Positron annihilation studies of defects in swift ion irradiated single crystals

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Outline

- **goals and means**
- positron annihilation (PA): basics, methods
- defects induced by irradiation with swift ions as seen by positron annihilation
- measurements on Kr and Bi irradiated sapphire single crystals
- measurements on Si, SiC and graphite
- comparison of vacancy defect creation in different materials

Our goals and means:

- Systematic studies on well-characterized samples irradiated under well-controlled conditions, to understand more details of defect creation by ion irradiation

  (Dubna)

- A combination of positron annihilation methods:

  -bulk lifetime and Doppler measurements

  (Budapest)

  -slow positron beam, Doppler-effect

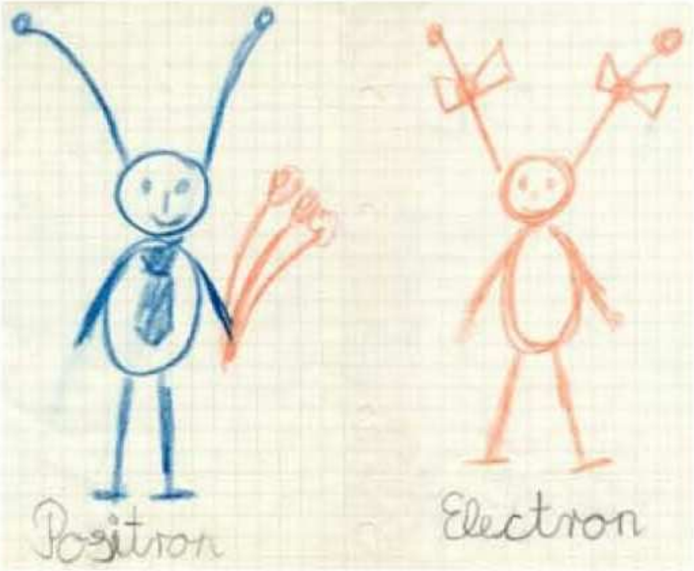
  (Coimbra)

  -slow positron beam, lifetime

  (Münich)

- Interpretation of results, joint understanding

WILL OUR EFFORT BE OF INTEREST AND USE?



Reserved Quantity

$$\rho(\bar{p}) = \text{const.} \sum_{j} |dr\ \exp(-i\bar{p}\bar{r})\cdot\Psi_j(\bar{r}).\ \Psi_+(\bar{r})|^2$$

(Independent Particle Model) j-electron state

Annihilation rate:

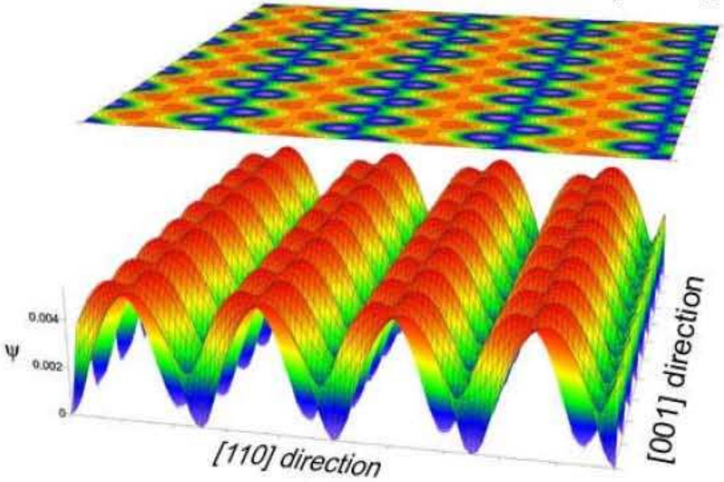
$$\lambda \sim \int_{\bar{p}} \rho(\bar{p})d\bar{p}$$

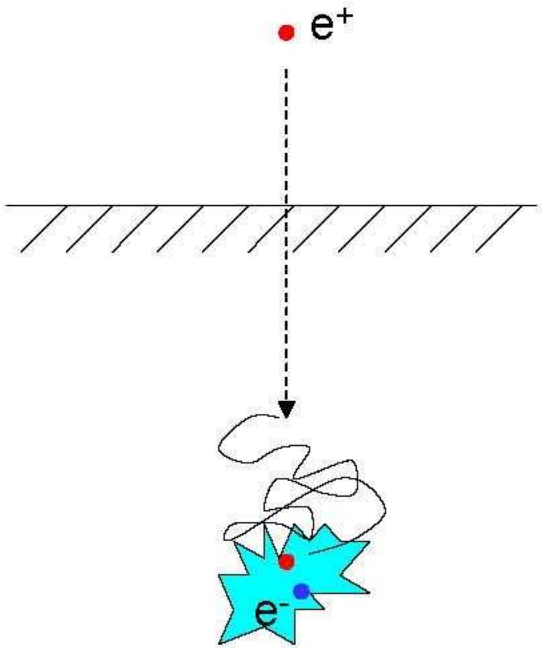
Lifetime:

$$\tau = \lambda^{-1}$$

Positron in condensed matter

- Thermalization
  - energy loss through electron/phonon excitation
  - 1 - 3 ps
  - Penetration depth ≈ E/ρ
- Diffusion
  - $L_+ \approx 100$ nm
  - Positron wave function in [110] plane of GaAs





- Annihilation
  - mainly with emitting of two γ-quanta

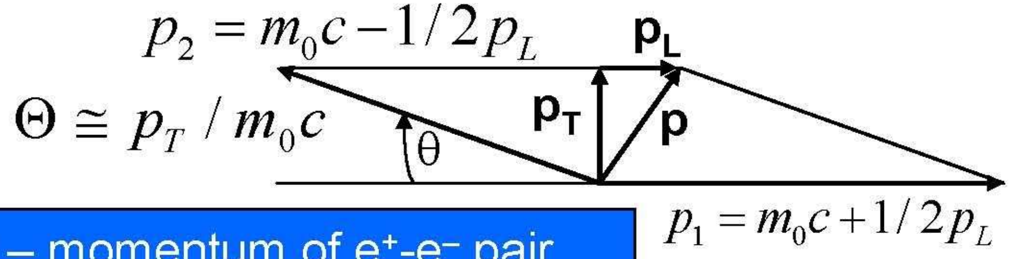
$$3\gamma / 2\gamma = 0.27\%$$

2γ-annihilation

- Sensitivity to electron momentum

energy and momentum conservation leads to

  - angular correlation of annihilation radiation
  - Doppler broadening of annihilation line



$$p_2 = m_0 c - 1/2\, p_L$$

$$\Theta \cong p_T / m_0 c$$

$$p_1 = m_0 c + 1/2\, p_L$$

p – momentum of e^+-e^- pair

p_1, p_2 – γ-quanta's momentum

- Sensitivity to electron density
  - Positron Lifetime Spectroscopy (PALS)

positron diffusion: $L_+ = \sqrt{D_+ \tau_b}$ during τ_b – positron bulk lifetime

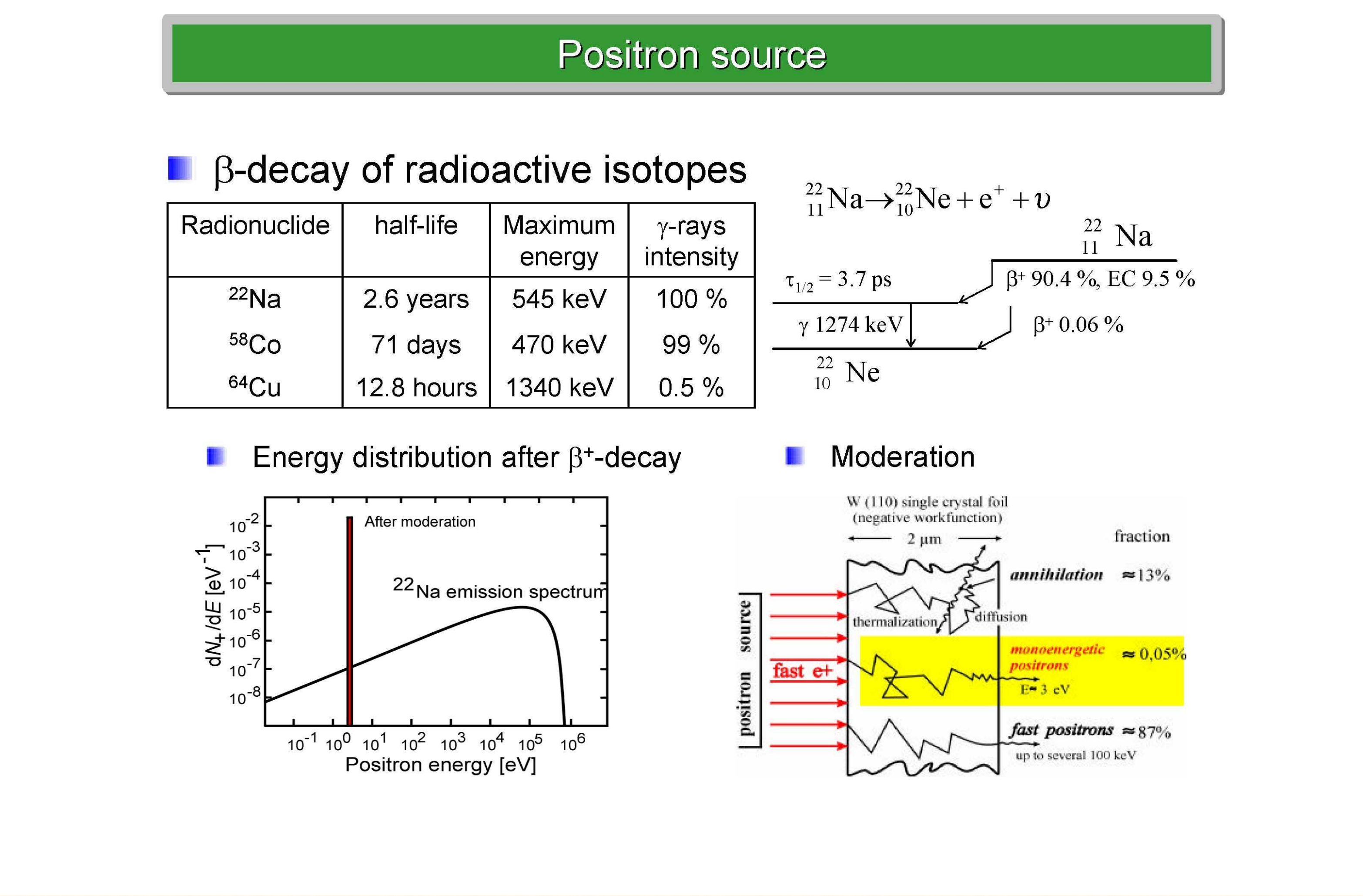
annihilation rate:

$$\lambda = 1/\tau_b = \pi \cdot r_0 \cdot c \int \psi_+(\mathbf{r}) \psi_-(\mathbf{r}) \gamma \, d\mathbf{r}$$

the lower the electron density is, the higher is the positron lifetime

Access to positrons:

pair creation, radioactive decay



Positron source

- β-decay of radioactive isotopes

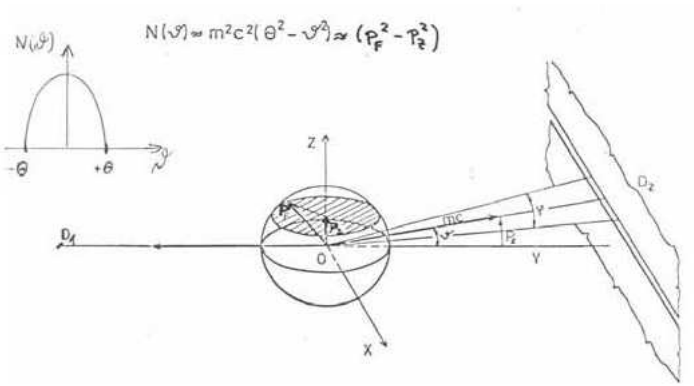
Radionuclide	half-life	Maximum energy	γ-rays intensity
^{22}Na	2.6 years	545 keV	100 %
^{58}Co	71 days	470 keV	99 %
^{64}Cu	12.8 hours	1340 keV	0.5 %

