Identification of Vacancy Defects using Positron Annihilation

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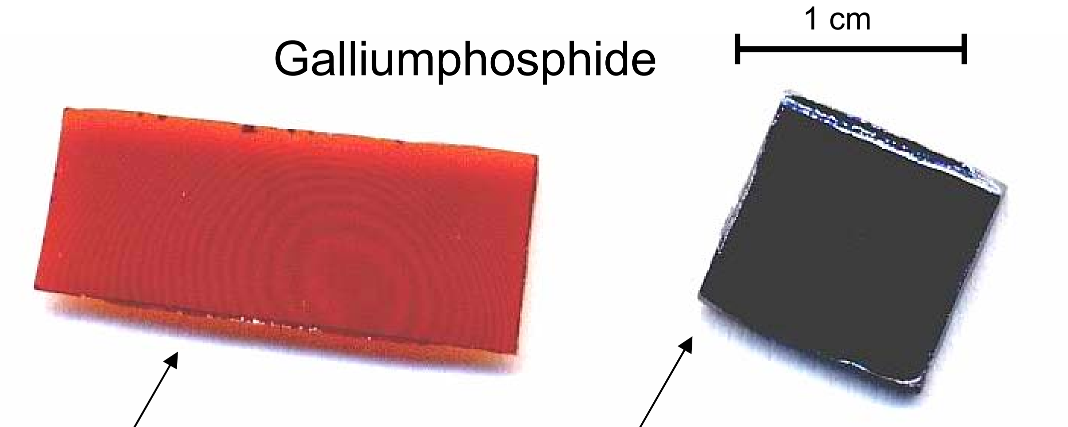
- Why are so tiny defects important at all?
- Positron trapping by vacancies
- Other techniques of positron annihilation
- Vacancy clusters

Point defects determine optical and electronic properties of semiconductors

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

Galliumphosphide



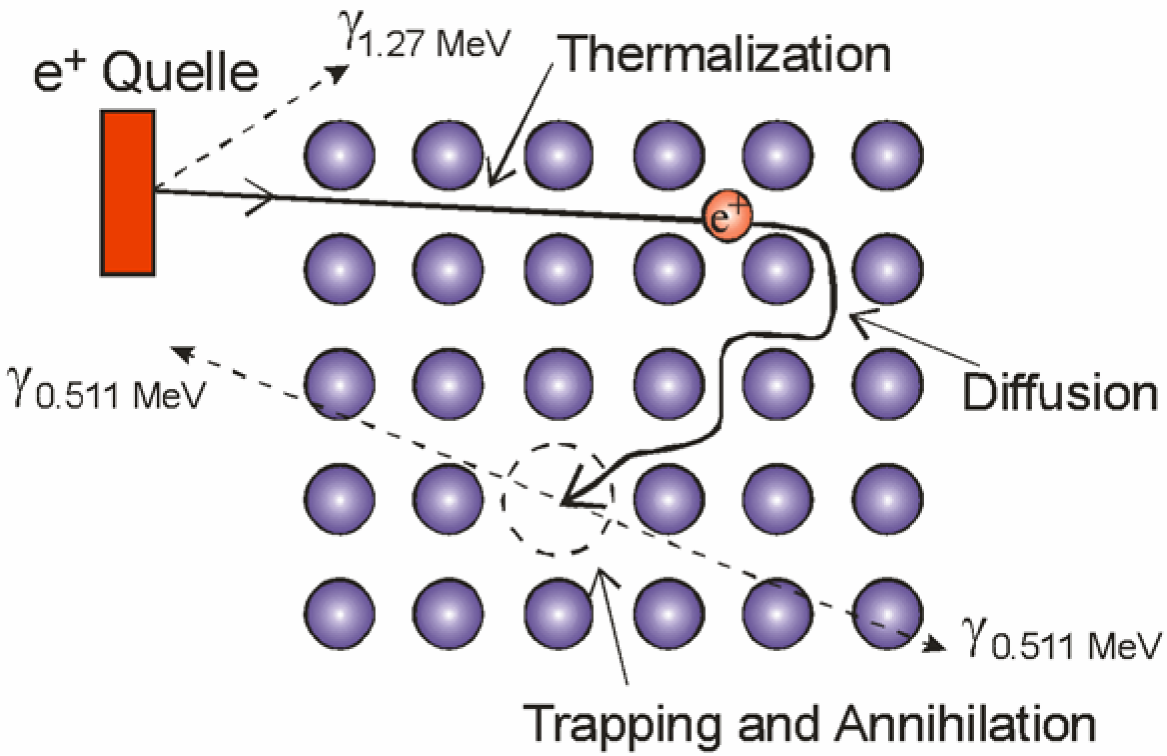
without vacancies
transparent

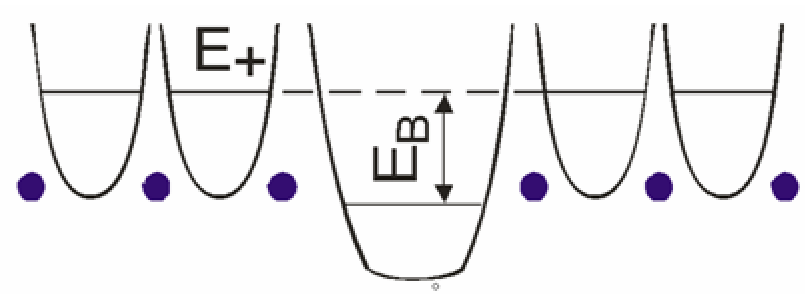
with 0,001% vacancies
opaque
1 vacancy in 100000 atoms

