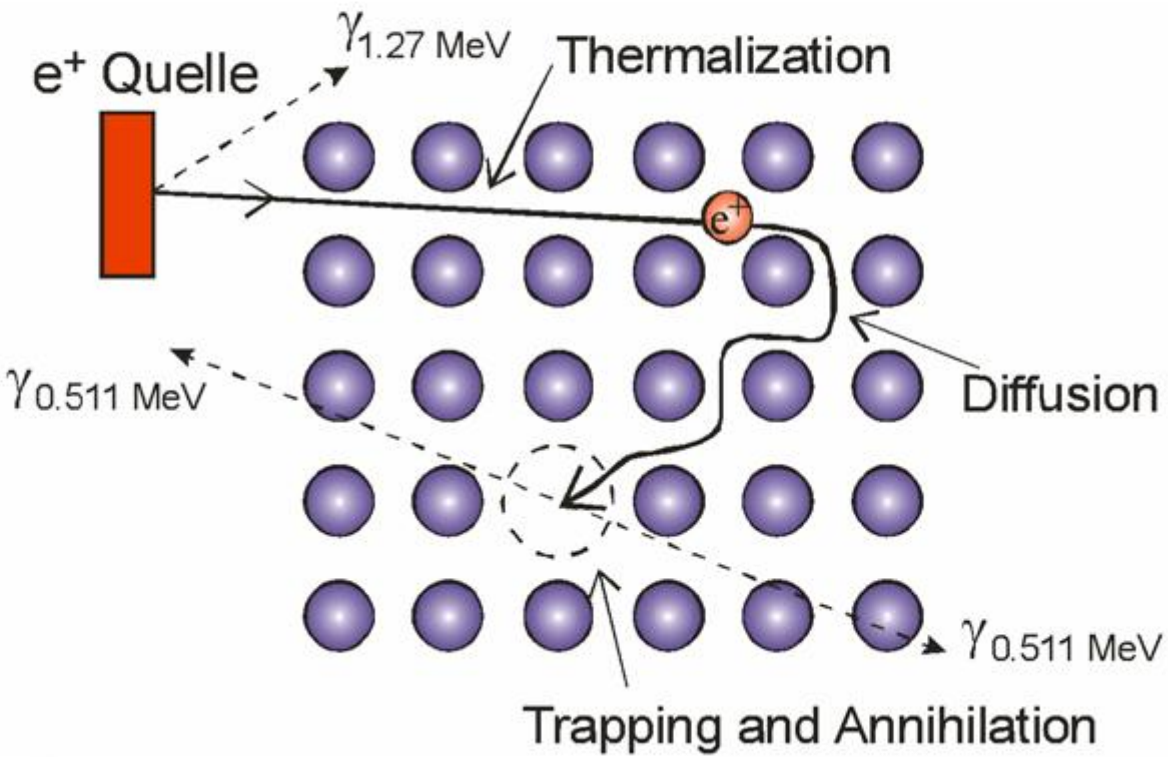


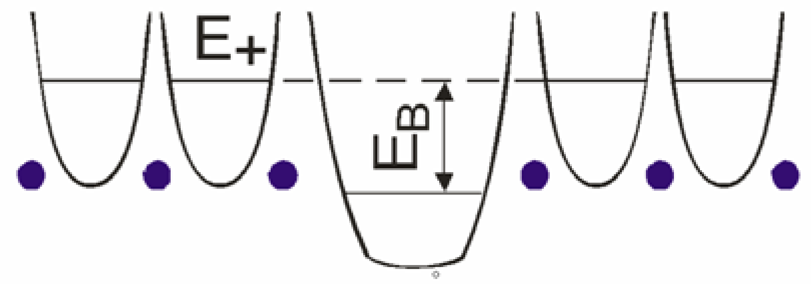
FIG. 1. Positron-lifetime spectra after source-background subtraction in electron-irradiated (6×10^{18} e^-/cm^2) high-purity iron at various stages of isochronal annealing. The dramatic occurrence of a long-lifetime component after 230 K annealing is clearly visible.

- positron lifetime is very sensitive for vacancy-type defects
- here: lifetime increases after irradiation
- and further increase after first annealing: vacancy clustering

The positron lifetime spectroscopy

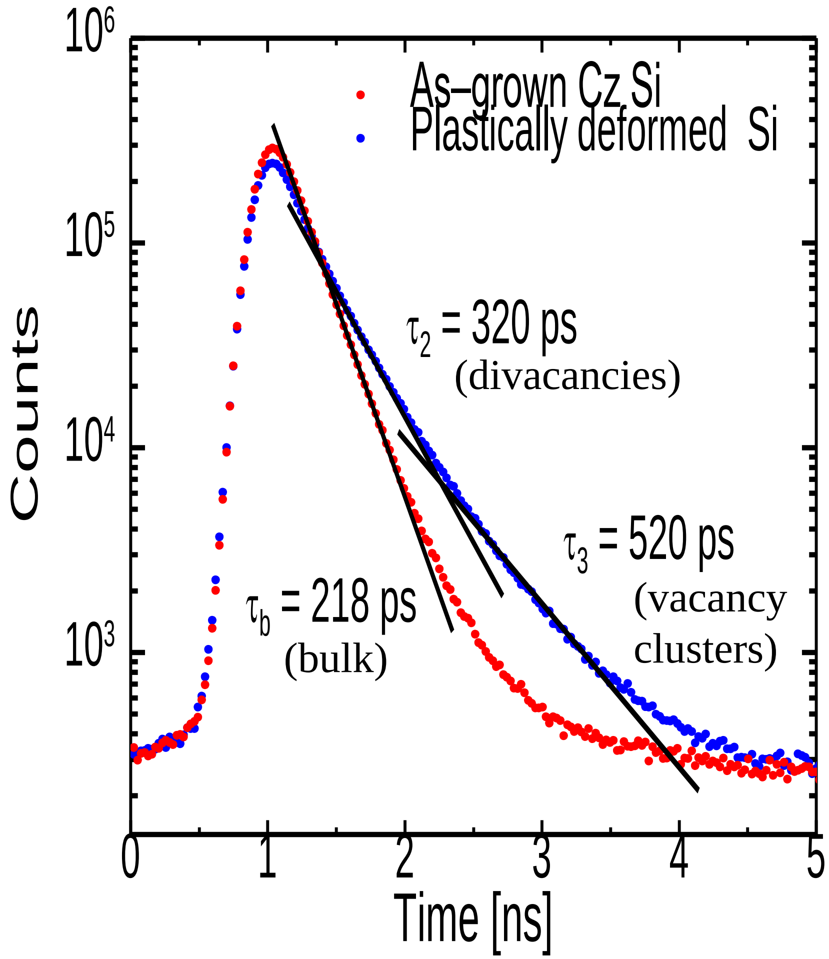
^{22}Na





- 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

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

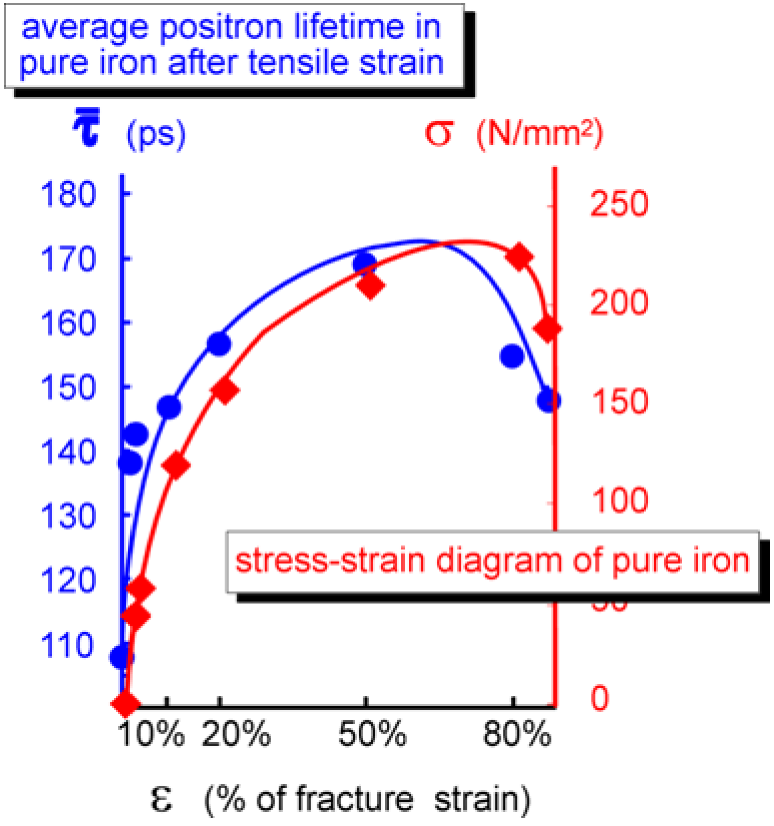
$$\boxed{\kappa_d = \mu C_d} = \frac{I_2}{I_1}\left(\frac{1}{\tau_b} - \frac{1}{\tau_d}\right)$$