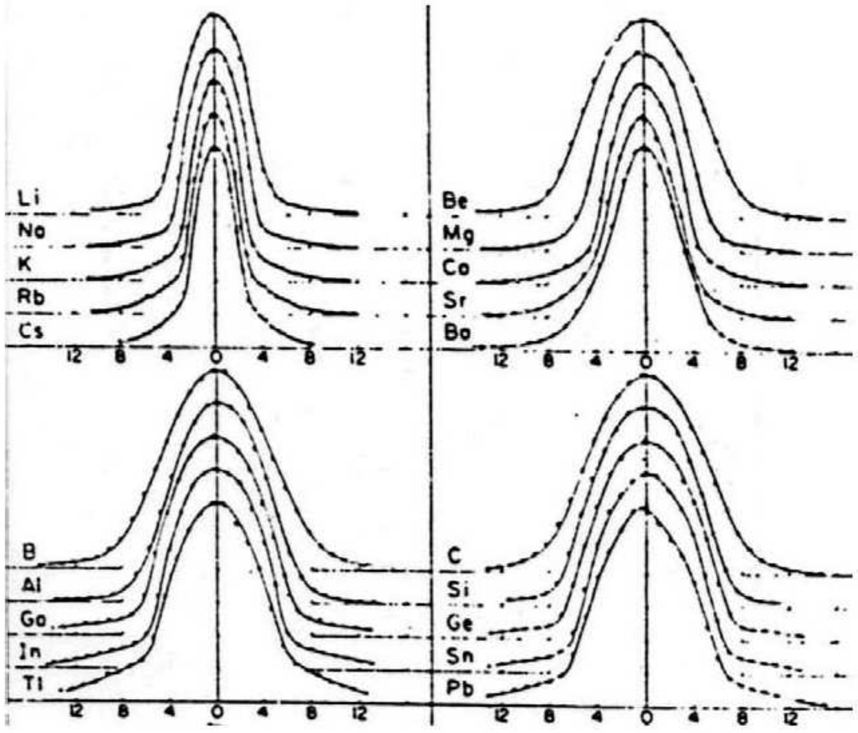
$$^{22}_{11}\mathrm{Na} \rightarrow ^{22}_{10}\mathrm{Ne} + e^{+} + \upsilon$$

- Energy distribution after β+-decay

- Moderation

2γ–angular correlation (ACAR) results

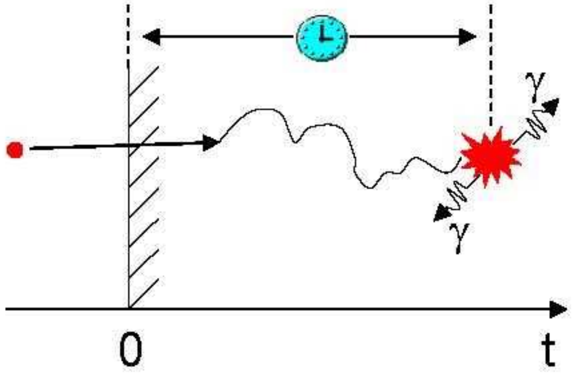




Positron Annihilation Lifetime Spectroscopy (PALS)

Technique

- γ-detection: scintillator + photomultiplier
- Time between positron penetration and it's annihilation in a sample is measured
- $3\text{-}6\times10^6$ are accumulated in a spectrum



Mathematics

- probability **n(t)** that e^+ is alive at time **t**:

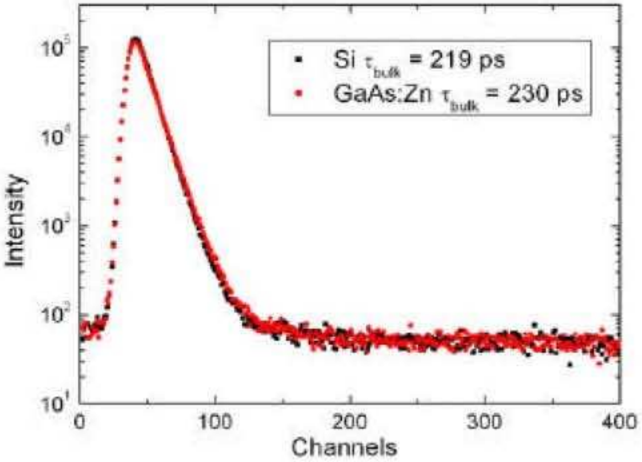
$$\boxed{\frac{\mathrm{d}n(t)}{\mathrm{d}t} = -\lambda\, n(t)} \quad n(0) = 1$$

  λ - positron annihilation rate
- Positron lifetime spectrum in bulk:

$$n(t) = e^{-\lambda_{bulk}\, t} \longrightarrow$$

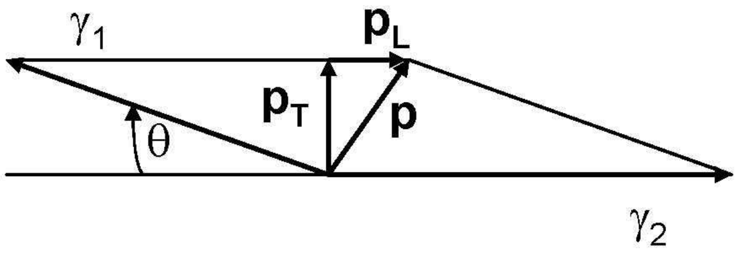
slope of the exponential decay

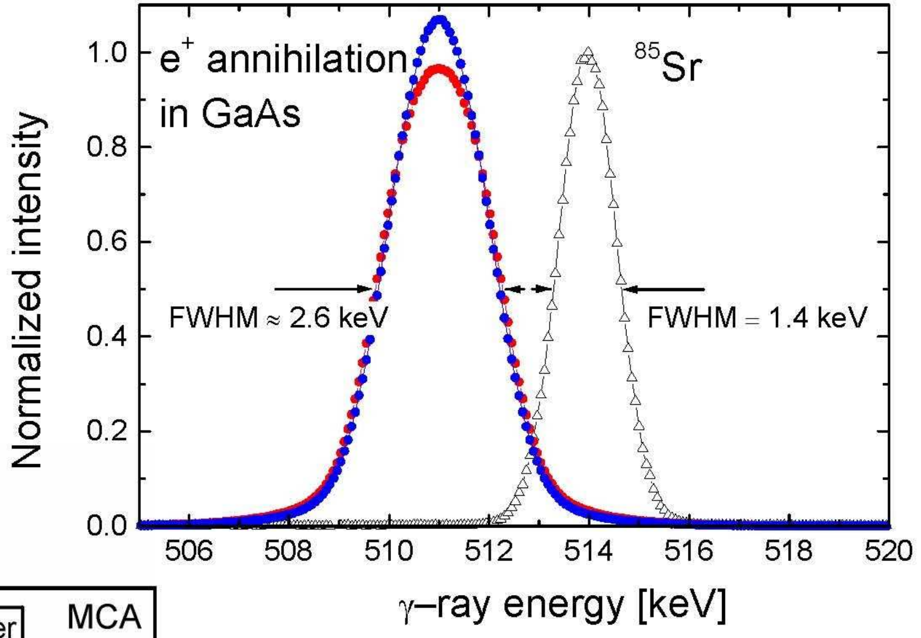
$$\lambda_{bulk} = \frac{1}{\tau_{bulk}}$$



Annihilation-Line Doppler broadening spectroscopy

- Doppler effect
  - electron momentum in propagation direction of 511 keV γ-ray leads to Doppler broadening of annihilation line