- 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

The positron lifetime spectroscopy

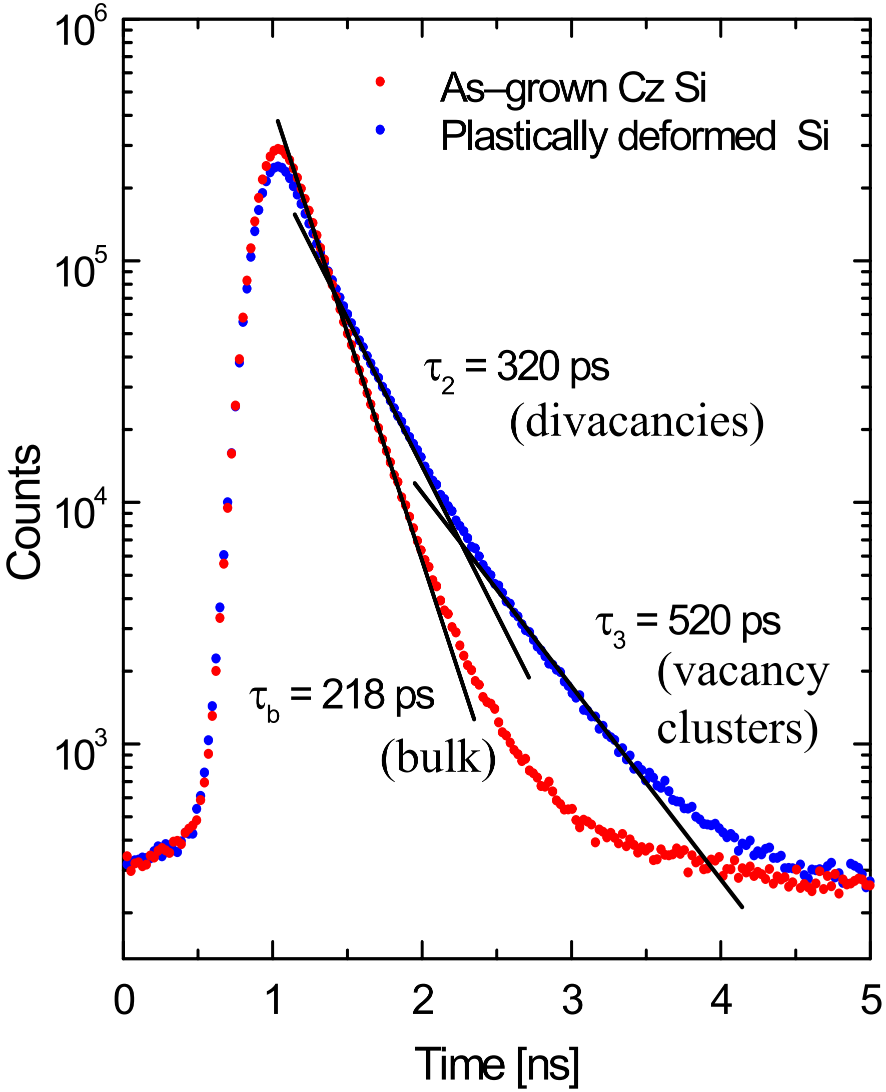
^{22}Na





- 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

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

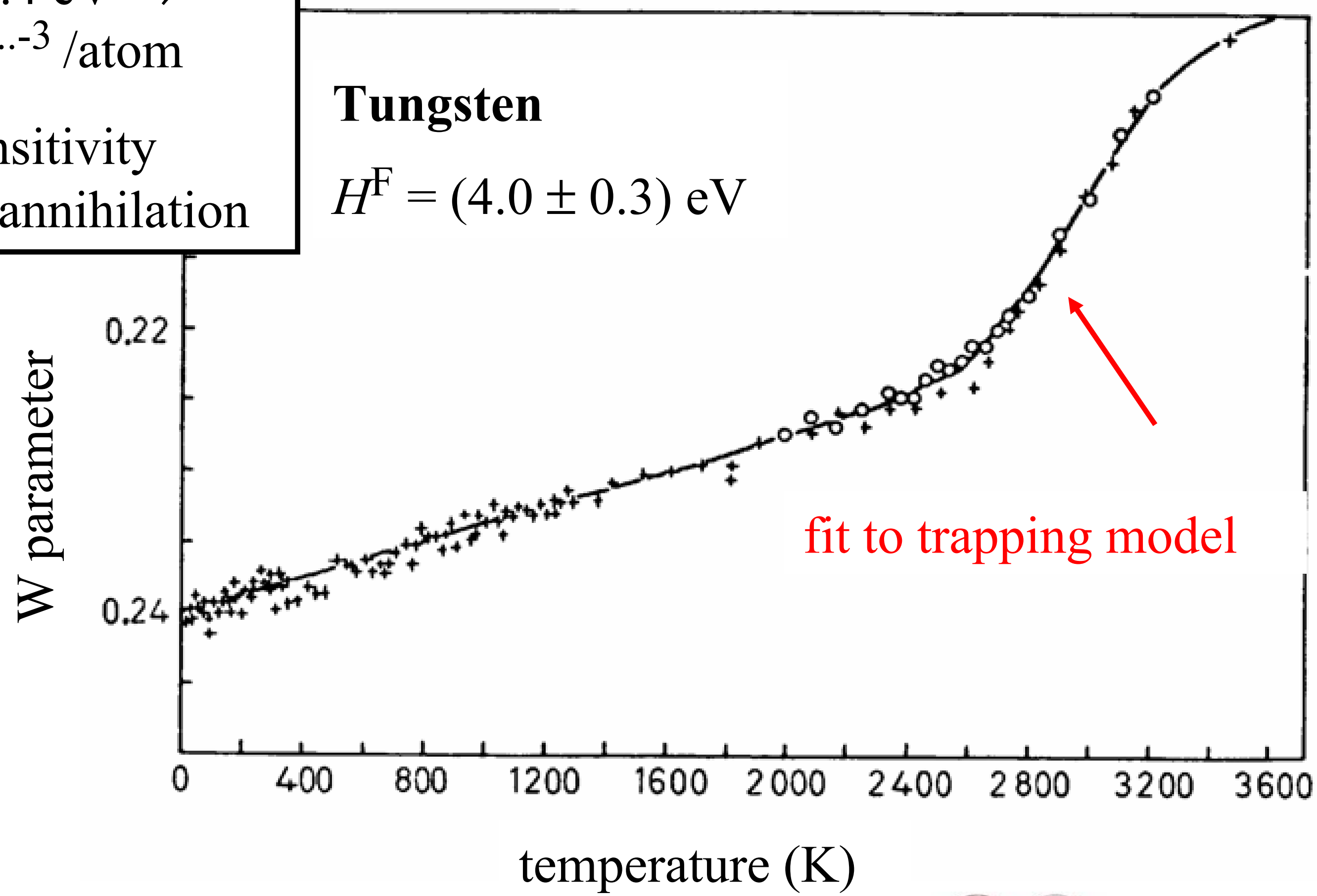