trapping rate

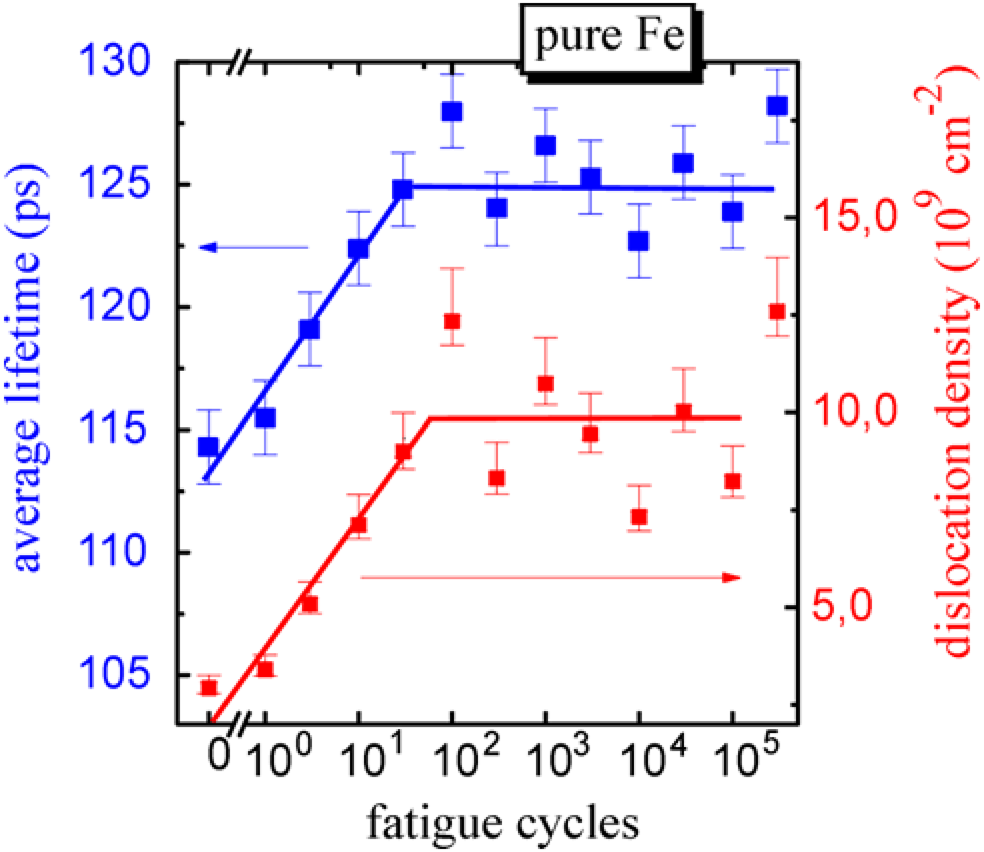
defect concentration

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

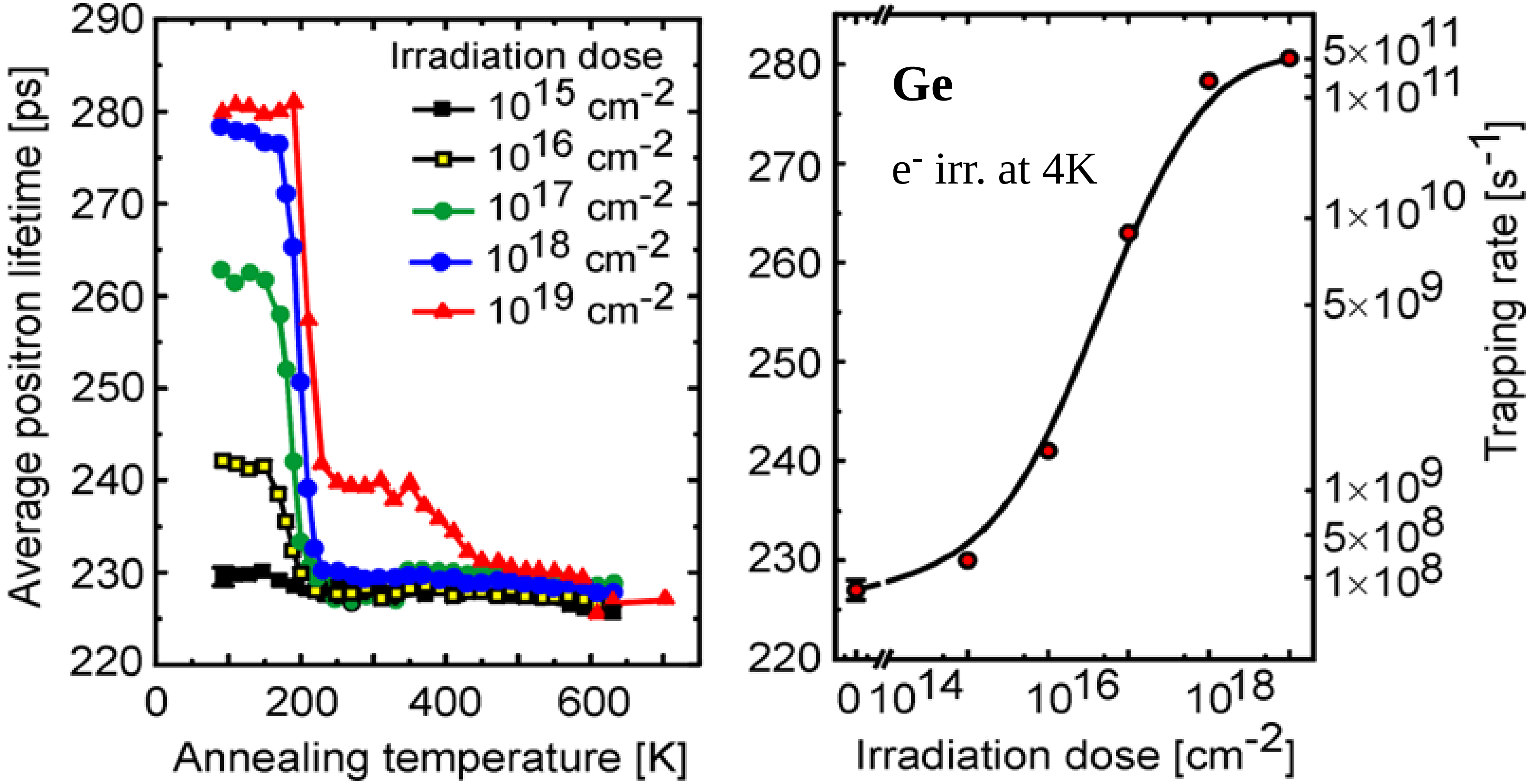
stress-strain diagram of pure iron



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

Defects in electron-irradiated Ge

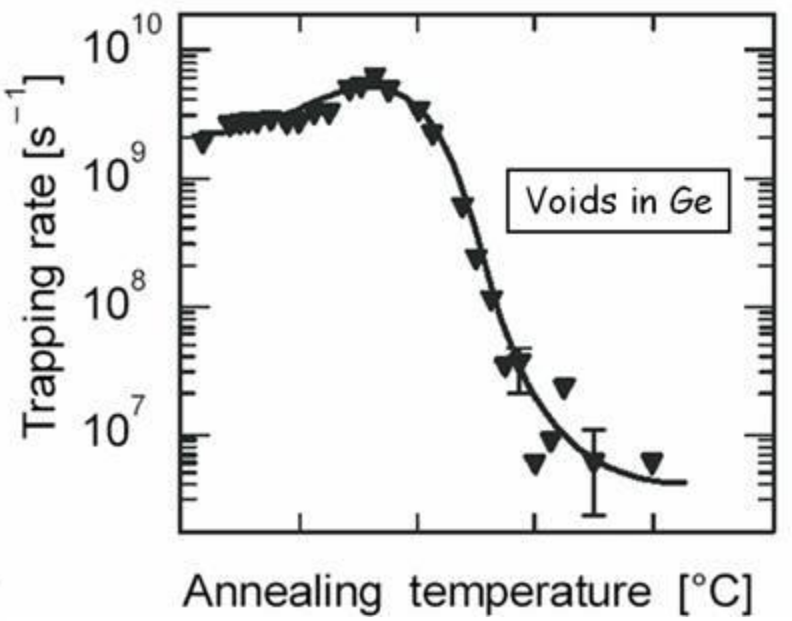
- Electron irradiation (2 MeV @ 4K) induces Frenkel pairs (vacancy - interstitial pairs)
- steep annealing stage at 200 K
- at high irradiation dose: divacancies are formed (thermally more stable)



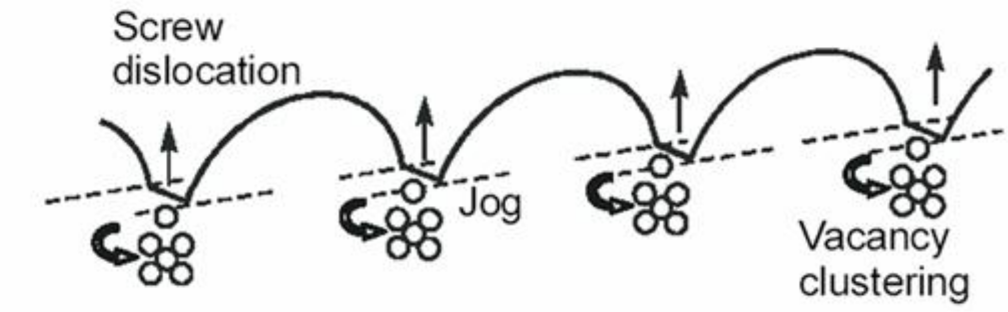
(Polity et al., 1997)