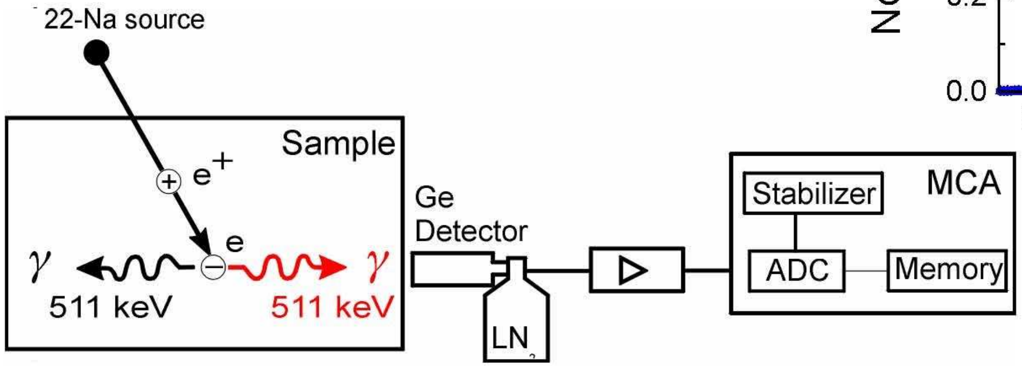




$E_1 - E_2 = p_L c$

E_1, E_2 – energy of γ quanta

- Technique



Annihilation-Line Doppler broadening spectroscopy

Data Treatment

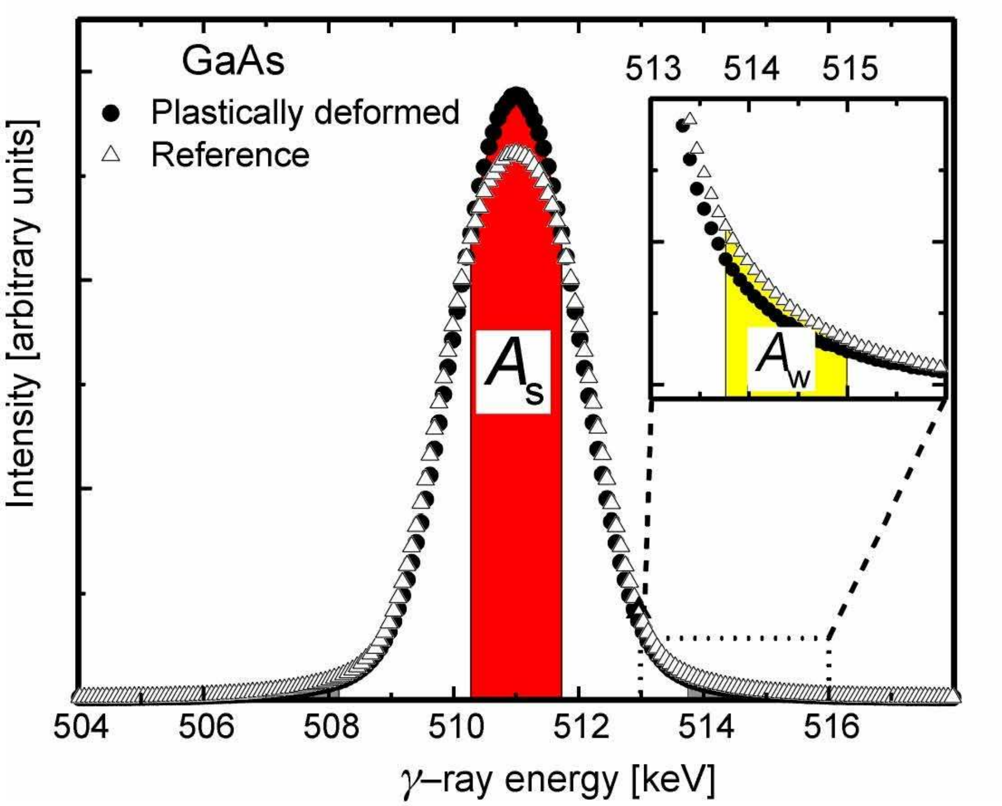
Line Parameters

- "Shape" parameter

$$S = \frac{A_s}{A_0}, \quad A_s = \int_{E_0-E_s}^{E_0+E_s} N_D\, dE$$

- "Wing" parameter

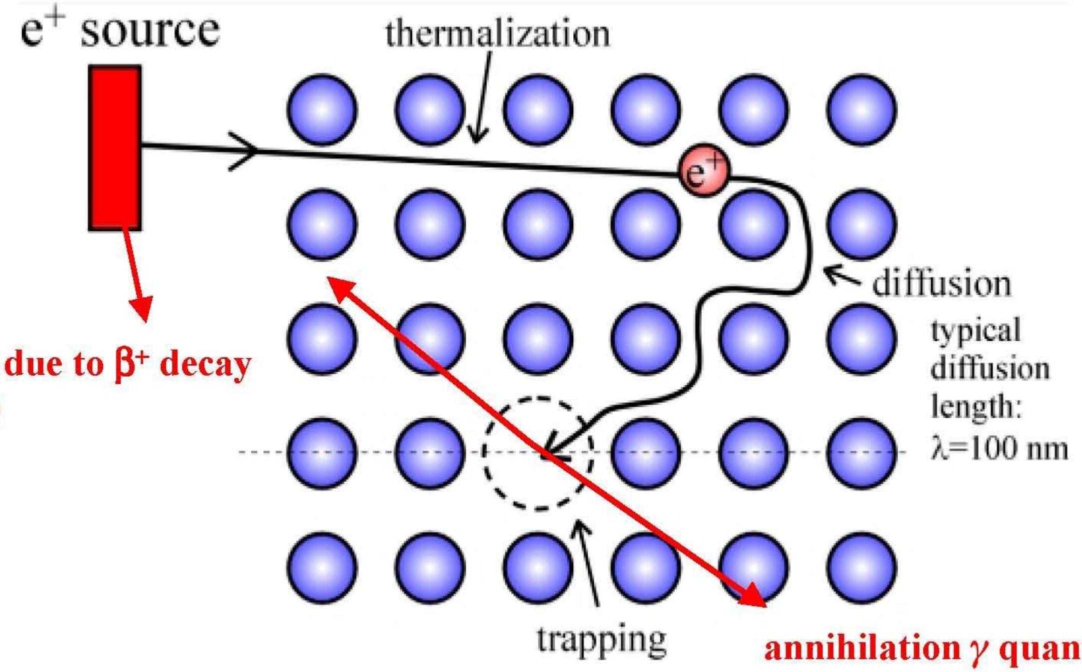
$$W = \frac{A_w}{A_0}, \quad A_w = \int_{E_1}^{E_2} N_D\, dE$$



Information

- Both S and W are sensitive to the concentration and defect type
- W is sensative to chemical surrounding of the annihilation site, due to high momentum of core electrons participating in annihilation

Positron trapping at crystal lattice defects

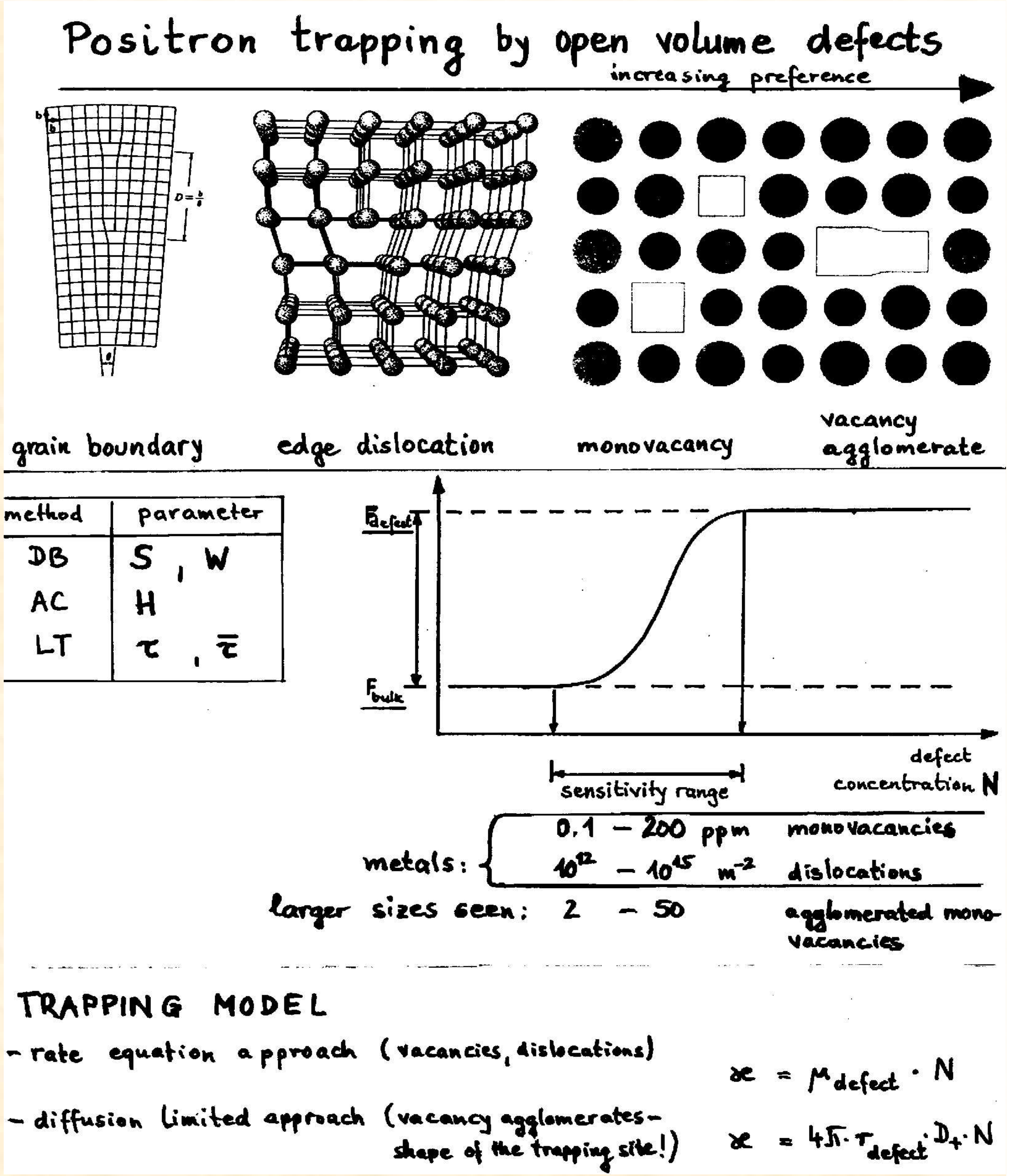


γ quantum due to β^+ decay (1.27 MeV)

annihilation γ quantum ($m_0c^2 = 511$ keV)

- positron wave-function can be localized in the attractive potential of a defect
- annihilation parameters change in the localized state (e.g. positron lifetime)
- defects can be detected (identification and quantification)

Trapping in general: Defectology



Positron trapping by open volume defects

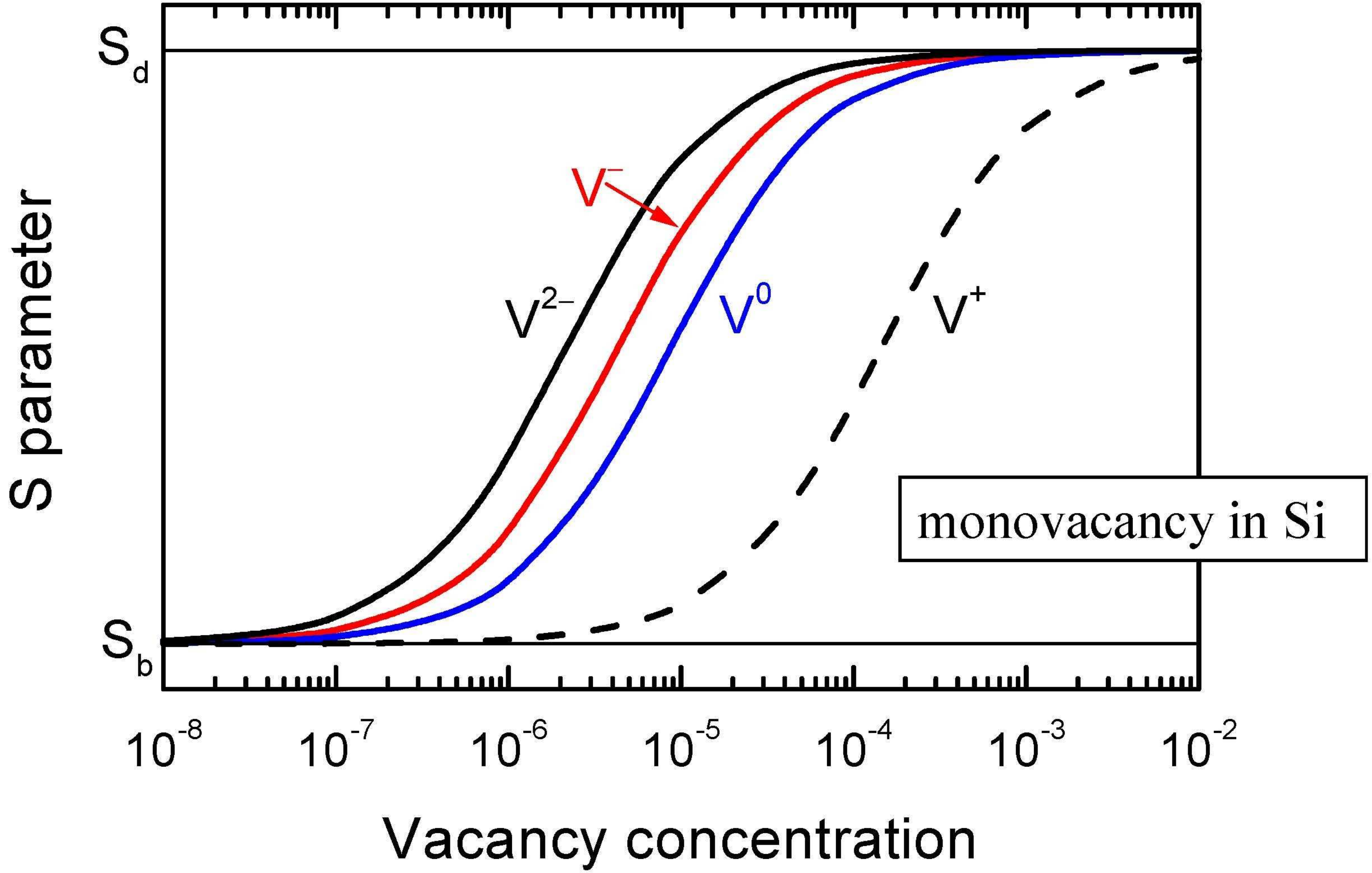
method	parameter
DB	S , W
AC	H
LT	τ , $\bar{\tau}$

metals:	0.1 – 200 ppm	monovacancies
	10^{12} – 10^{15} m^{-2}	dislocations
larger sizes seen:	2 – 50	agglomerated monovacancies