trapping rate

defect concentration

Vacancies in thermal Equilibrium

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

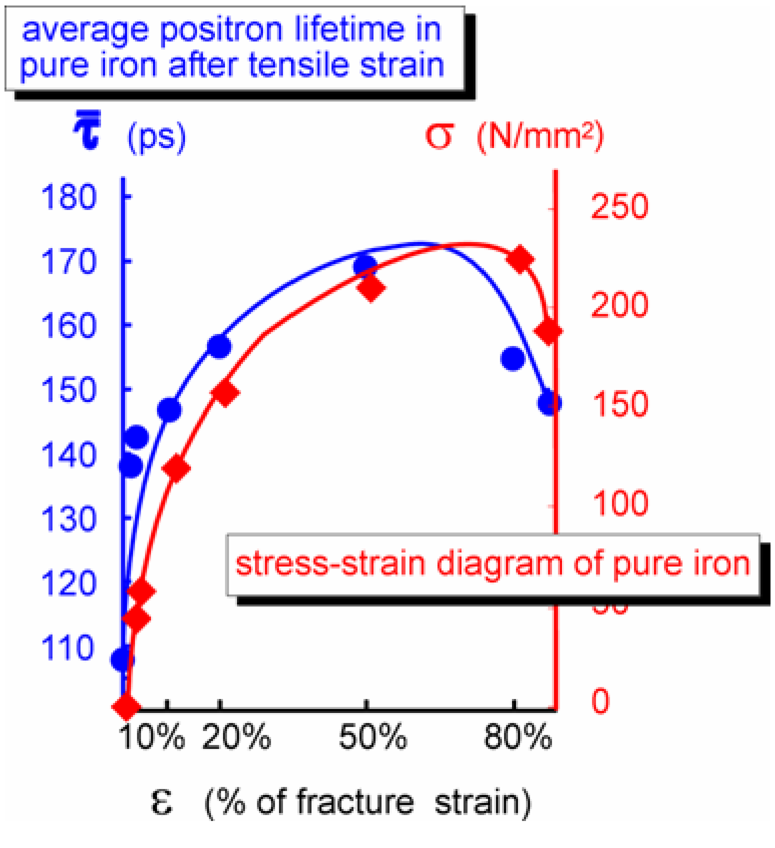
$$C_{1v}(T) = \exp\left(\frac{S_{1v}^{F}}{k}\right)\exp\left(\frac{H_{1v}^{F}}{kT}\right)$$