Vacancy clusters in semiconductors

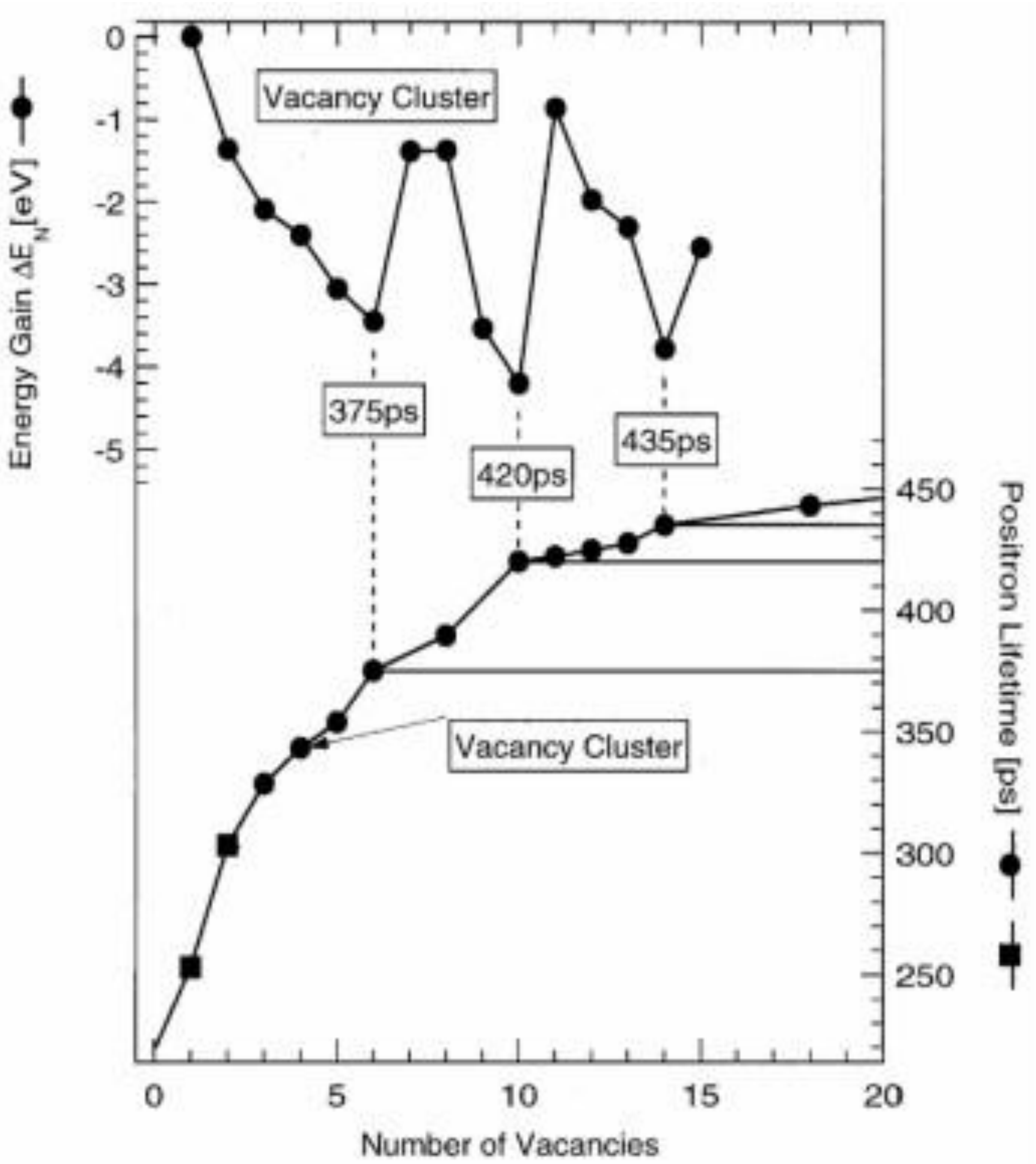
- vacancy clusters were observed after neutron irradiation, ion implantation and plastic deformation
- due to large open volume (low electron density) -> positron lifetime increases distinctly
- example: plastically deformed Ge
- lifetime: τ = 525 ps
- reason for void formation: jog dragging mechanism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



Krause-Rehberg et al., 1993



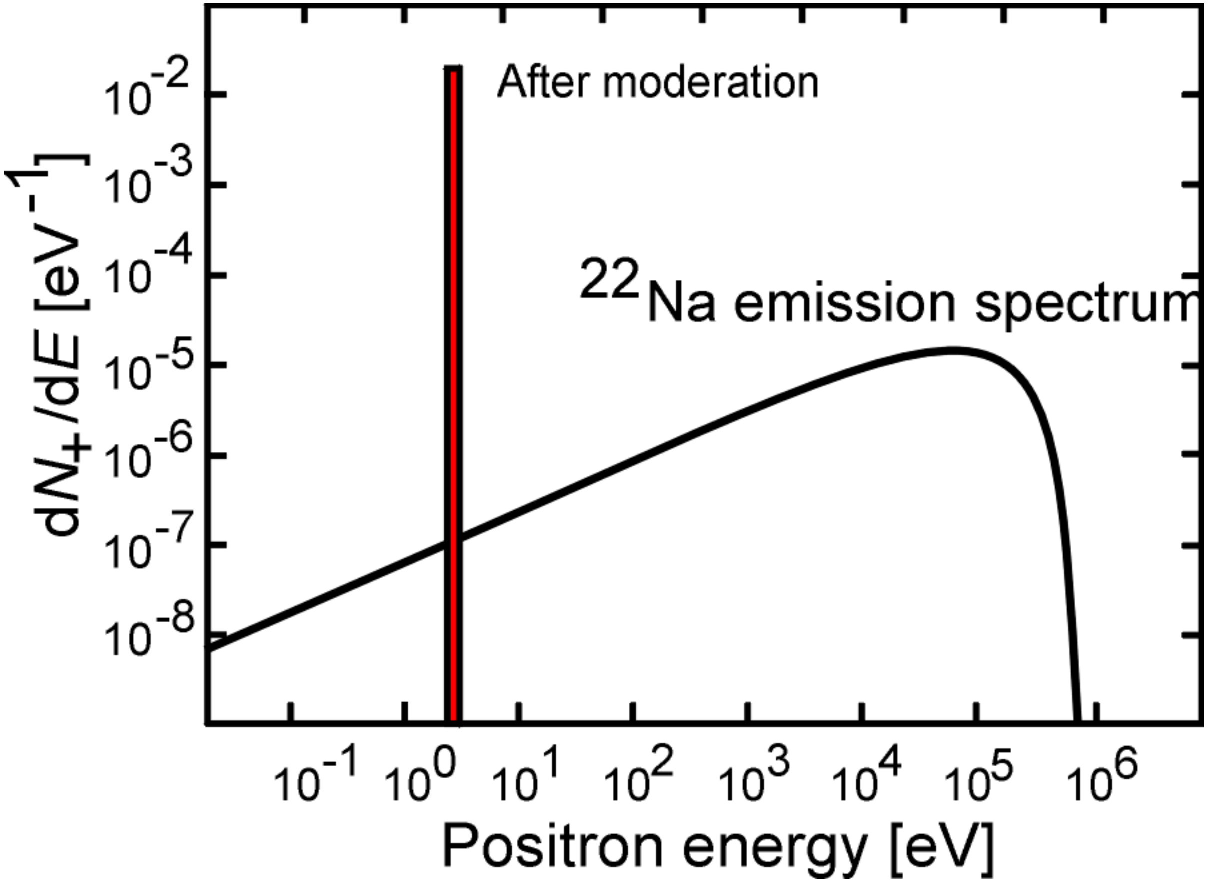
Theoretical calculation of vacancy clusters in Si



- 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

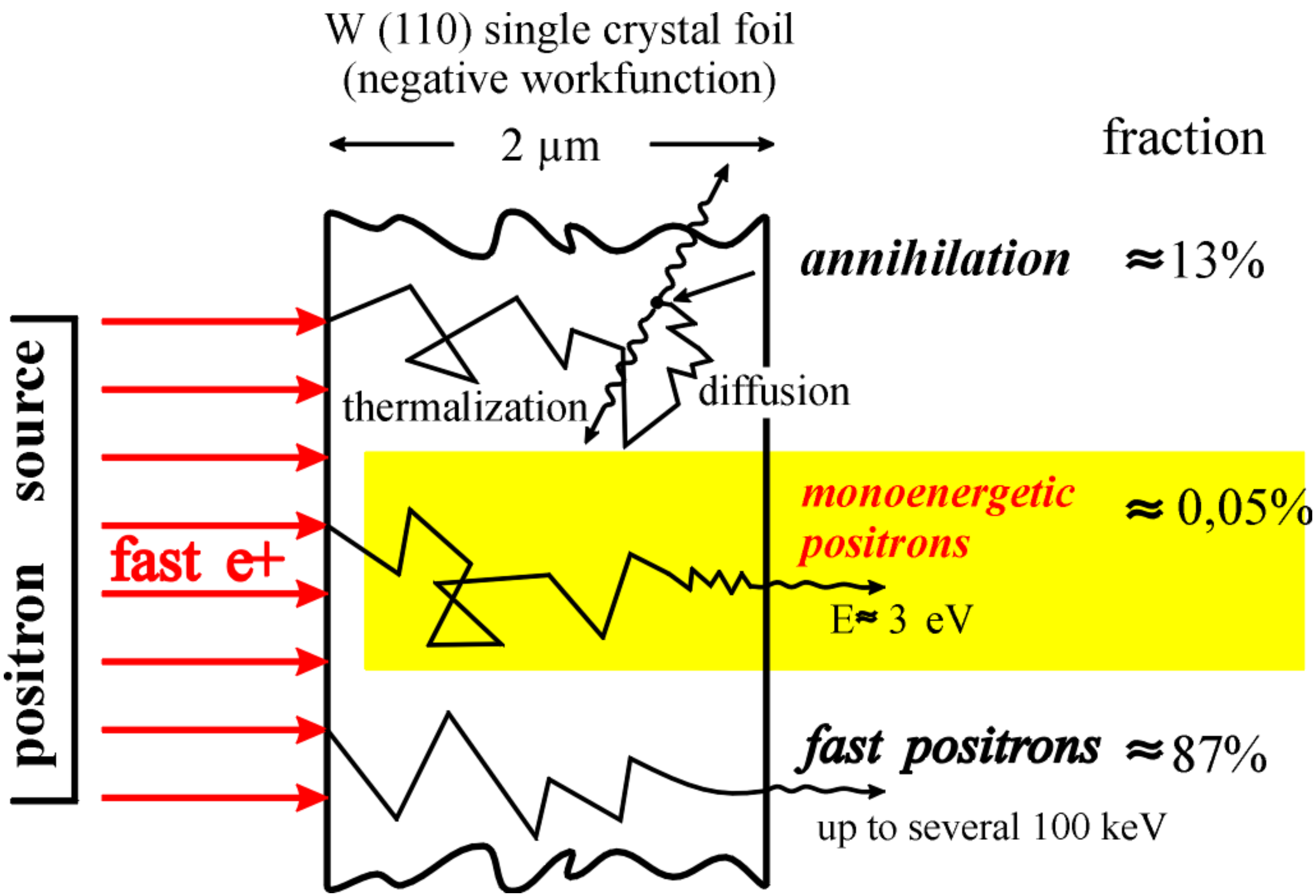
The Slow-Positron Beam Technique



- broad positron emission spectrum from beta sources
- deep implantation into solids
- no use for study of defects in thin layers
- moderation necessary