TRAPPING MODEL

- rate equation approach (vacancies, dislocations) $\varkappa = \mu_{defect} \cdot N$
- diffusion limited approach (vacancy agglomerates – shape of the trapping site!) $\varkappa = 4\pi \cdot r_{defect} \cdot D_+ \cdot N$

Sensitivity limit of positron annihilation

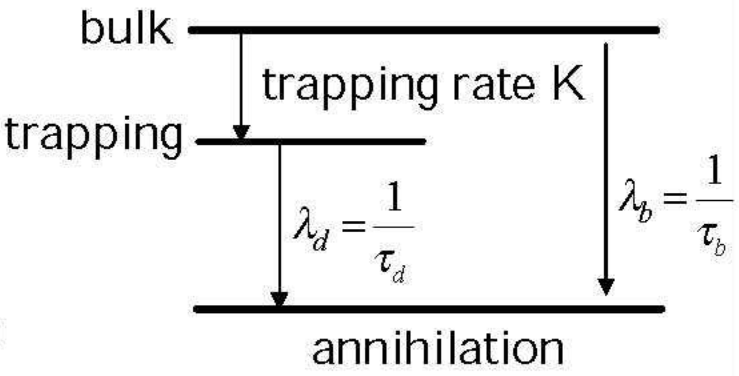


Positron Annihilation Lifetime Spectroscopy

Physics

one-defect trapping model

- annihilation from bulk with $\lambda_b=1/\tau_b$ s^{-1}
- trapping to vacancy-defect with **K** s^{-1}
- annihilation from the defect with $\lambda_d=1/\tau_d$
- two-component lifetime spectrum



bulk

trapping rate K

trapping

$$\lambda_d = \frac{1}{\tau_d}$$

$$\lambda_b = \frac{1}{\tau_b}$$

annihilation

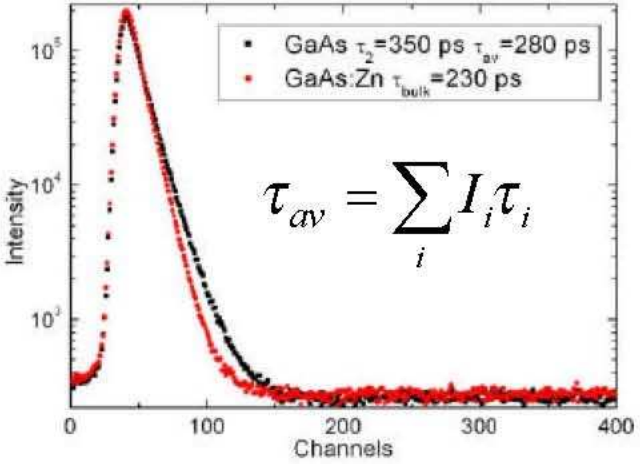
$$N(t) = I_1/\tau_1 \exp(-t/\tau_1) + I_2/\tau_2 \exp(-t/\tau_2)$$

Information

- vacancy type (mono-, di-, vacancy cluster)

  τ_2 – reflects the electron density
- defect concentration C

$$K = \frac{I_2}{I_1}\left(\frac{1}{\tau_b} - \frac{1}{\tau_2}\right) \approx C$$

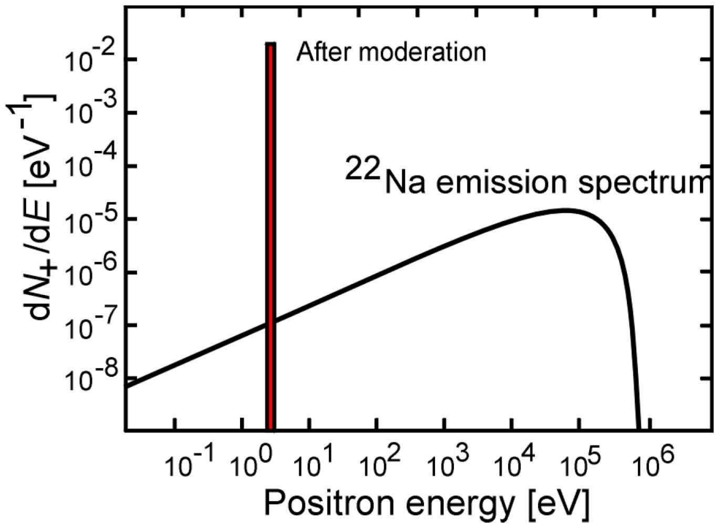


$$\tau_{av} = \sum_i I_i \tau_i$$

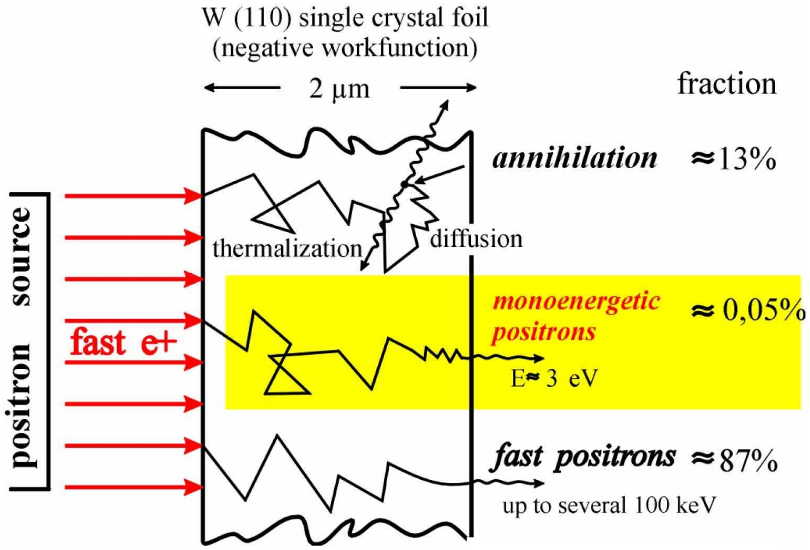
Monoenergetic positrons obtained by moderation

- semiconductor technology: thin layers (epitaxy, ion implantation)
- broad energy distribution due to β^+ decay
- some surfaces: negative workfunction ⇒ moderation (but rather inefficient)

Energy distribution after β^+ decay

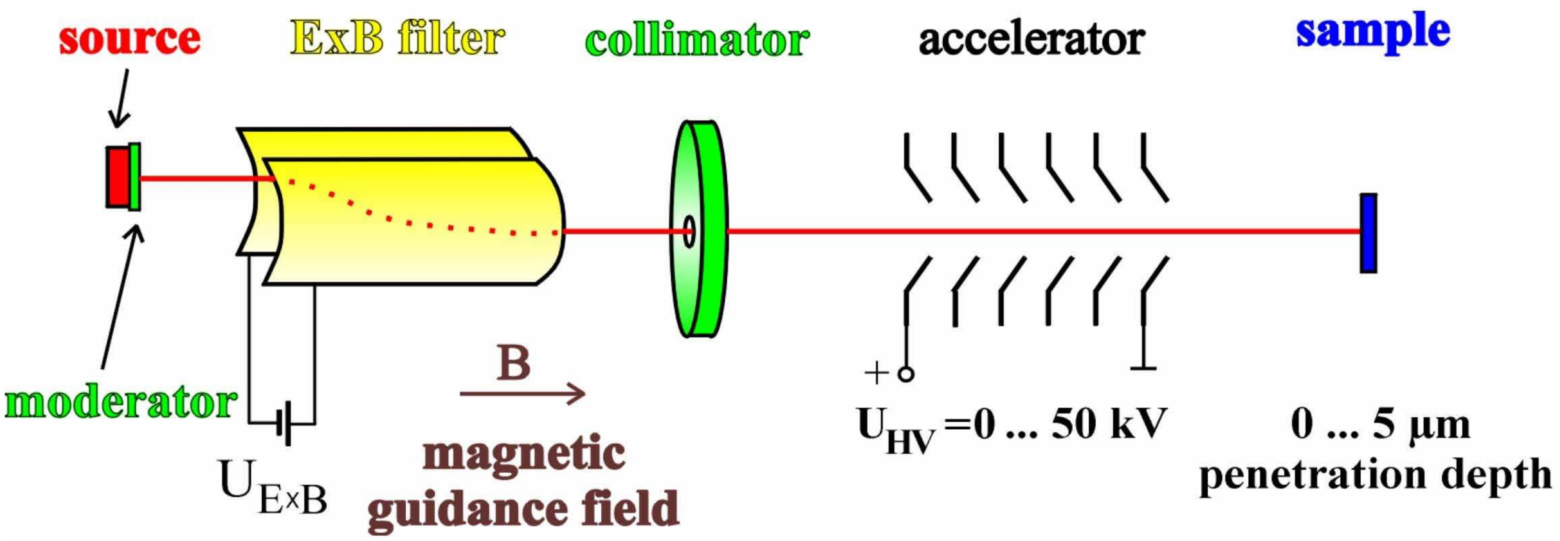


Effect of moderation

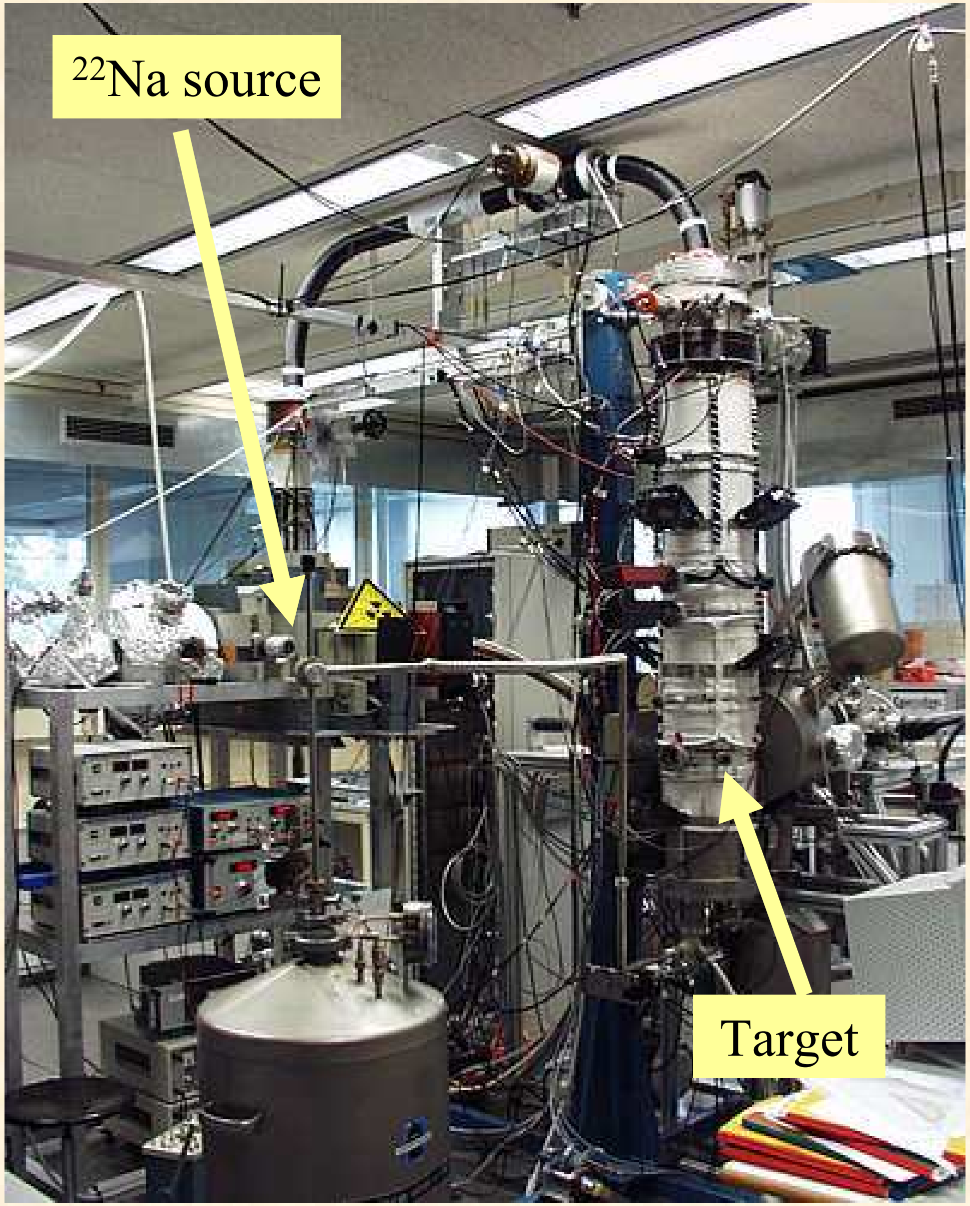


Conventional positron beam technique

- positron beam can be formed using mono-energetic positrons
- often: magnetically guided for simplicity