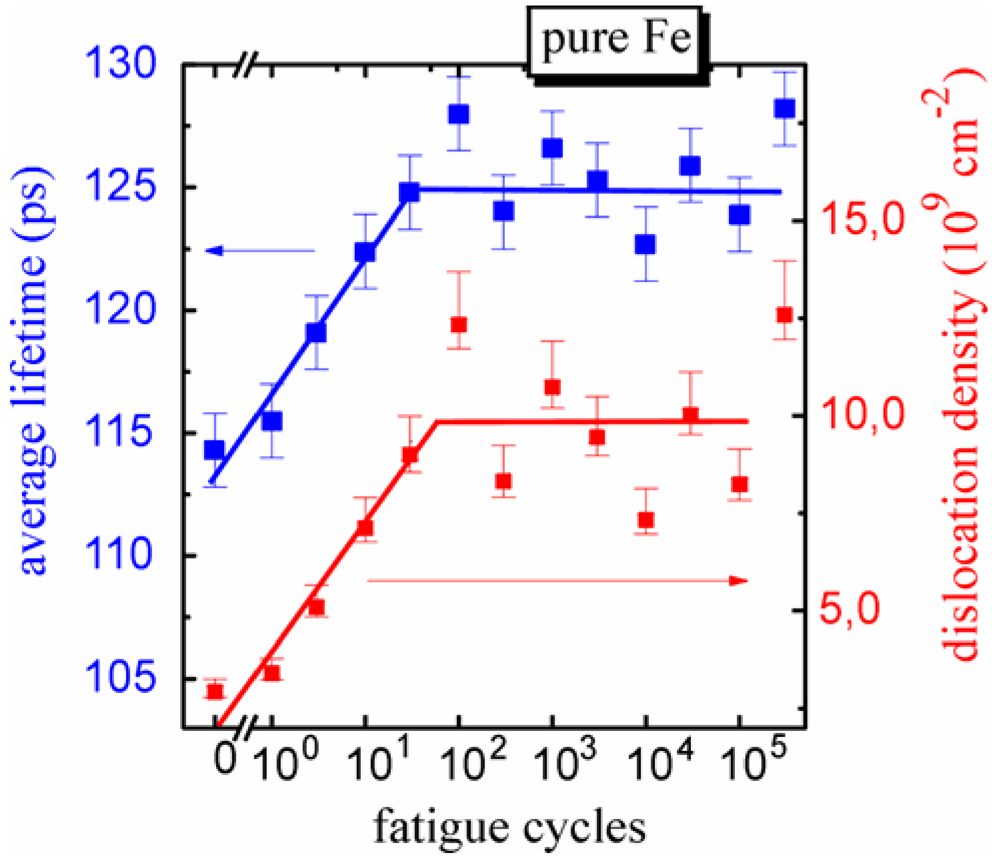


(Ziegler, 1979)

Defects in Iron after tensile strength and fatigue treatment

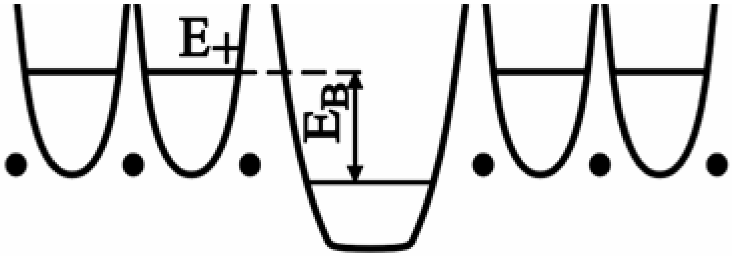
- We performed an extensive study of defects in mechanically damaged iron and steel
- Positrons are very sensitive: detection of defects already in the Hooks range of the stress-strain experiment
- Vacancy cluster and dislocations are detectable in both cases

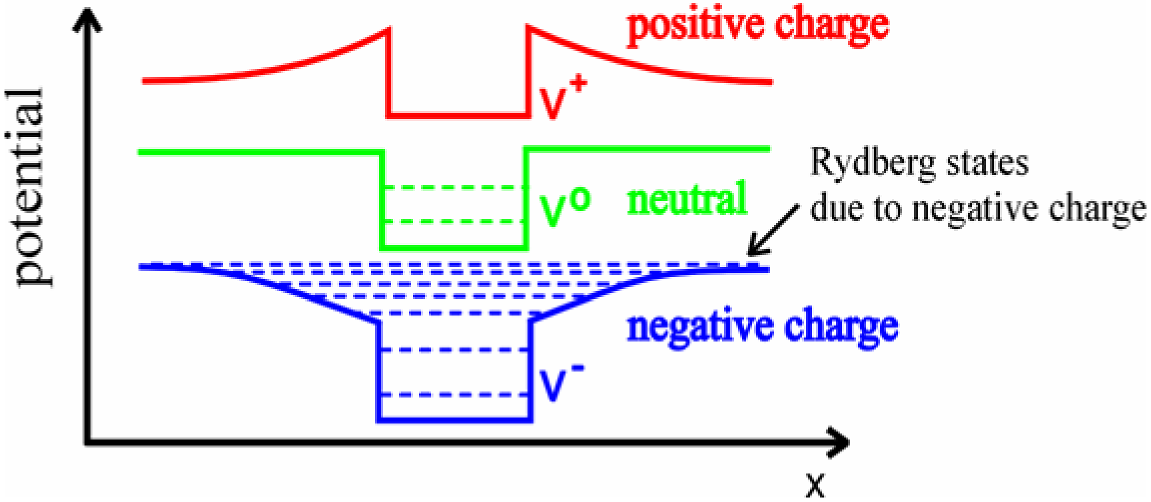




Somieski et al., J. Physique IV 5, C1/127-134 (1995)