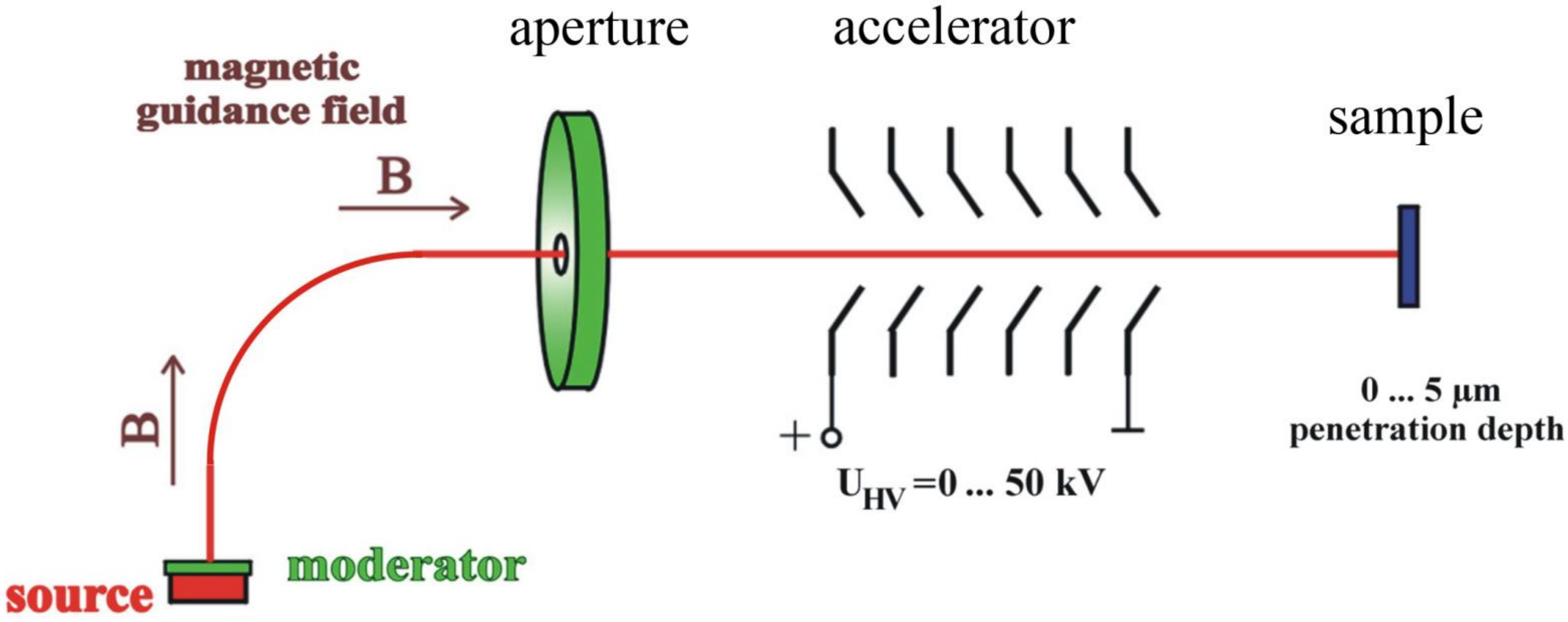
Mean implantation depth of un-moderated positrons (1/e): Si: 50µm

Moderation of Positrons



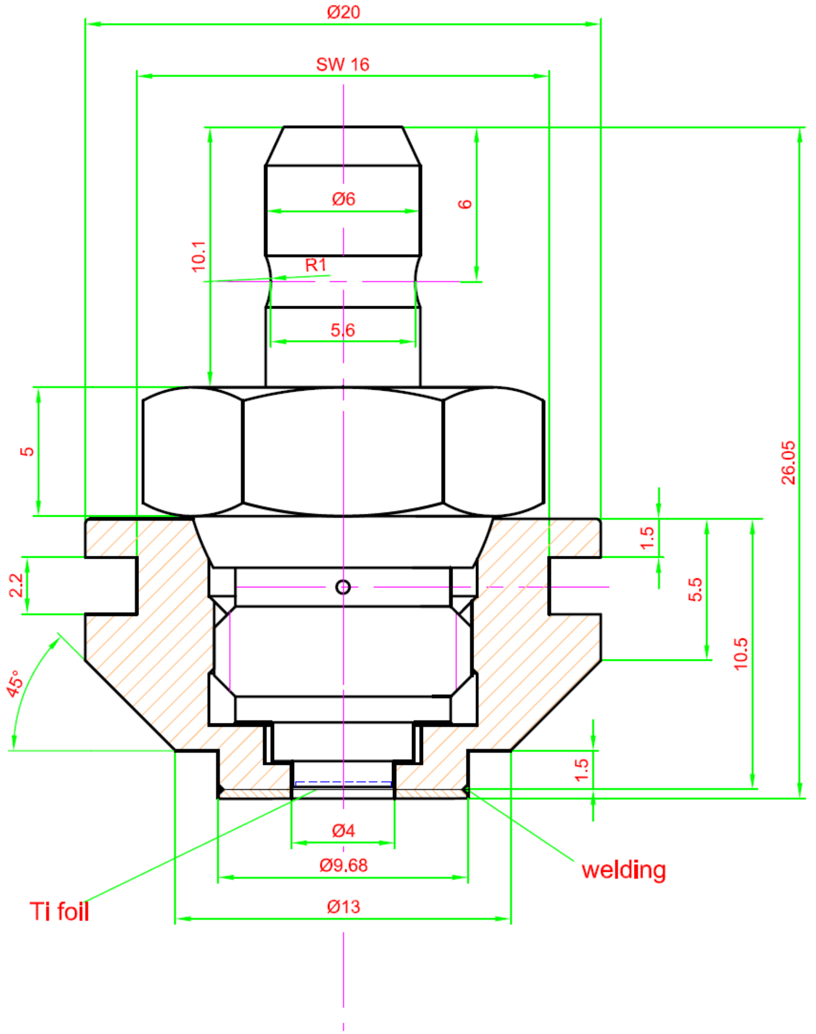
moderation efficiency: ≈10^{-4}

Positron Beam System at Halle University



- Energy selection done by a bended tube: slow positrons follow the longitudinal magnetic field

Positron Source

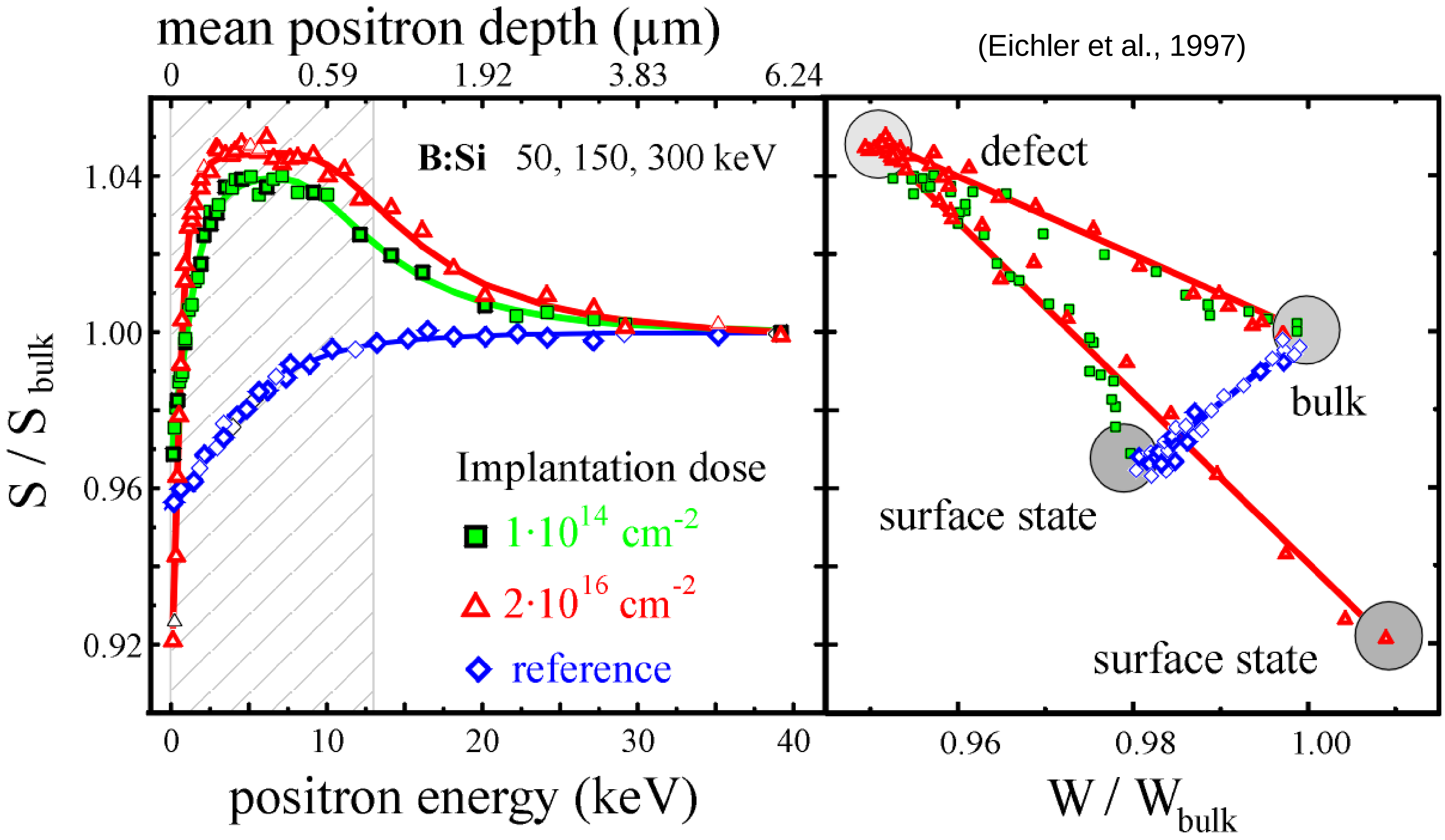


Source capsule made from Ti

- We developed a source capsule for T = 4…473K
- tested individually by He leak tester to be UHV-tight
- thin Ti window (5 µm) tested to survive up to 6 bar overpressure
- maximum activity: 50 mCi (1.8 GBq)
- 22Na produced / capsules filled at iThemba Labs