- defect studies by Doppler-broadening spectroscopy
- characterization of defects only by line-shape parameters or positron diffusion length
- for positron lifetime spectroscopy: beam can be bunched



Pulsed slow positron beam in Munich

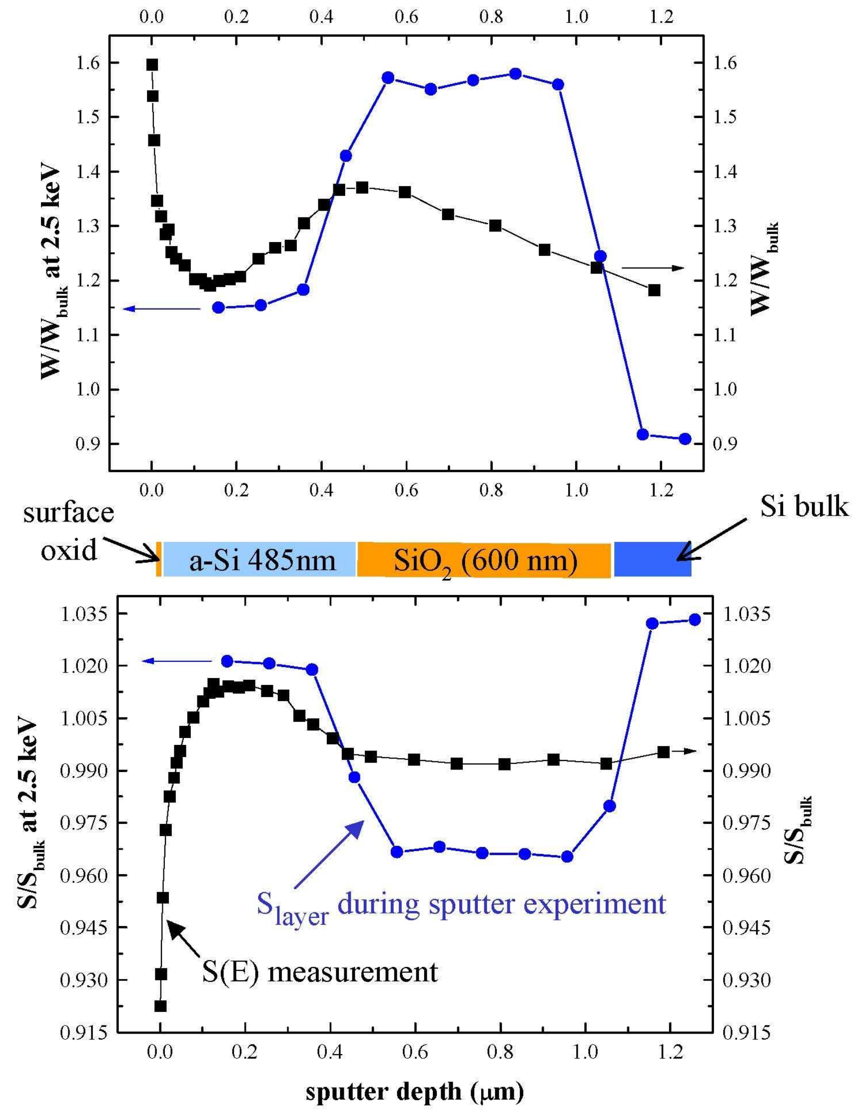
50 MHz pulsing rate

240 ps FWHM time resolution

80-540 K sample temperature

typically 400 cps counting rate

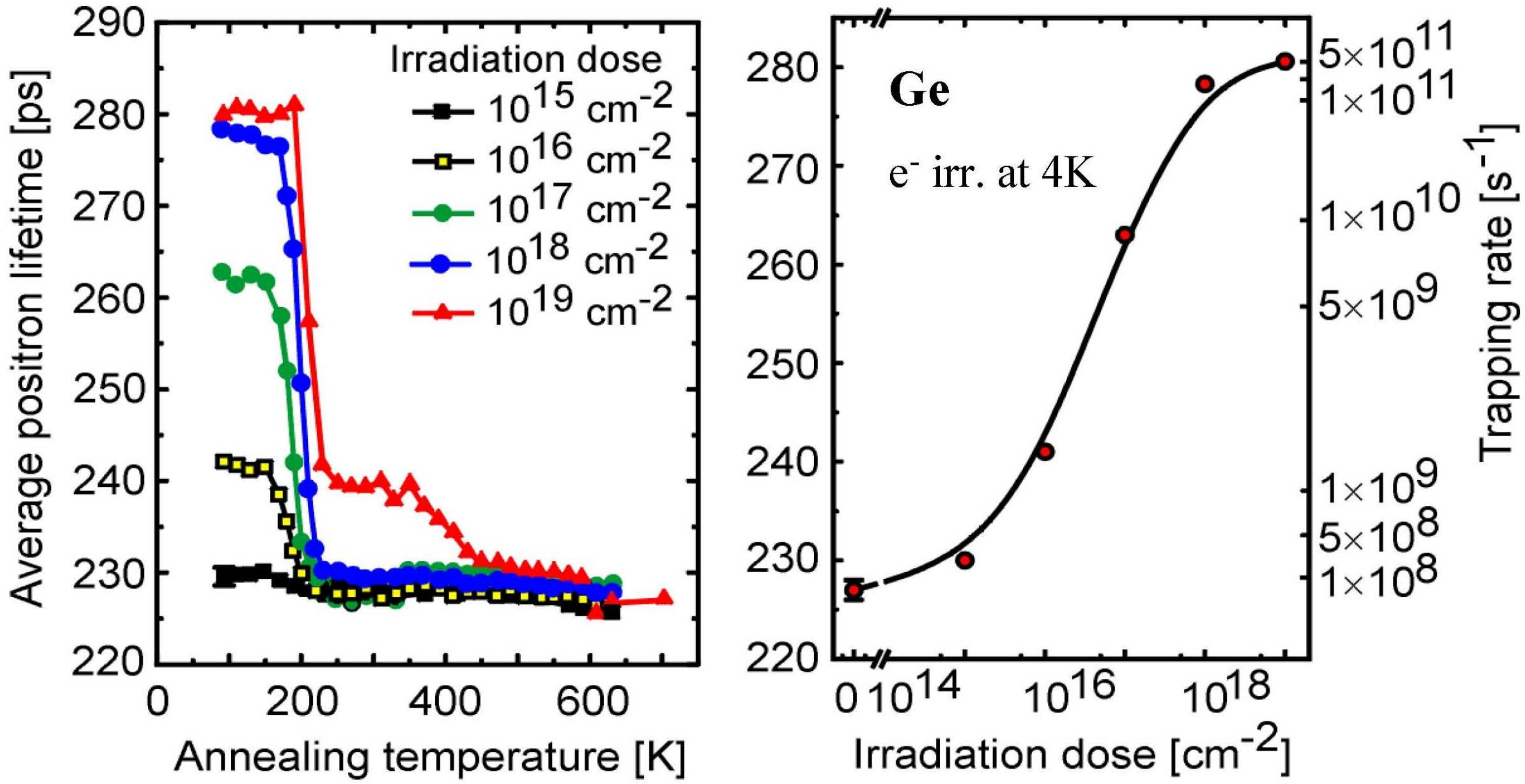
Annihilation parameters as function of depth



- annihilation parameters are taken in a suitable depth after each sputtering step
- e^+ energy choosen so that:
  - must be no influence of surface
  - still sharp e^+ implantation profile
- annihilation parameters of all layers are precisely obtained
- important especially for deep layers
- depth resolution is limited by e^+ diffusion, not by implantation profile