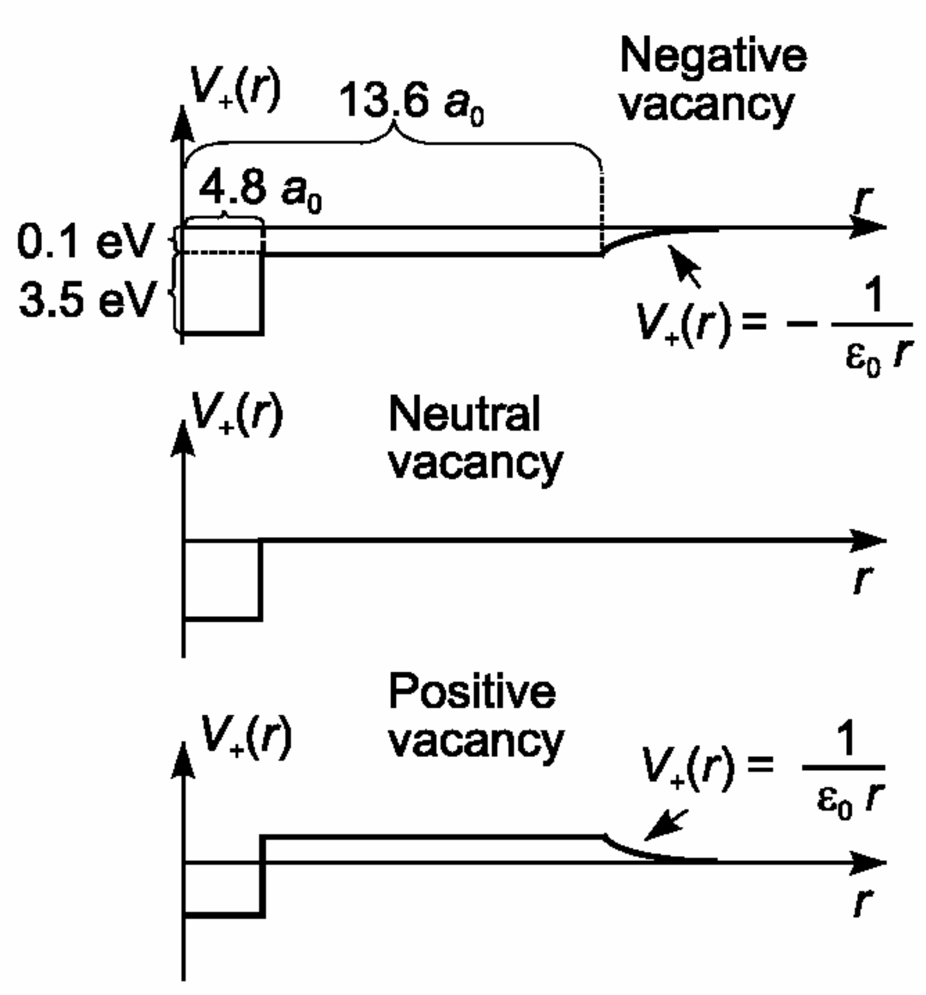
Vacancies in a semiconductor may be charged





- 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

Vacancies may be charged



Puska et al. 1990

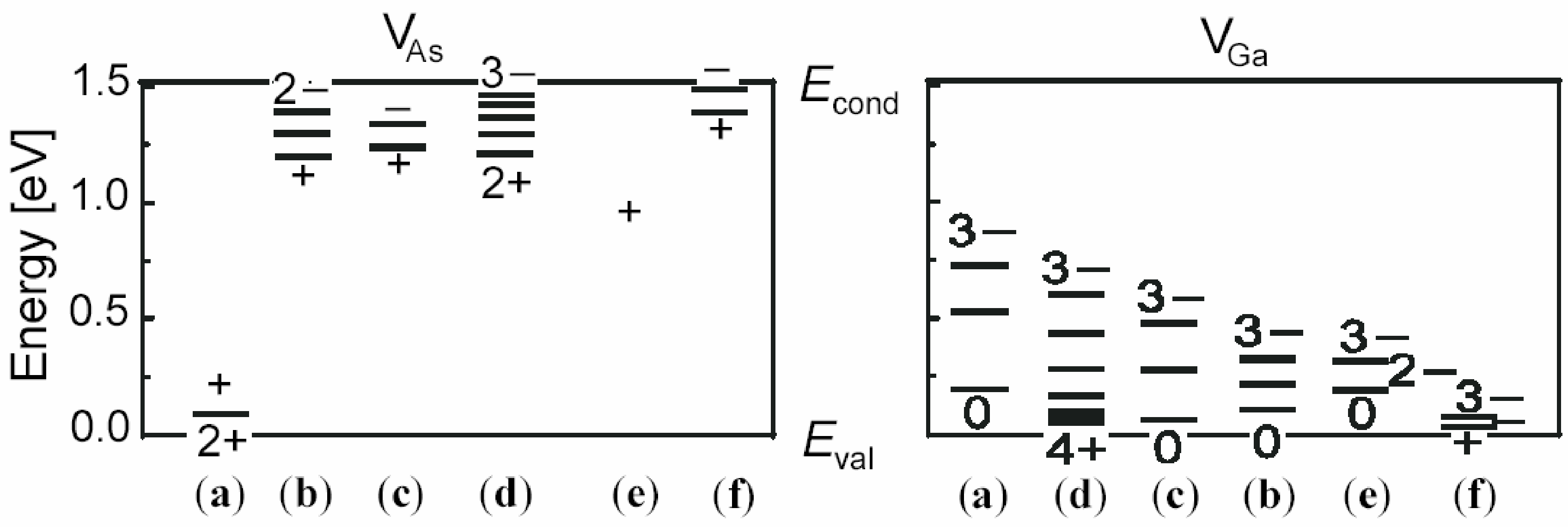
For a negative vacancy:

- Coulomb potential is rather extended but weak
- it supports trapping only at low temperatures
- at higher temperatures: detrapping dominates and vacancy behaves like a vacancy in a metal or a neutral vacancy

Positive vacancies repel positrons

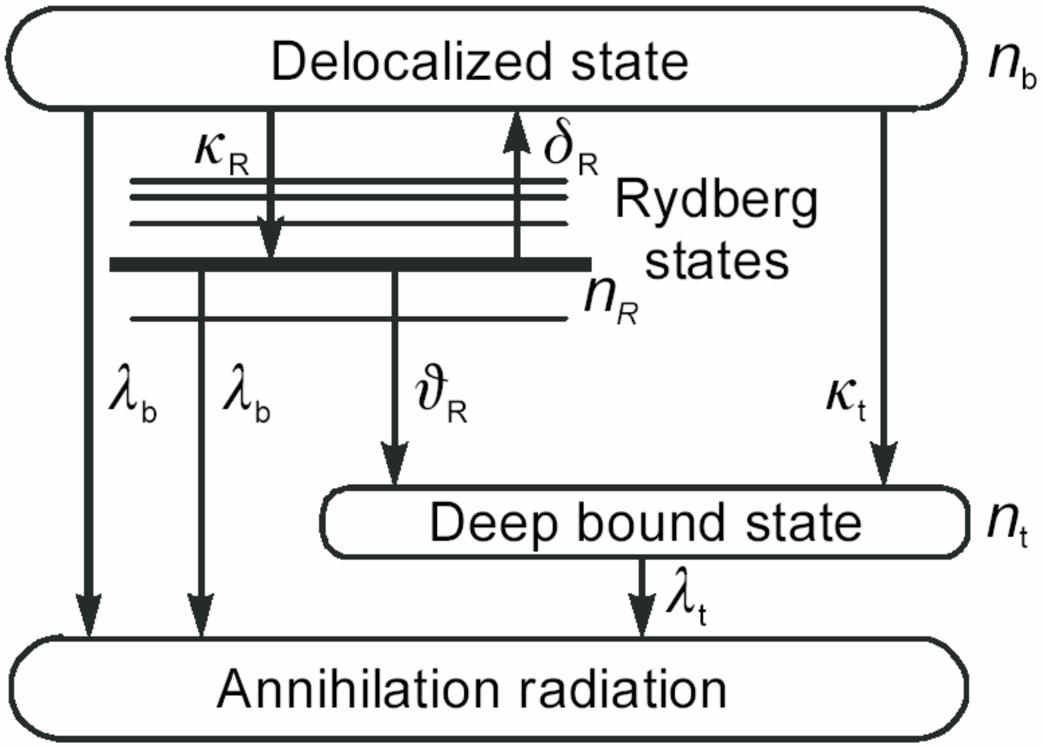
Theoretical calculation of vacancy levels in GaAs

- Theoretical description not simple
- relaxation of vacancy possible -> Jahn-Teller distortion / negative-U effect



Ionization levels of arsenic vacancies, gallium vacancies, and antisites according to theoretical calculations of (**a**) Baraff and Schlüter (1985a), (**b**) Puska (1989a), (**c**) Jansen and Sankey (1989), (**d**) Xu and Lindefelt (1990), (**e**) Zhang and Northrup (1991), and (**f**) Seong and Lewis (1995), (**g**) Zhang and Chadi (1990), (**h**) Pöykkö et al. (1997). E_{val} and E_{cond} are the edges of the valence and the conduction band, respectively.

Positron trapping by negative vacancies



- trapping process can be described quantitatively by trapping model
- Coulomb potential leads to Rydberg states
- from there: positrons may re-escape by thermal stimulation
- once in the deep state: positron is captured until annihilation
- detrapping is strongly temperature dependent

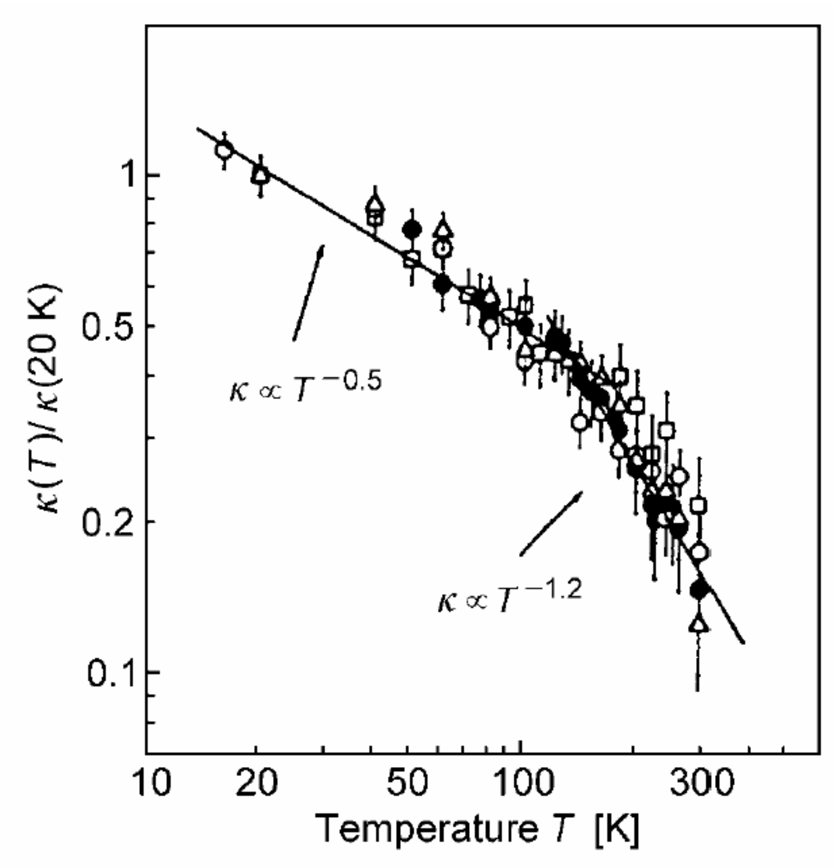
$$\delta_R = \frac{\kappa_R}{\rho_v}\left(\frac{m^* k_B T}{2\pi\hbar^2}\right)^{3/2} \exp\left(-\frac{E_R}{k_B T}\right)$$