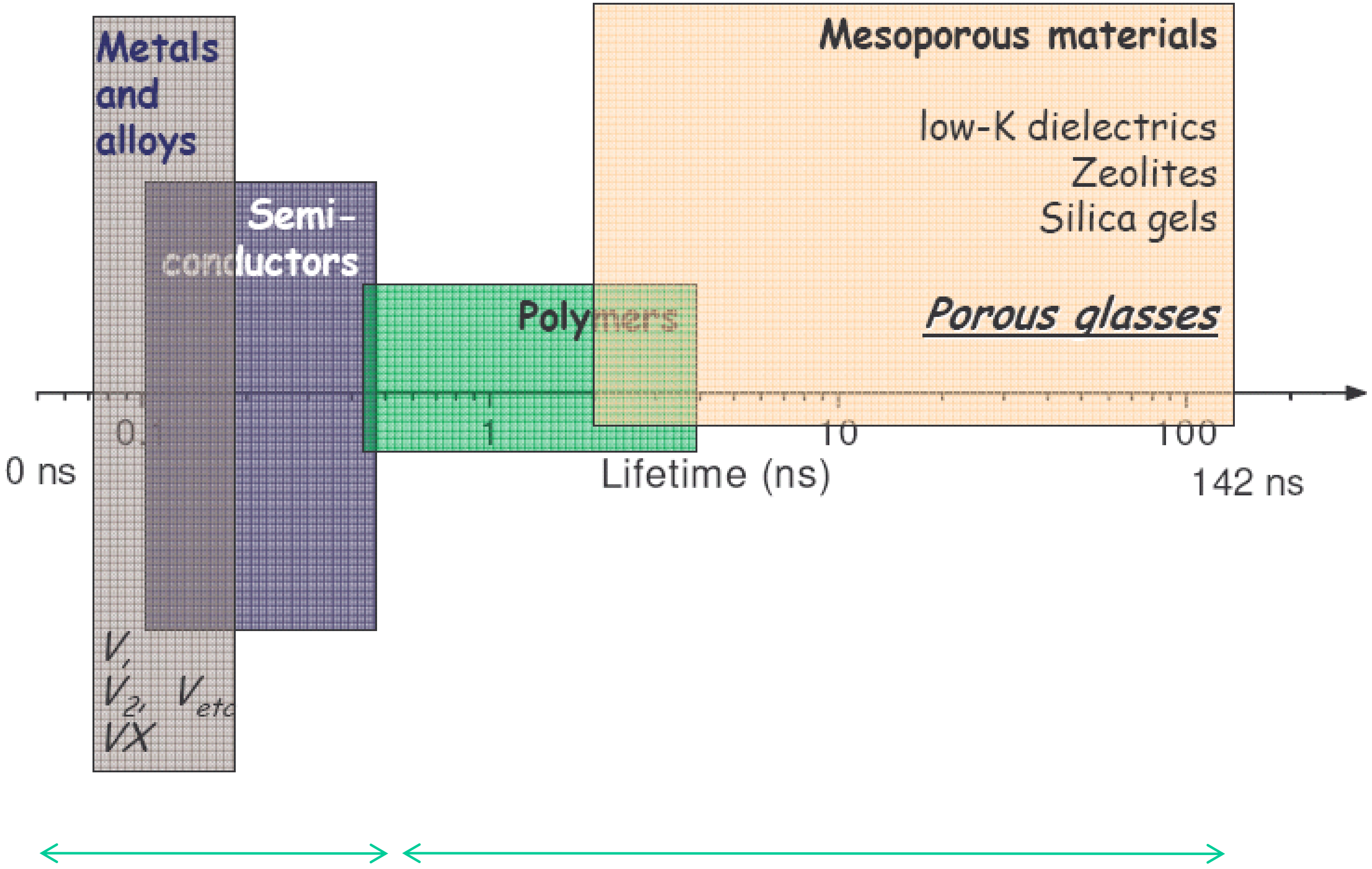
Defects in Si induced by Ion Implantation

- ion implantation is most important doping technique in planar technology
- main problem: generation of defects ⇒ positron beam measurements



(Eichler et al., 1997)

Typical Positron and Positronium Lifetimes

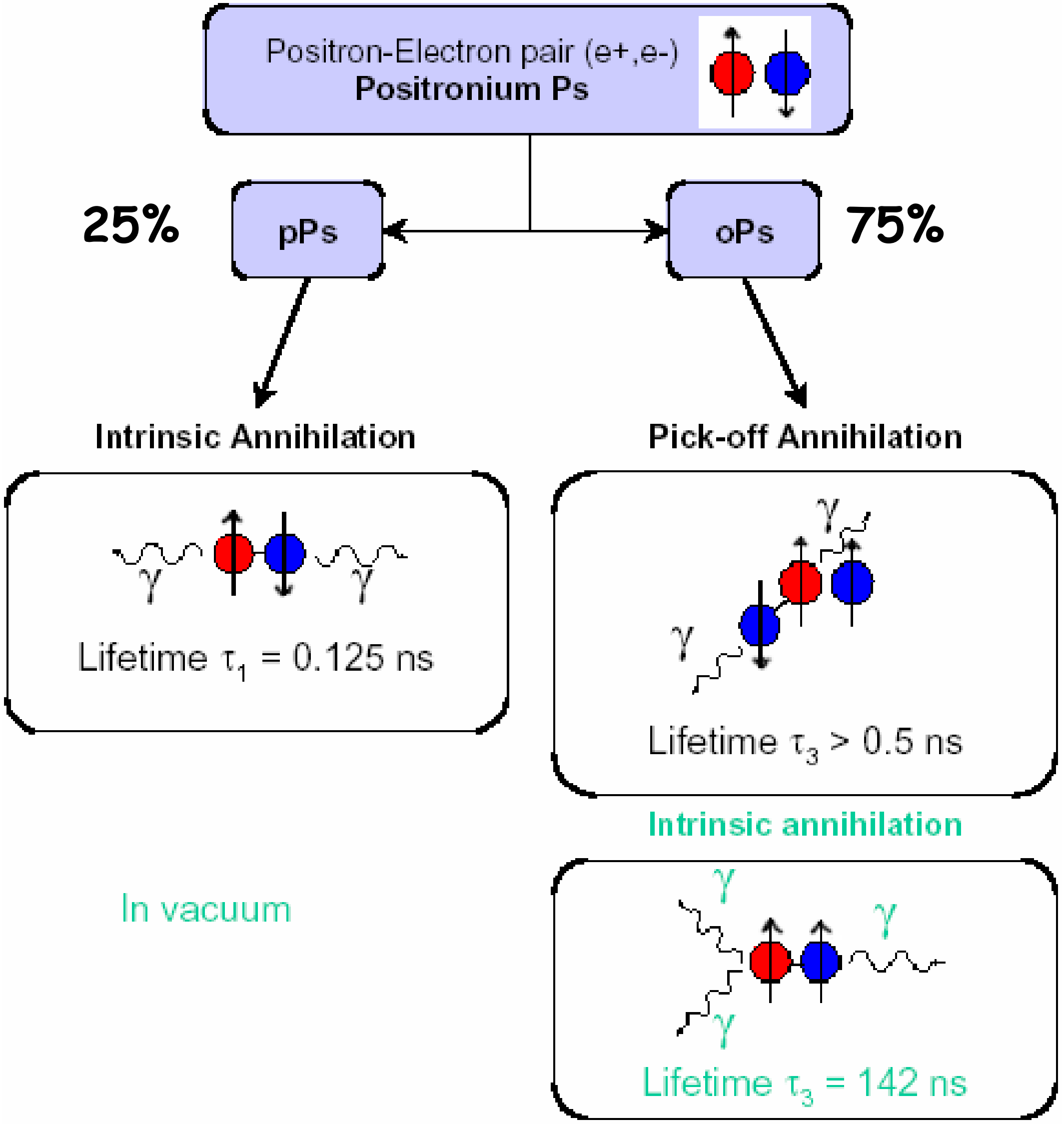


Positron

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

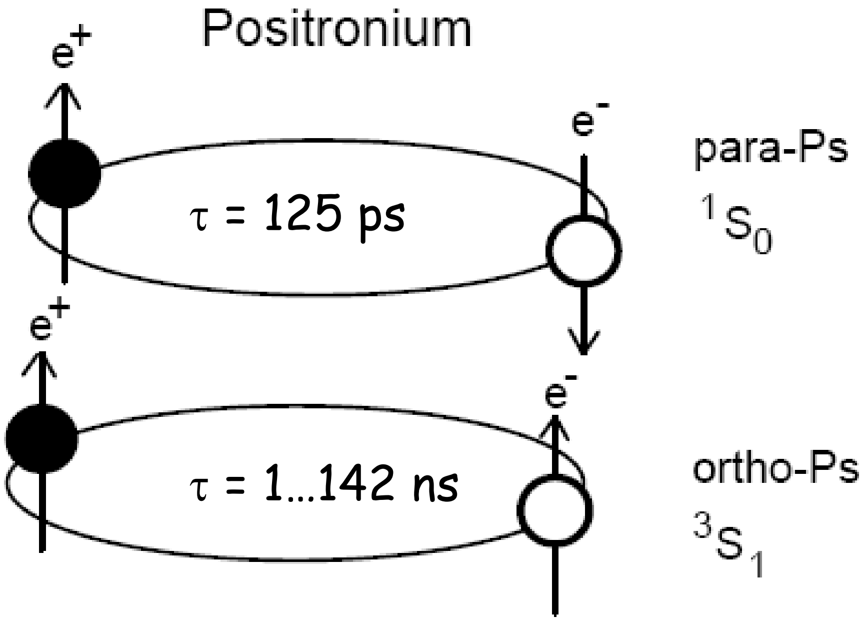
Lifetime τ_3 = 142 ns

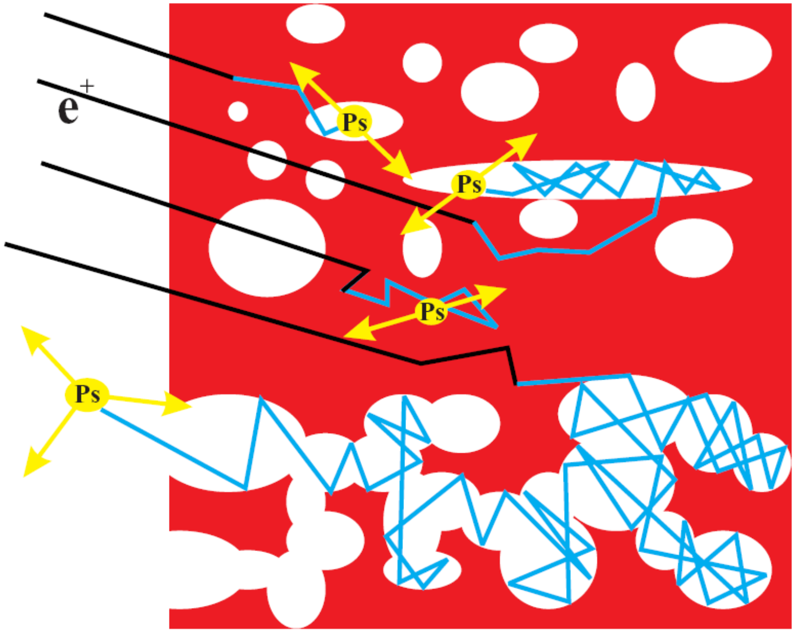
Pick-off annihilation

pick-off annihilation:

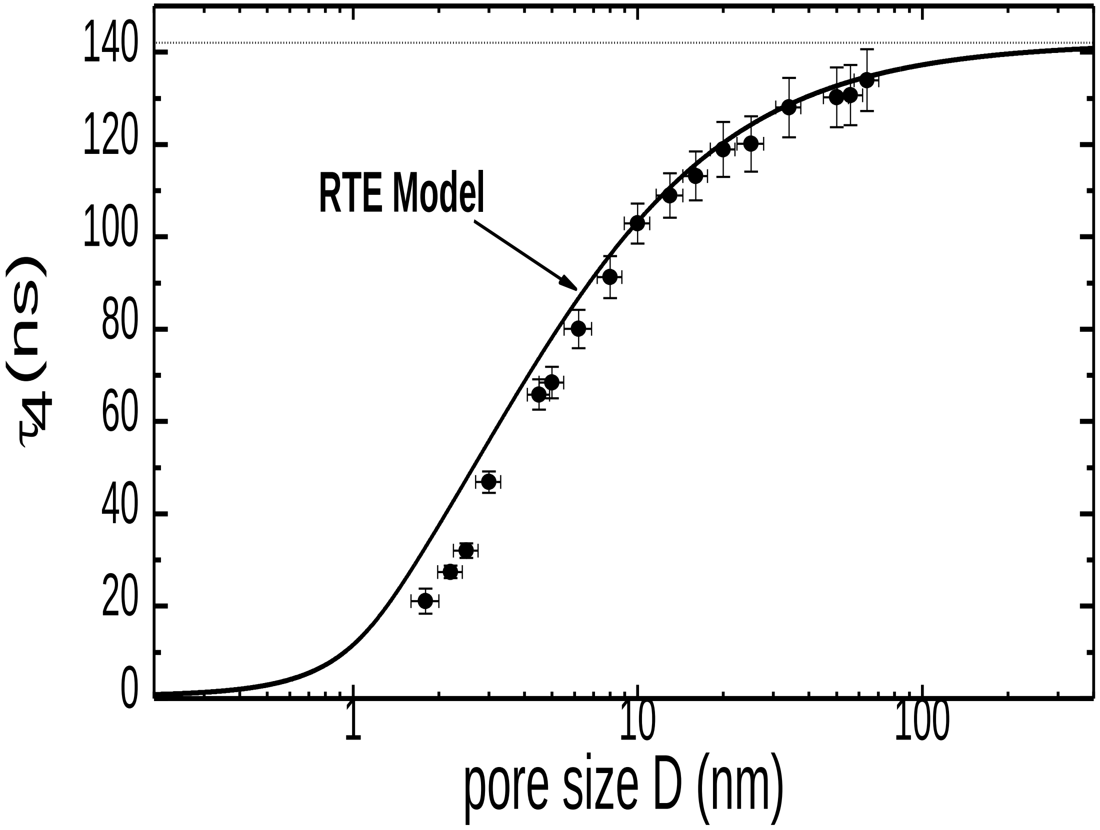
- o-Ps is converted to p-Ps by capturing an electron with anti-parallel spin
- happens during collisions at walls of pore
- lifetime decreases rapidly
- lifetime is function of pore size 1.5 ns to 142 ns

positrons form Ps

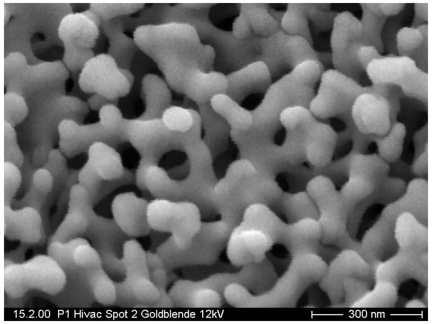




o-Ps lifetime τ_4 versus pore size



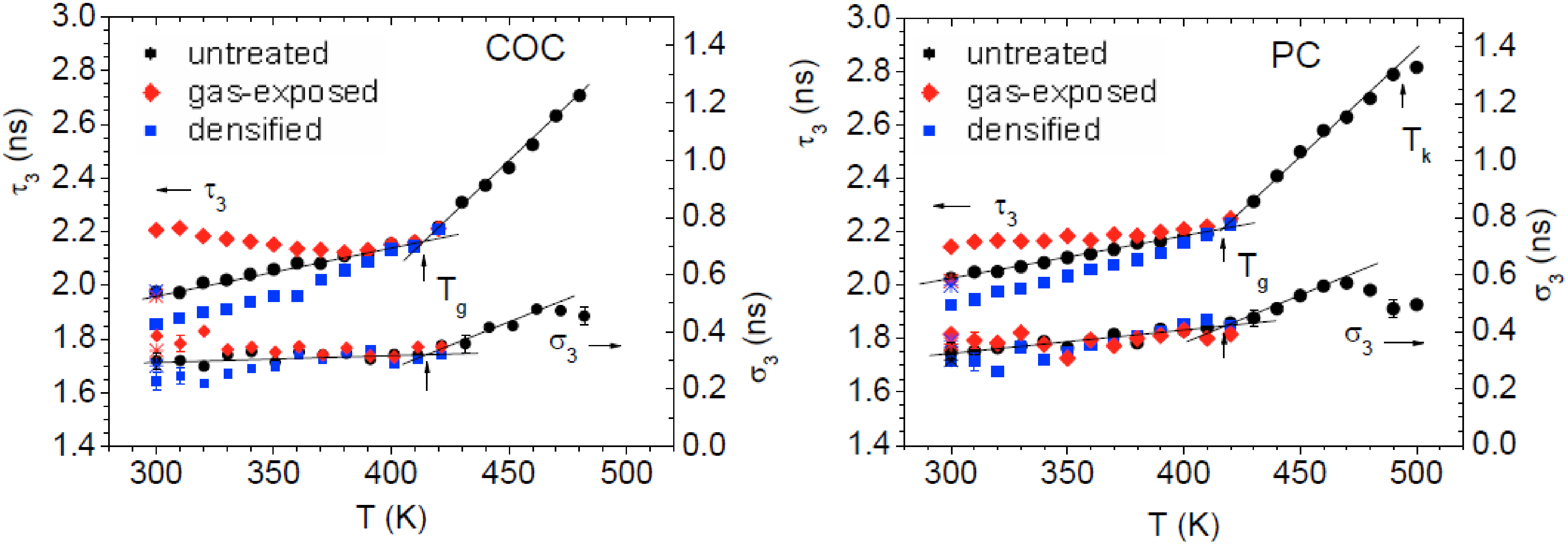
- we measured porous CPG glass in a broad pore size range



- 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.

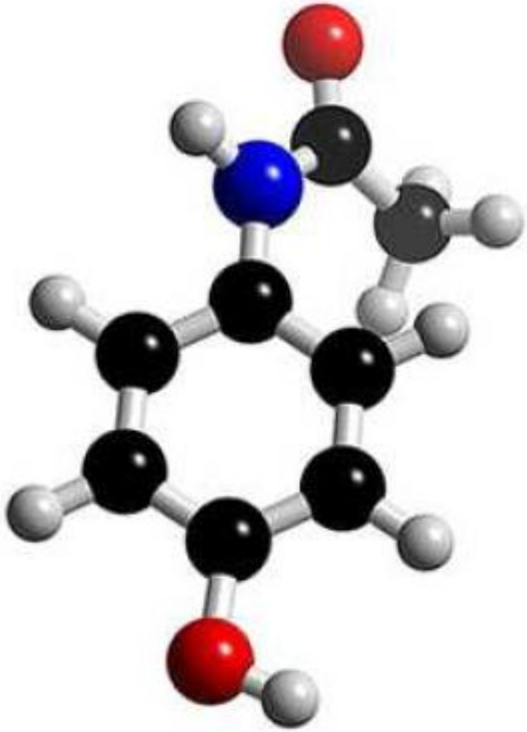
Open-volume in Polymers



The mean, τ_3, and the mean dispersion, σ_3, of *o*-Ps lifetimes as a function of temperature *T* for densified at 200 MPa (blue), gas-exposed (read) and untreated (black) COC and PC.

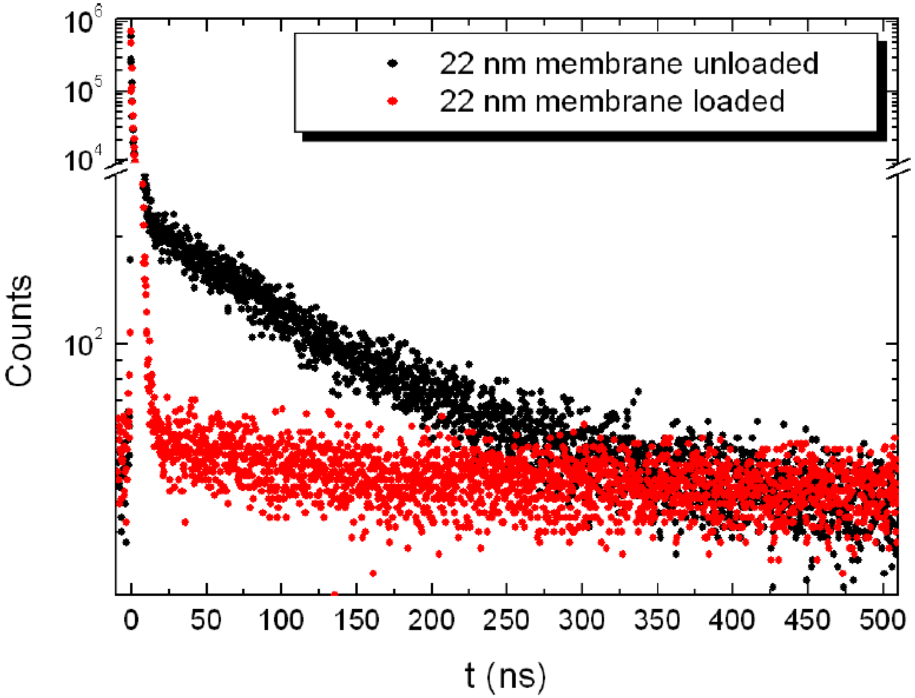
Tao, S. J. *J. Chem. Phys.* **1972**, *56*, 5499-5510. / Eldrup, M.; Lightbody, D.; Sherwood, J. N. *Chem. Phys.* **1981**, *63*, 51-58.