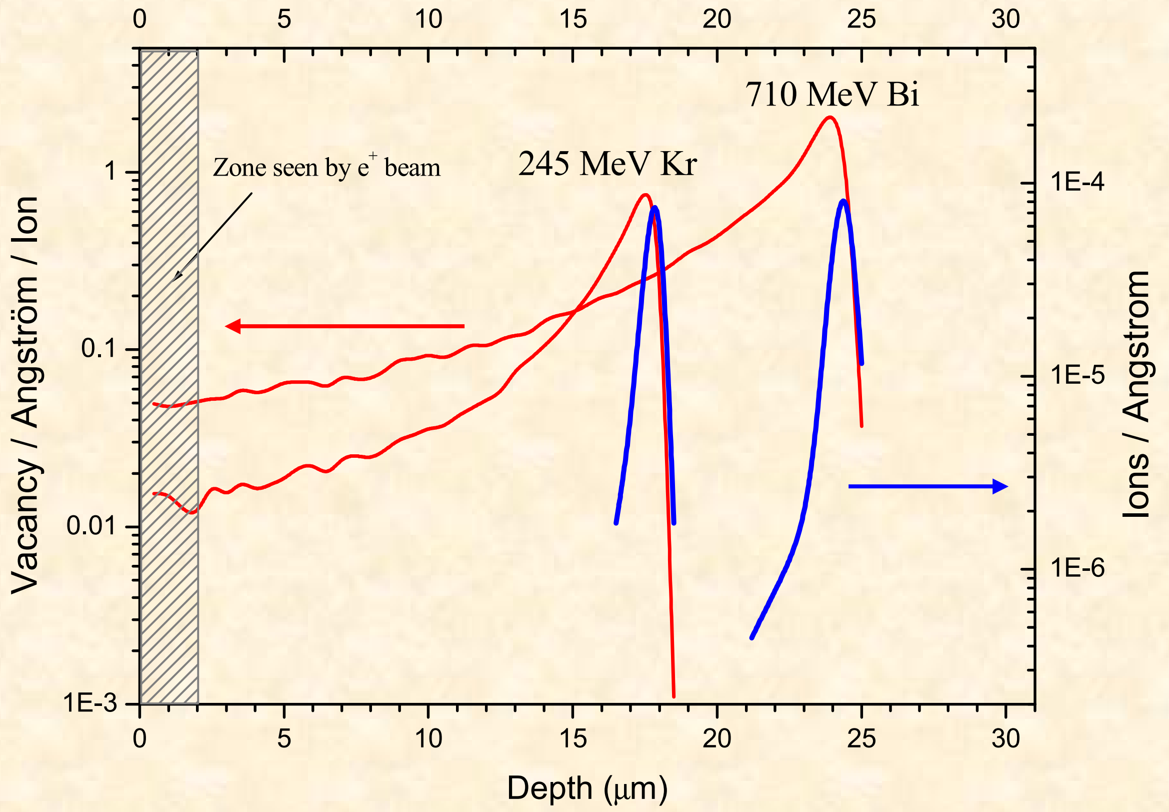
Defects in electron-irradiated Ge

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



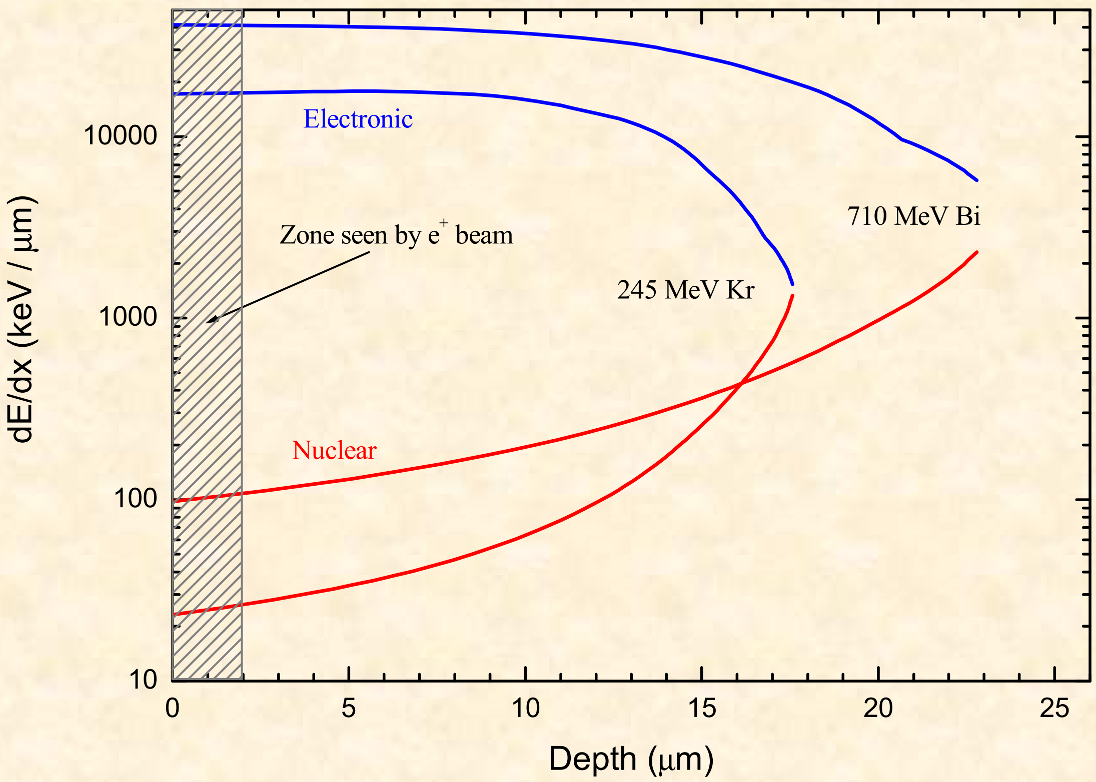
(Polity et al., 1997)

Vacancy and ion profiles compared with the zone probed by positrons in irradiated sapphire

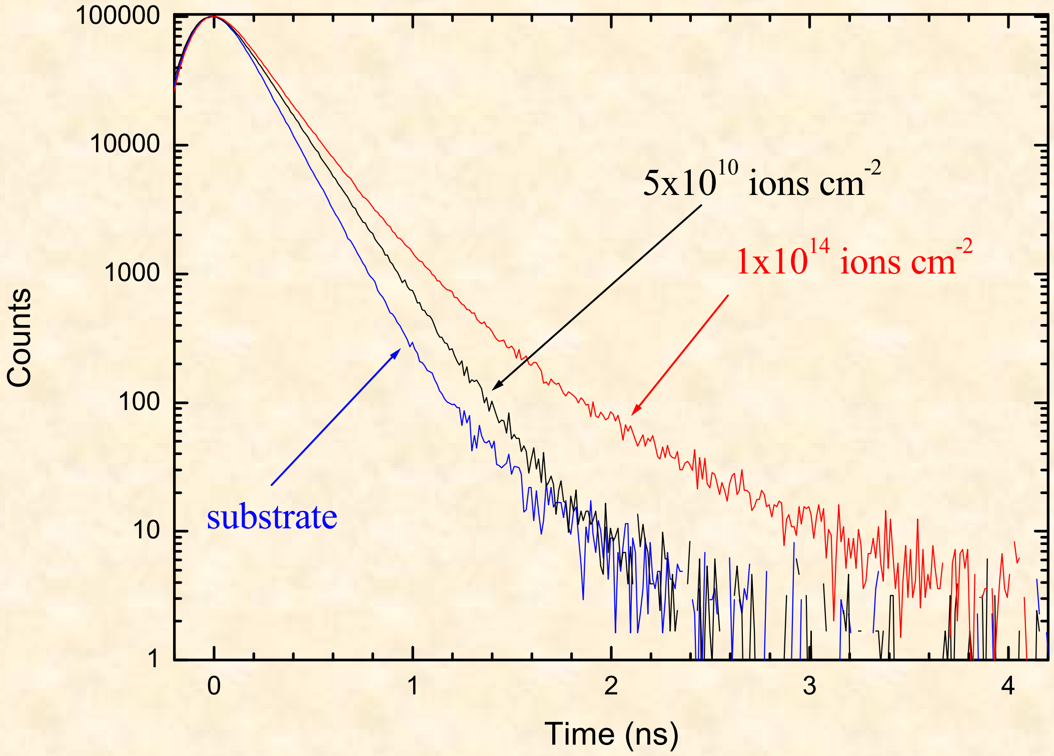


positrons sample the first part of the implantation profile

Electronic and nuclear stopping power vs. depth in irradiated sapphire



Lifetime spectra in irradiated sapphire (at approx. 2 μm depth)



different lifetime values:

- in the substrate (145 ps)

  → bulk annihilation only

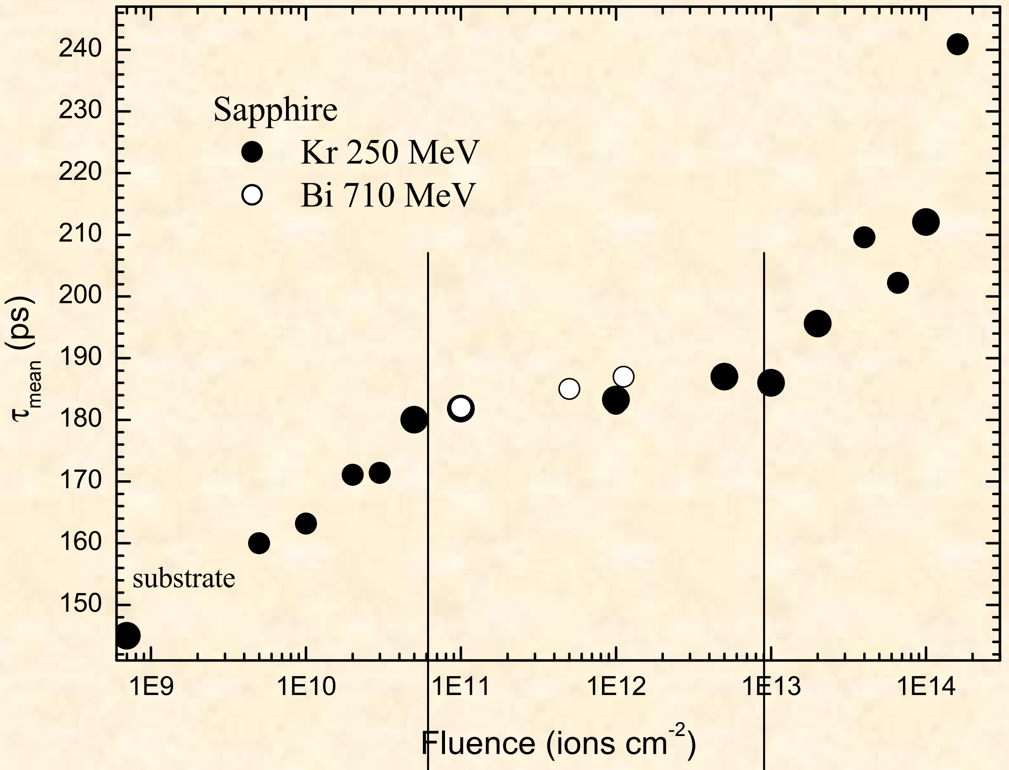
- at lower fluence (185 ps)

  → bulk + monovacancies

- at higher fluence (185 ps + 500 ps)

  → bulk + monovacancies
  + larger voids

Mean lifetime vs. fluence in irradiated sapphire

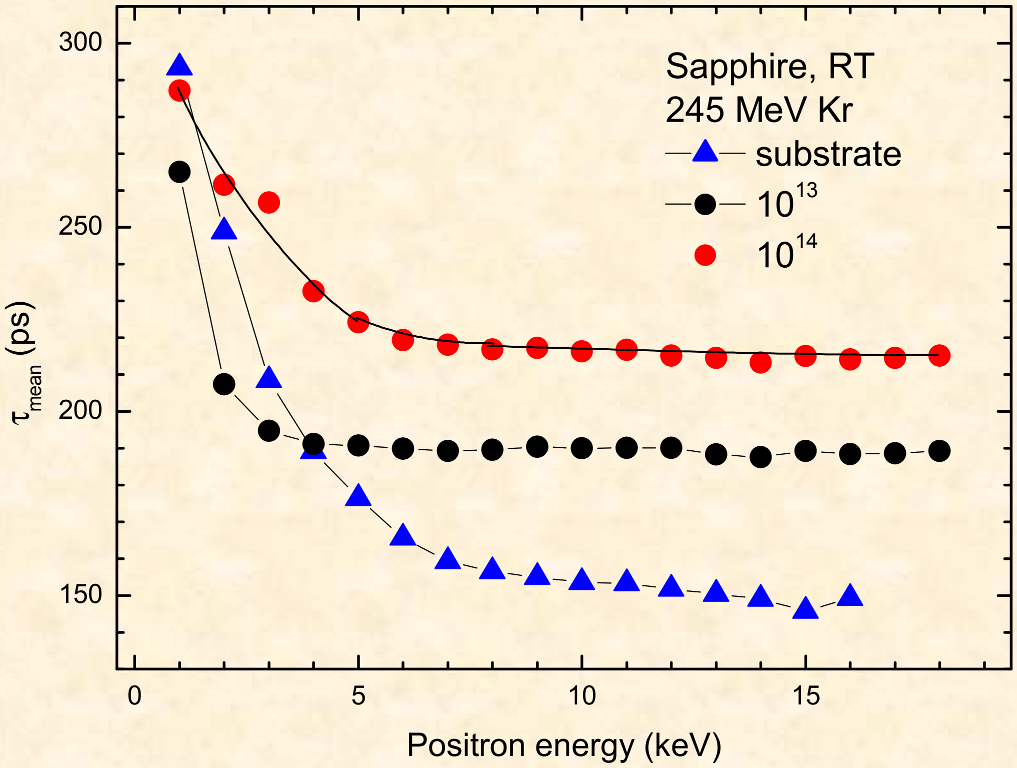


trapping in vacancies

saturated trapping in vacancies

trapping in larger defects (500 ps)

Mean positron lifetime vs. positron energy in irradiated sapphire



positron diffusion length: decrease at high fluence?