E_R binding energy of positron in Rydberg state

ρ_v vacancy density

Manninen, Nieminen, 1981

Negative vacancies show temperature-dependent positron trapping



positron trapping in negatively charged Ga vacancies in SI-GaAs

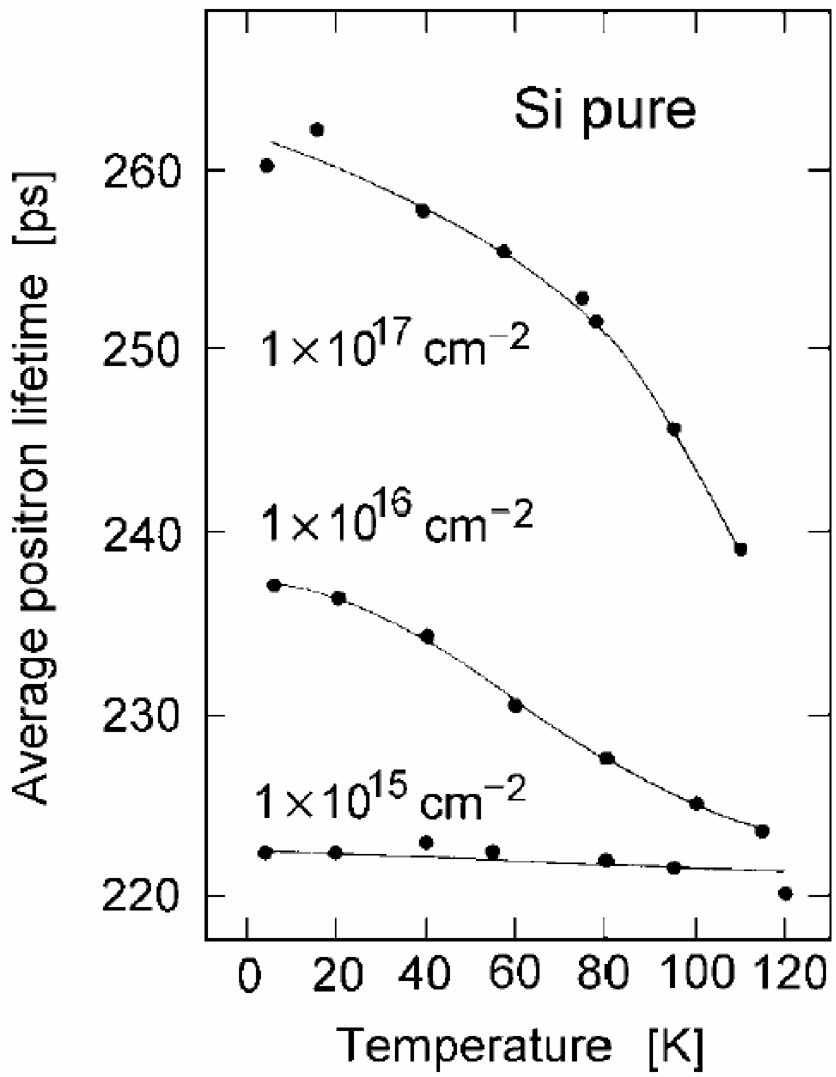
- temperature dependence of positron trapping is rather complex

$$\kappa = \frac{\vartheta_R \rho_v \kappa_{R0} T^{-1/2}}{\vartheta_R \rho_v + \kappa_{R0} \left(\frac{m^* k_B}{2\pi\hbar^2} \right)^{3/2} T \exp\left(-\frac{E_R}{k_B T} \right)}$$

- low temperature: $\sim T^{-0.5}$ due to diffusion limitation in Rydberg states
- higher T: stronger temperature dependence due to thermal detrapping from Rydberg state