Loading of Mesopores by Drugs



- CPG membranes have been loading with Acetaminophen ($C_8H_9NO_2$) – also known as Paracetamol
- different pore sizes were studied
- filling by dropping membrane in hot melt of drug
- degree of filling can be studied with positrons

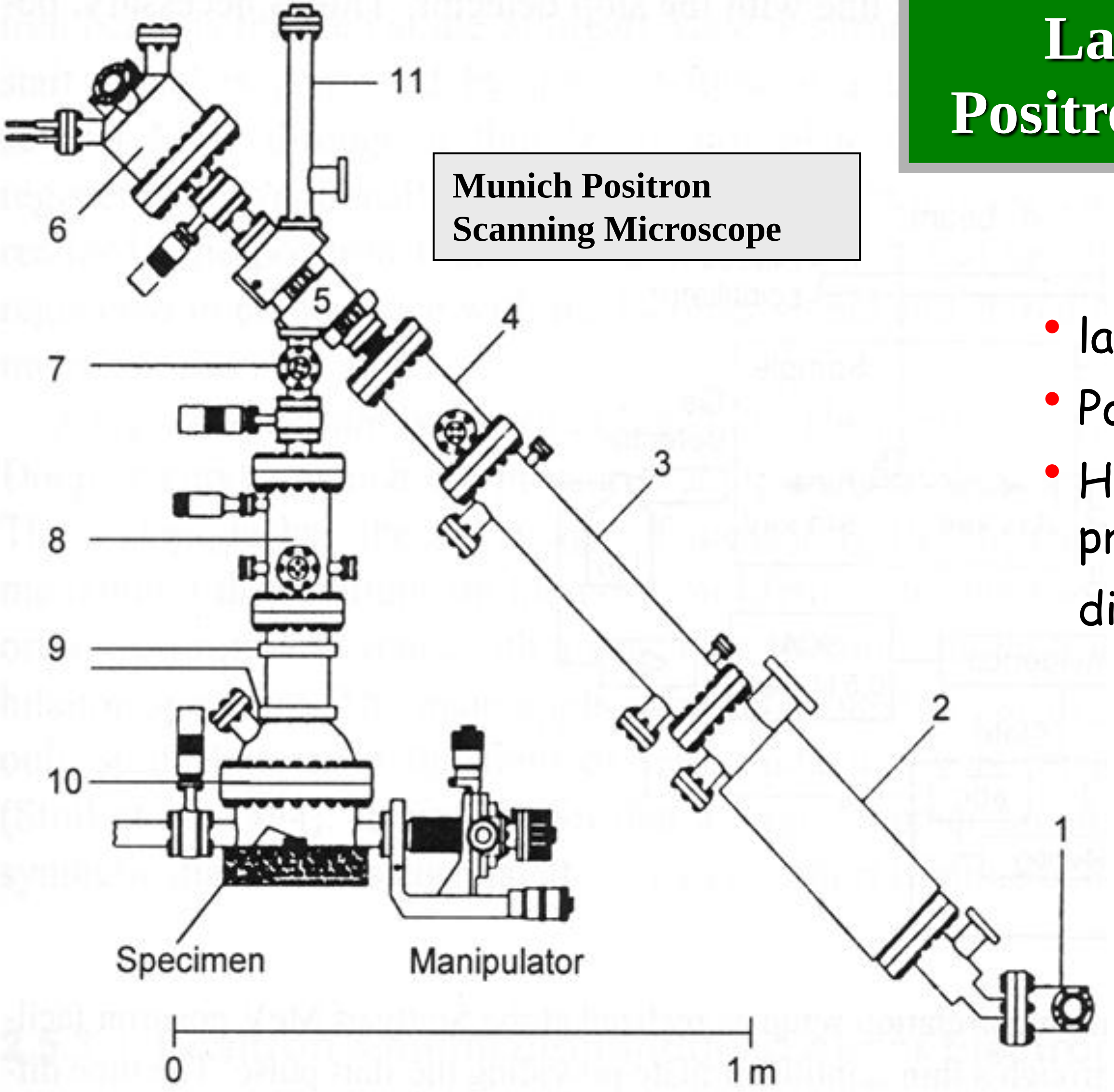
Loading of Mesopores by Drugs



- Filling almost complete for large pores (22 nm)
- lifetime spectra show much smaller intensity for long-lived component
- remaining pores are smaller

Probe	Membrandicke	vor Bel.: τ_4 und I_4		nach Bel.: τ_4 und I_4	
22 nm	300 μm	121 ns	6,2 %	111 ns	0,5 %
9,3 nm	300 μm	98 ns	7,8 %	58 ns	0,9 %
3 nm	500 μm	47 ns	11,7 %	52 ns	5,0 %
2,2 nm	300 μm	30,7 ns	14,3 %	19,7 ns	4,0 %

Lateral Resolution with Positron-Scanning-Microscope

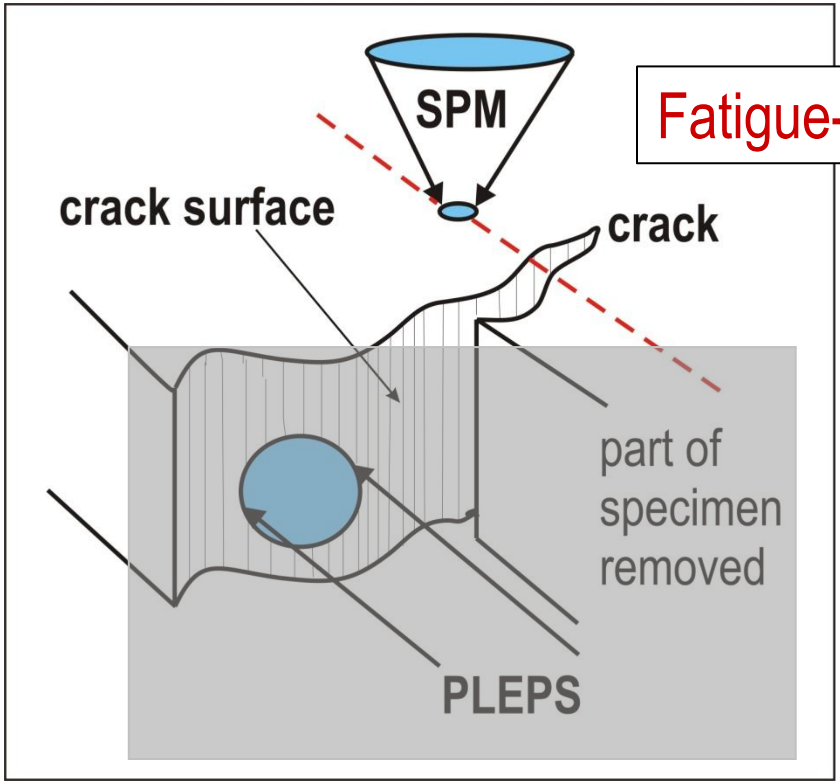


Munich Positron Scanning Microscope

- lateral resolution 2 µm
- Positron lifetime spectroscopy
- However lateral resolution principally limited by positron diffusion ($L_+ \approx$ 100nm)