→ lower trap (defect) concentration?

Vacancy concentration in sapphire after Kr irradiation with 5×10^{10} ions cm^{-2} fluence

•estimated Al vacancy concentration from TRIM (only elastic processes): 3.5×10^{16} displacements cm^{-3}

•nearly saturated positron trapping (as found) is highly unlikely at this dose

•found: vacancy with 186 ps lifetime → monovacancy, most likely V_{Al} (V_O may not form positron traps)

Vacancy concentration in sapphire after Kr irradiation with $5\text{x}10^{10}$ ions cm^{-2} fluence

- quantitative estimate:
  the positron trapping coefficient is approximately

$$\mu = {}^{1}\!/_{\tau_b C} \frac{\bar{\tau} - \tau_b}{\tau_d - \bar{\tau}} = 4 \times 10^{-6} \quad \text{cm}^3\text{s}^{-1}$$

(Assuming τ_b=145 ps bulk lifetime, τ_d=186 ps defect lifetime, τ=180 ps mean lifetime and 10^{16} cm^{-3} vacancy concentration.)

this value would be unusually high

→ vacancy creation by electronic energy transfer is dominant

in the case of Kr irradiation dE/dx=17 keV/nm

??? Literature: threshold for defect creation through inelastic process is estimated to dE/dx=20 keV/nm (swift ^{238}U)

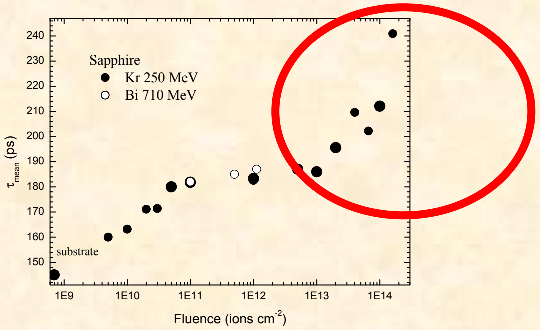
Larger positron traps in sapphire after Kr irradiation with higher than $2x10^{13}$ ions cm^{-2} fluence

spectrum decomposition:

500 ps positron lifetime

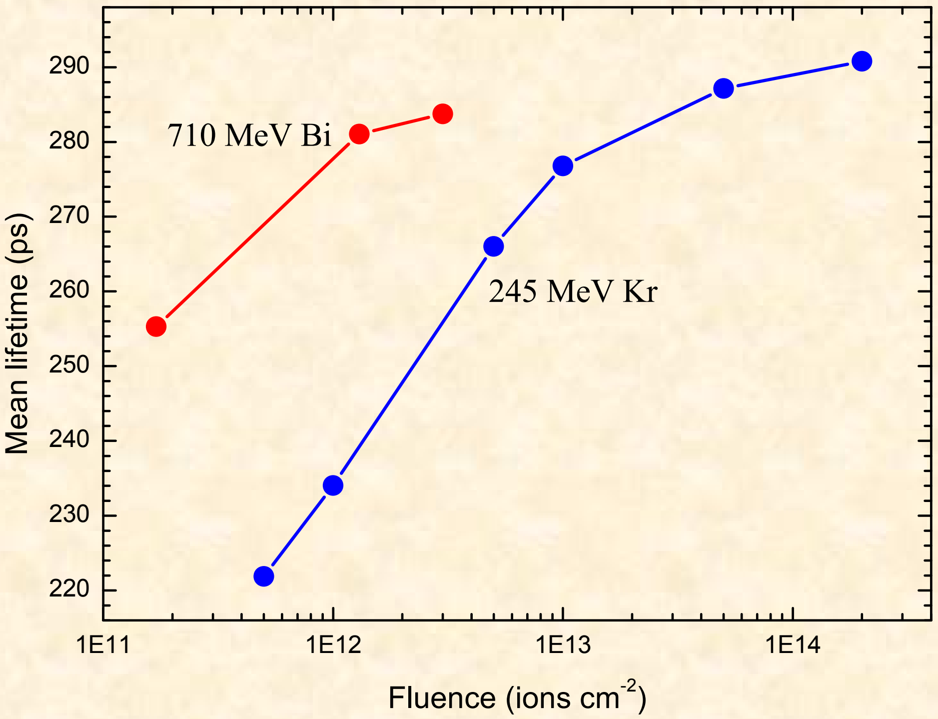
→larger defects (voids)

in the overlapping defect cascades



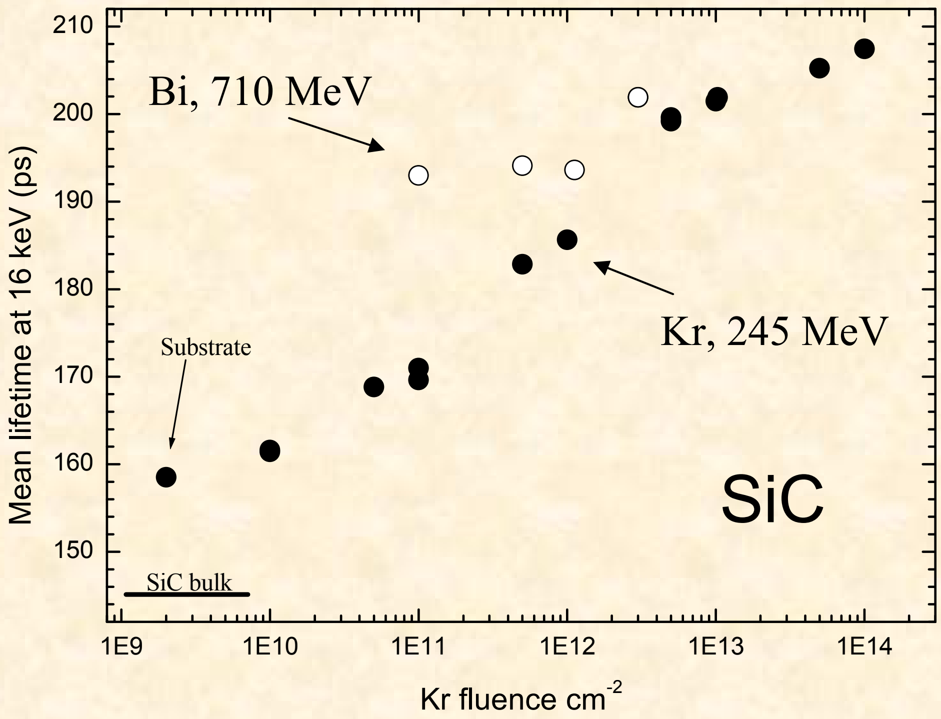
further studies to determine if amorphisation occurs

Mean positron lifetime vs. ion fluence in irradiated Si

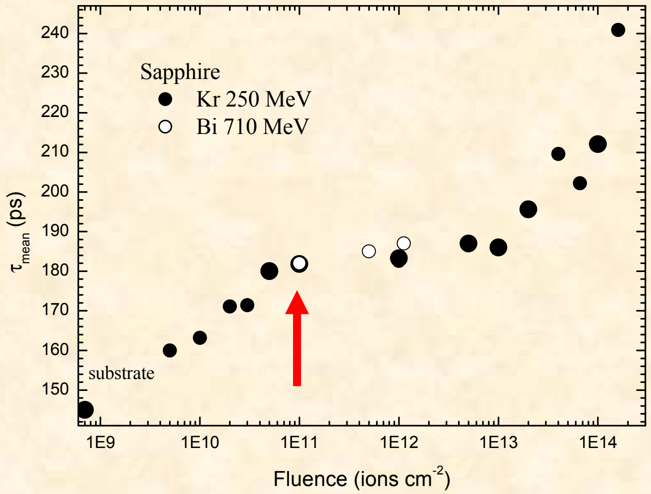


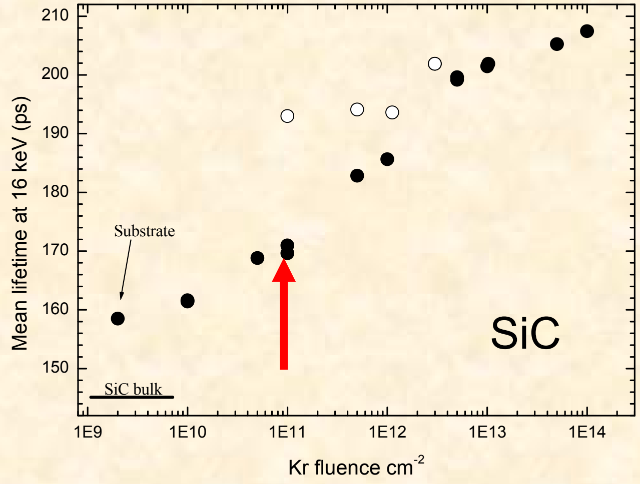
positron trap with 300 ps lifetime → Si divacancies are dominant traps (monovacancy anneals out below RT)

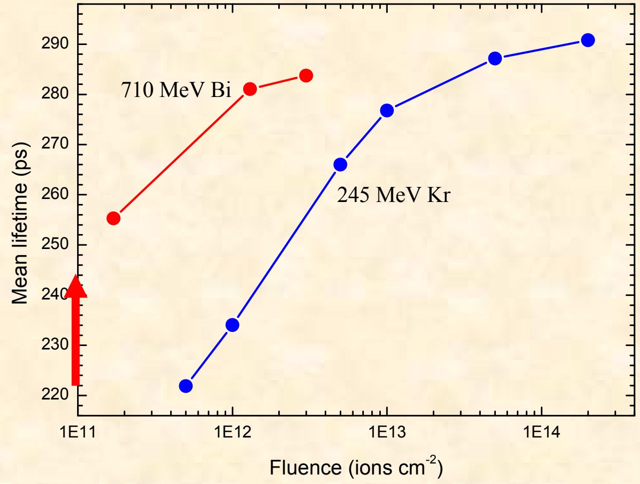
Mean lifetime vs fluence in irradiated 6H SiC



- positron trap with 225 ps lifetime → seems to indicate that V_{Si}-V_C divacancies are dominant traps

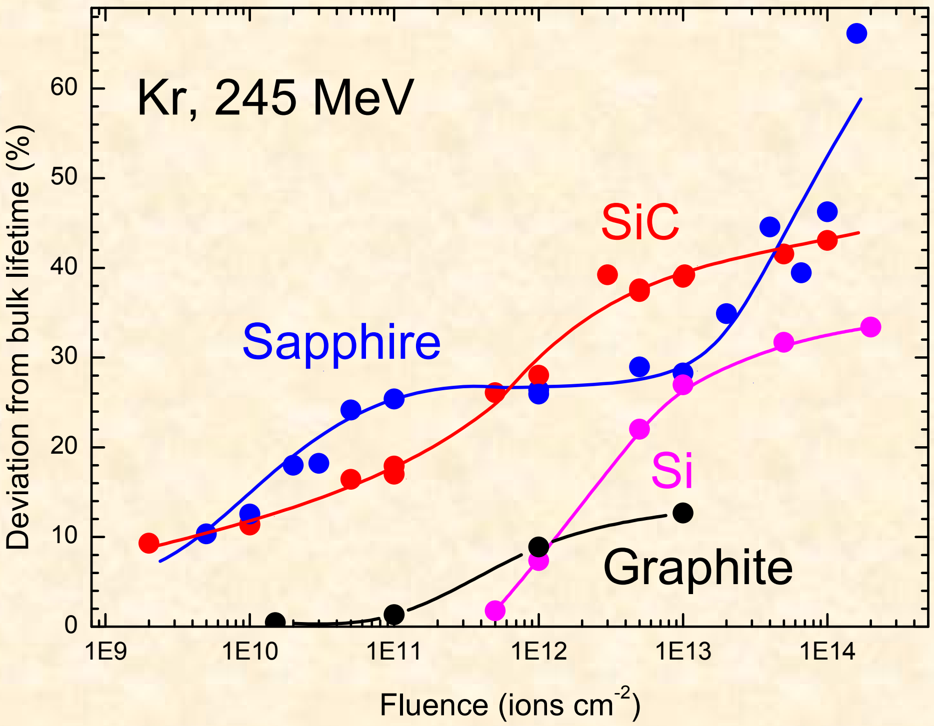






Si, SiC, sapphire comparison

Comparison between different single crystals irradiated with Kr ions at 245 MeV energy



sapphire: high vacancy concentration at low dose already

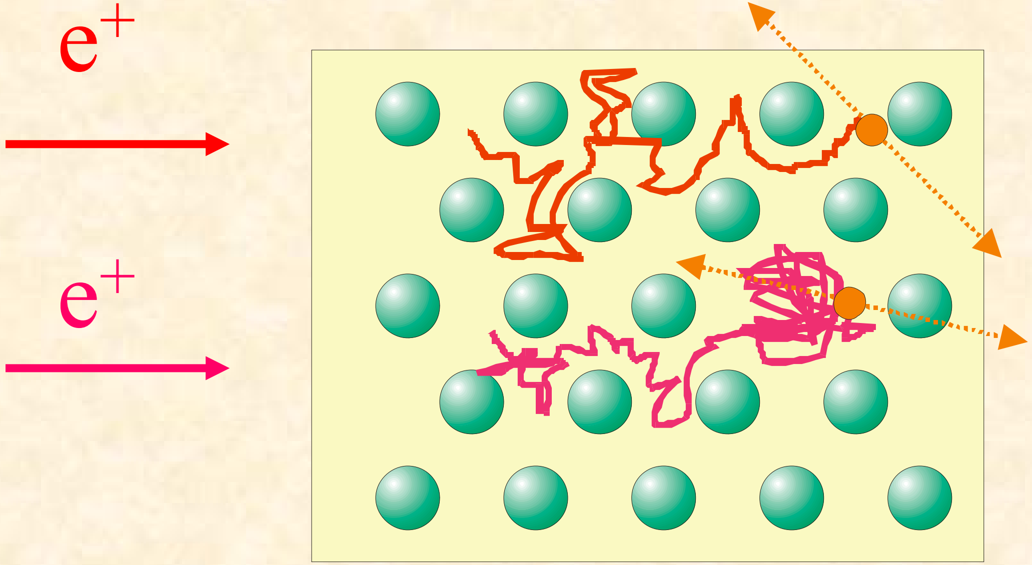
→ defect creation via inelastic processes (electronic excitation)

Positron annihilation in single crystals: a highly sensitive and selective method to detect vacancies and vacancy-related defects

annihilation in bulk:

- shorter lifetime
- larger Doppler shift (lower S, higher W)

positrons from ^{22}Na source or positron beam



annihilation in a vacancy:

- longer lifetime
- smaller Doppler shift (higher S, lower W)

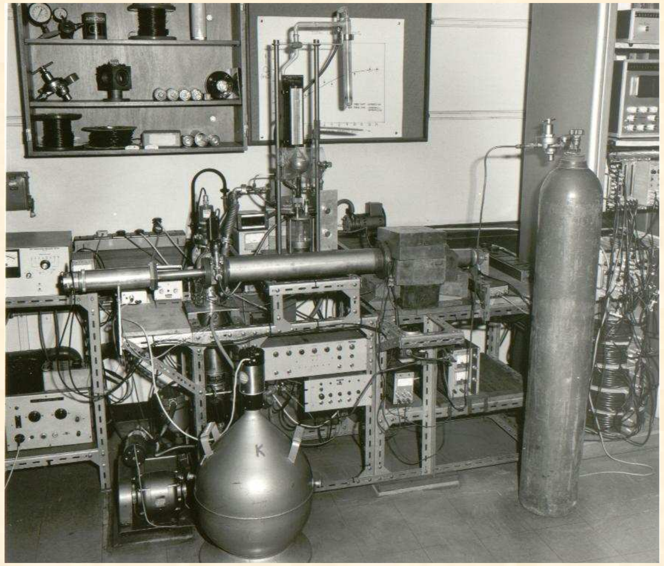
Surfaces, layered structures

- Mixing of various annihilation channels, high fraction of 3γ-annihilation!!!
  - Positron reemission
  - Backscattering
  - Surface positron trapping
  - Surface Ps-formation
  - Surface Ps diffusion
  - Ps trapping at the surface

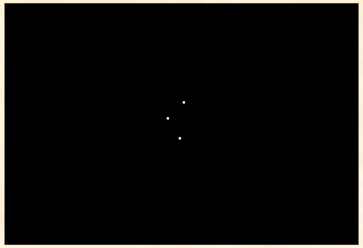
Summary

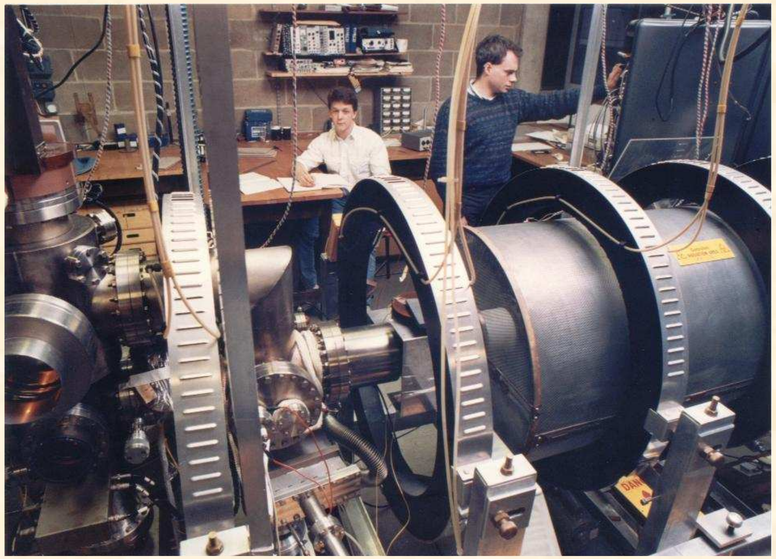
- Sapphire:
  - at lower fluences positrons detect Al monovacancies in the implanted zone
  - vacancies are created mainly through inelastic processes
  - at higher fluences larger positron traps (voids) are visible
- Si
  - positrons detect divacancies in the implanted zone
  - no evidence for defect creation by electronic processes
- SiC
  - positrons detect divacancies in the implanted zone
  - no overwhelming evidence for defect creation by electronic processes

Beam development - 1970 to 1990

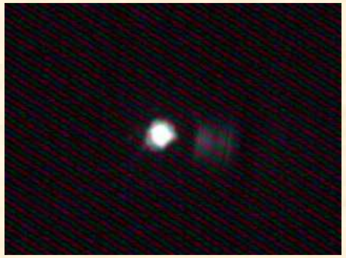


0.5 slow positrons per second

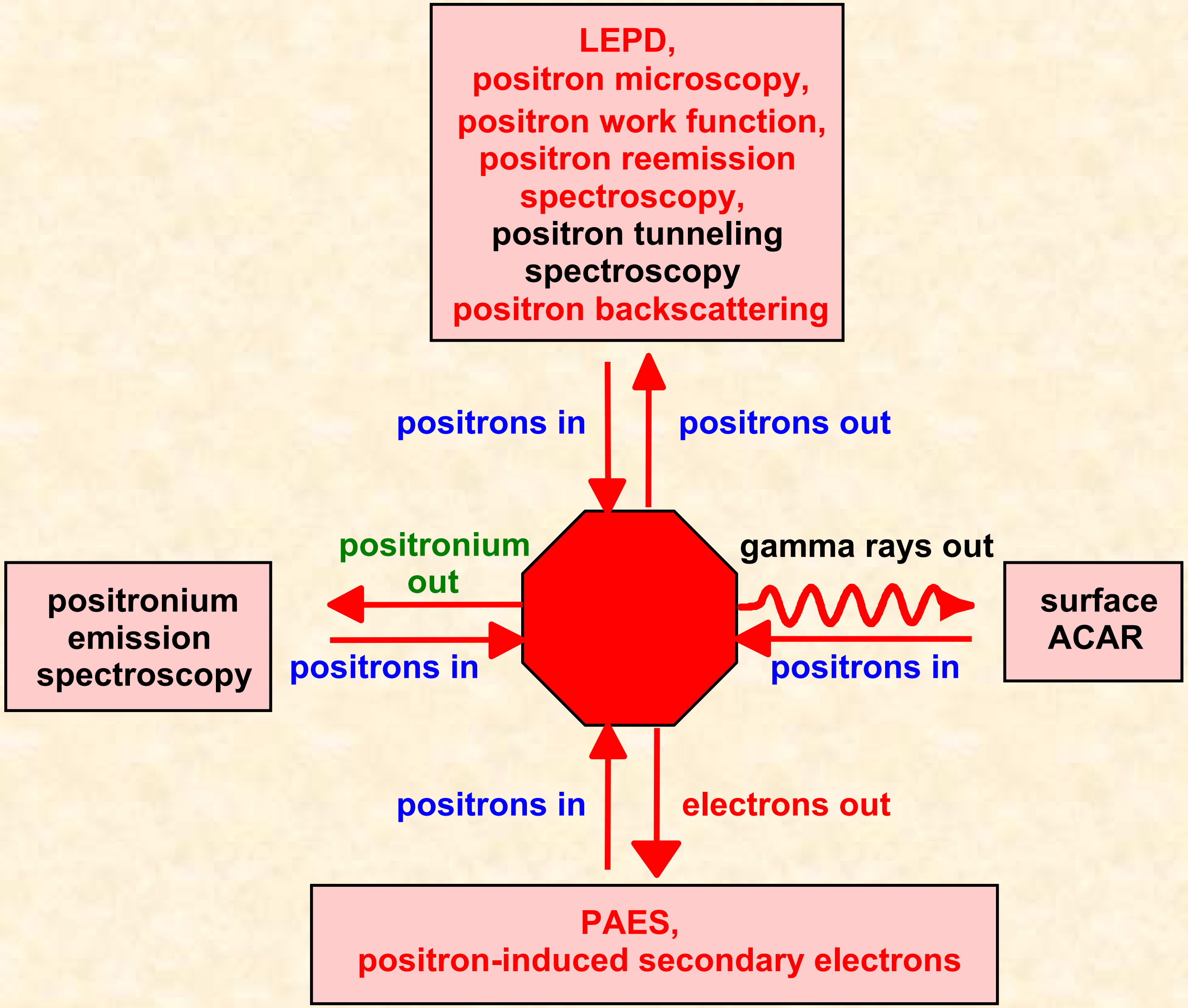




100,000 slow positrons per second



INDUSTRIAL APPLICATION - SURFACES?



LEPD,
positron microscopy,
positron work function,
positron reemission spectroscopy,
positron tunneling spectroscopy
positron backscattering

positronium emission spectroscopy

surface ACAR

PAES,
positron-induced secondary electrons