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

SPM on top of cracked sample

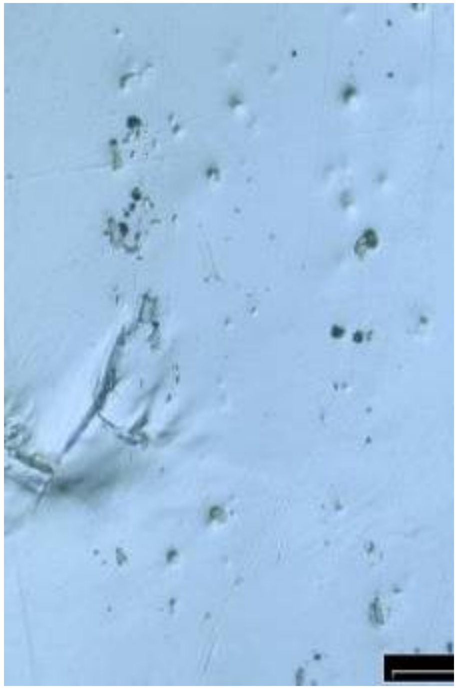


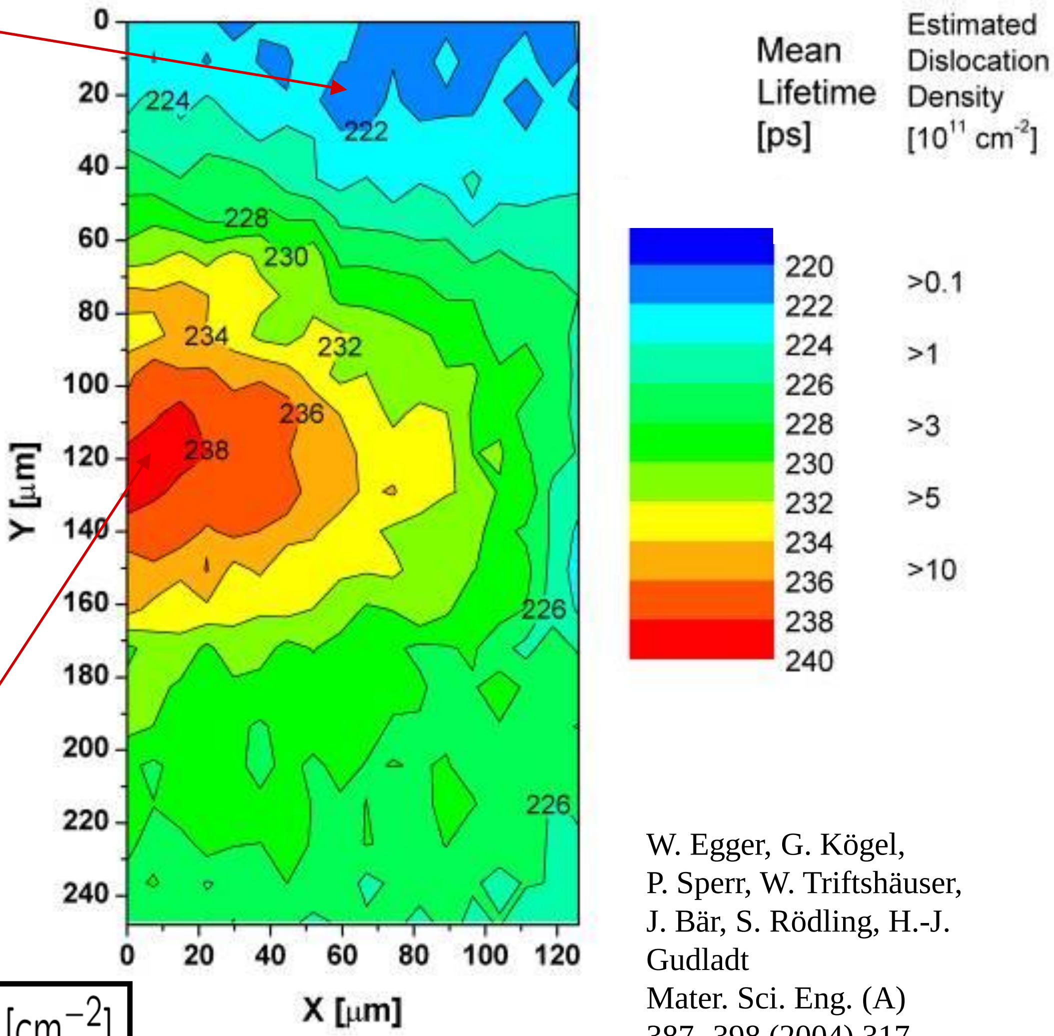
Fatigue-Crack in Al 6013

SPM: Lifetime-Image of Fatigue-Crack in Al 6013

resolution 5μm; step-size 10 μm

Trapping at Mg / Si-clusters!



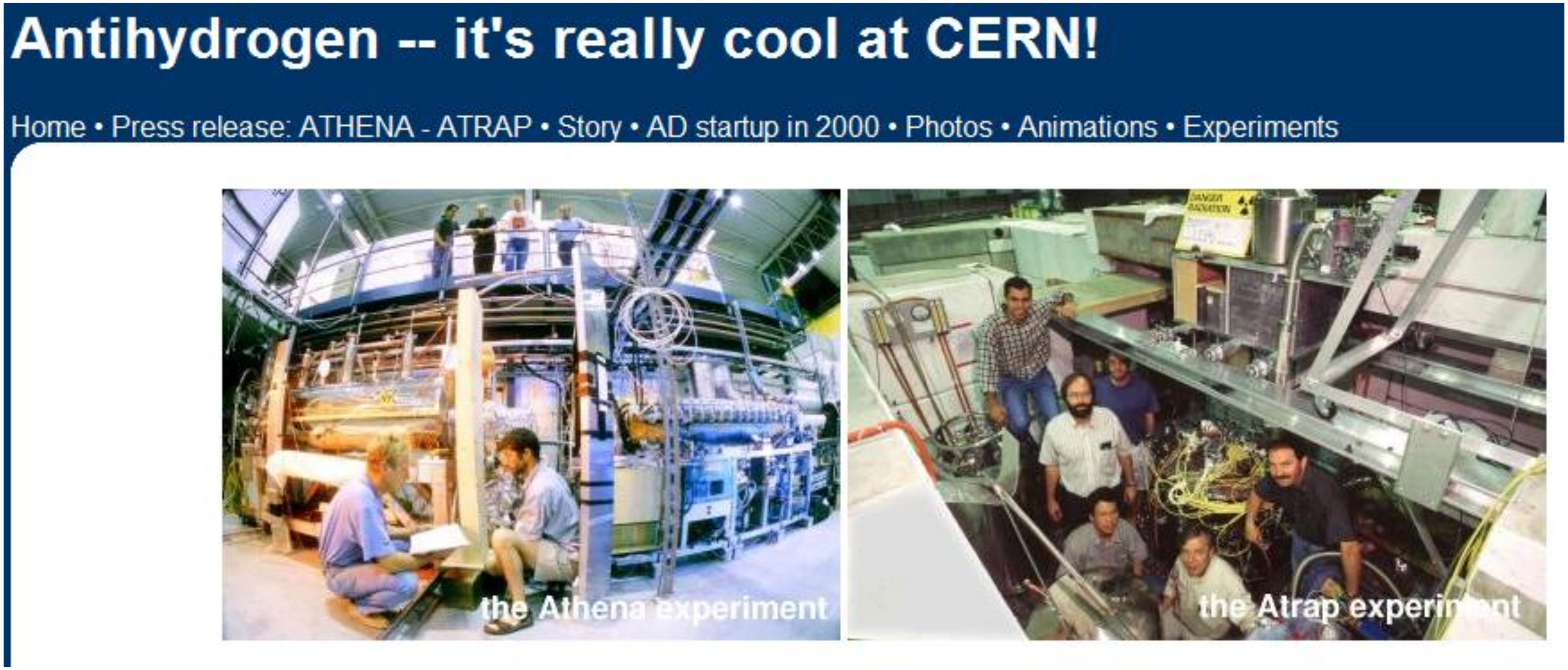


Only dislocations close to crack-tip !

$$c_{disl} = 4 \cdot 10^{11} (\tau - 220\,\mathrm{ps})/(240\,\mathrm{ps} - \tau)\ [\mathrm{cm}^{-2}]$$

W. Egger, G. Kögel,
P. Sperr, W. Triftshäuser,
J. Bär, S. Rödling, H.-J.
Gudladt
Mater. Sci. Eng. (A)
387- 398 (2004) 317

ATHENA, ATRAP and ASACUSA



Antihydrogen -- it's really cool at CERN!

Home • Press release: ATHENA - ATRAP • Story • AD startup in 2000 • Photos • Animations • Experiments

- Anti-Hydrogen experiments at CERN rely on 22-Na sources made in Faure at iThemba Labs
- aim: optical spectroscopy of Anti-Hydrogen-> looking for CPT violation

PRL **105,** 243401 (2010) PHYSICAL REVIEW LETTERS week ending 10 DECEMBER 2010

Synthesis of Cold Antihydrogen in a Cusp Trap

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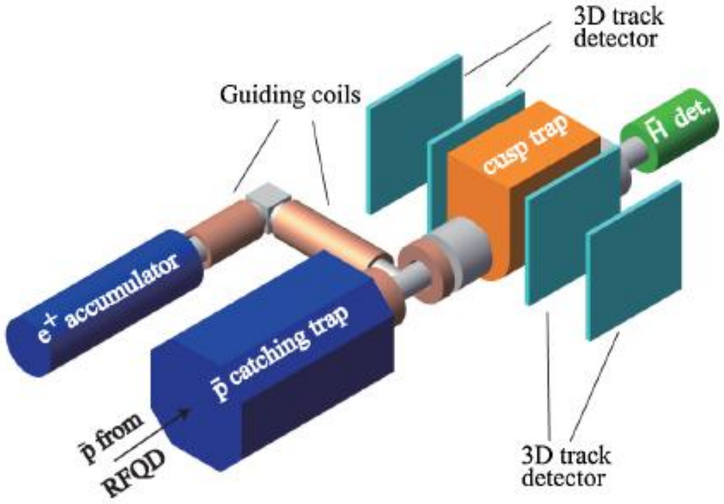
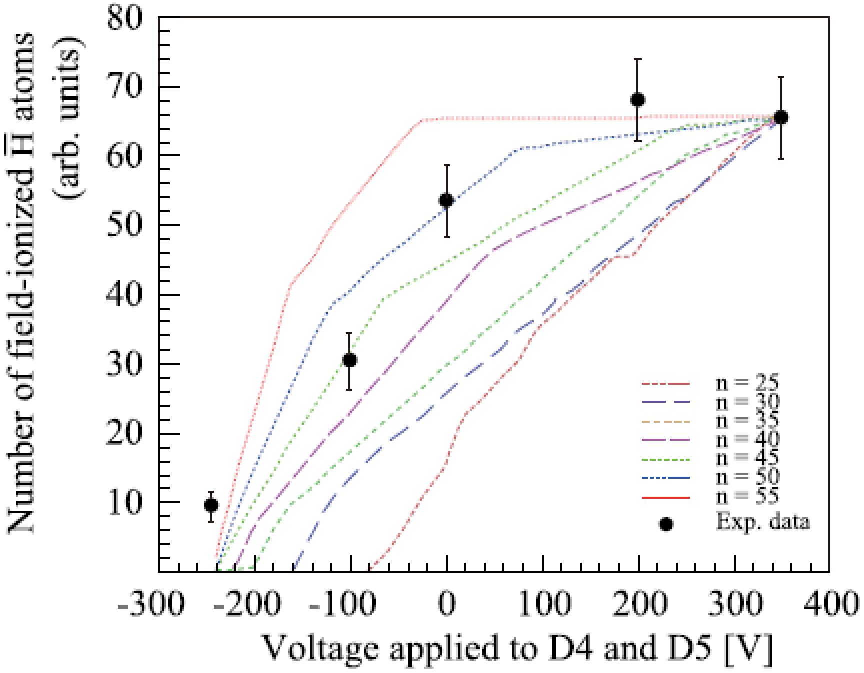


FIG. 2 (color online). A schematic drawing of the present experimental setup, which consists of the antiproton ($\bar{p}$) catching trap, the compact positron (e^+) accumulator, the cusp trap for antihydrogen ($\bar{H}$) synthesis, the 3D track detector, and the $\bar{H}$ detector downstream of the cusp trap.



Conclusions

Positrons are a unique tool for

- characterization of vacancy-type defects in crystalline solids
- embedded nano-particles (e.g. small precipitates)
- porosimetry
- intermolecular open-volume in Polymers

About 80 positron groups on all continents rely on 22-Na production at iThemba labs