Le Berre et al., 1995

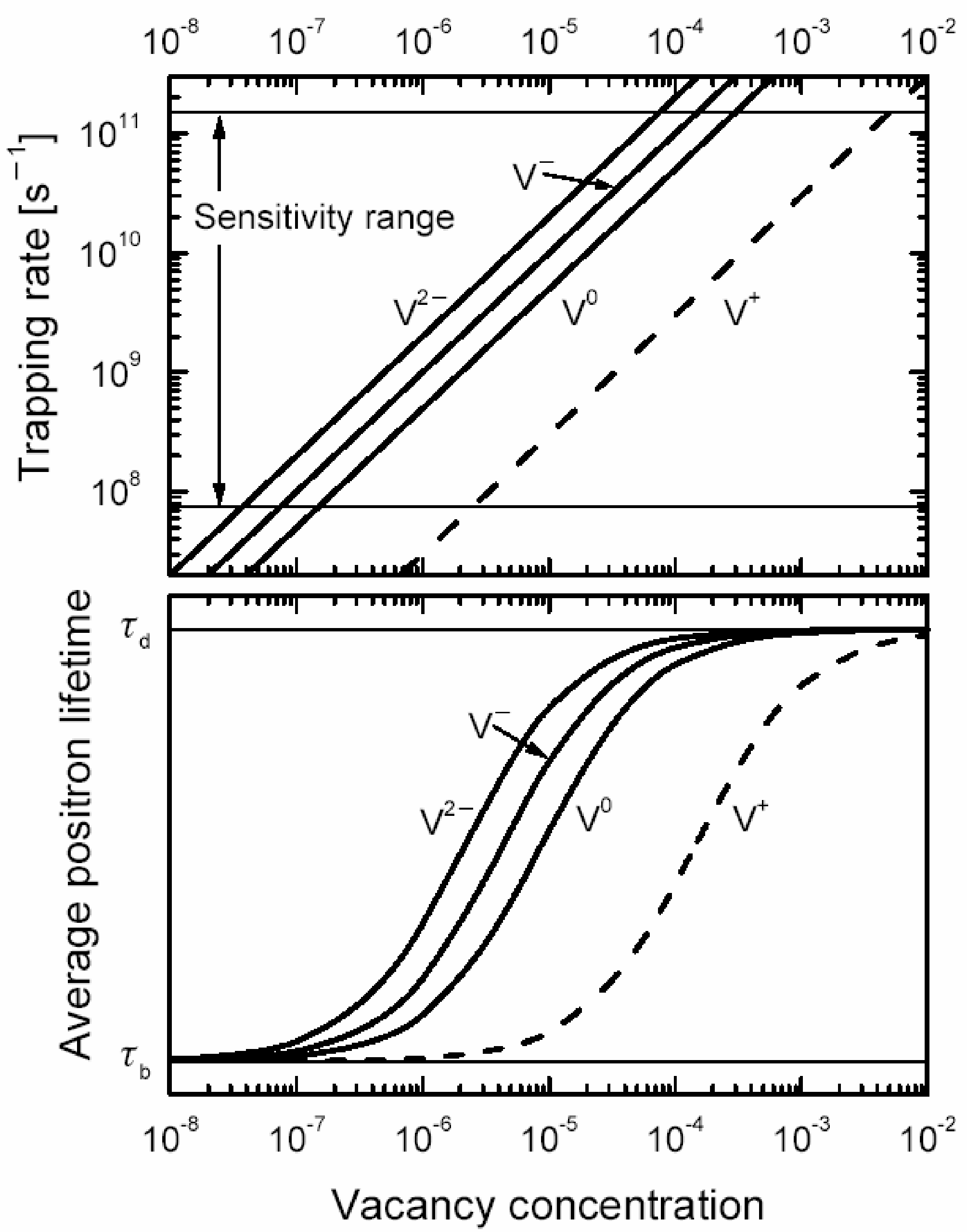
Temperature-dependent positron trapping



- temperature dependence of positron trapping can be used to determine the charge state of vacancies
- trapping to positive vacancies possible at elevated T
- however: has never been observed
- example: Positron trapping in e-irradiated Si
- trapping by negatively charged divacancies

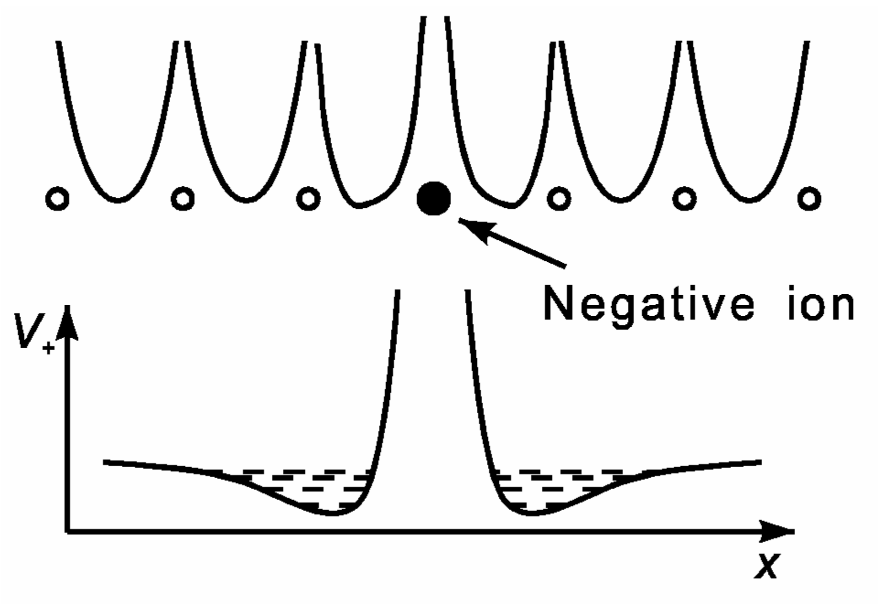
(Mäkinen et al. 1989)

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

Negative ions act as shallow positron traps

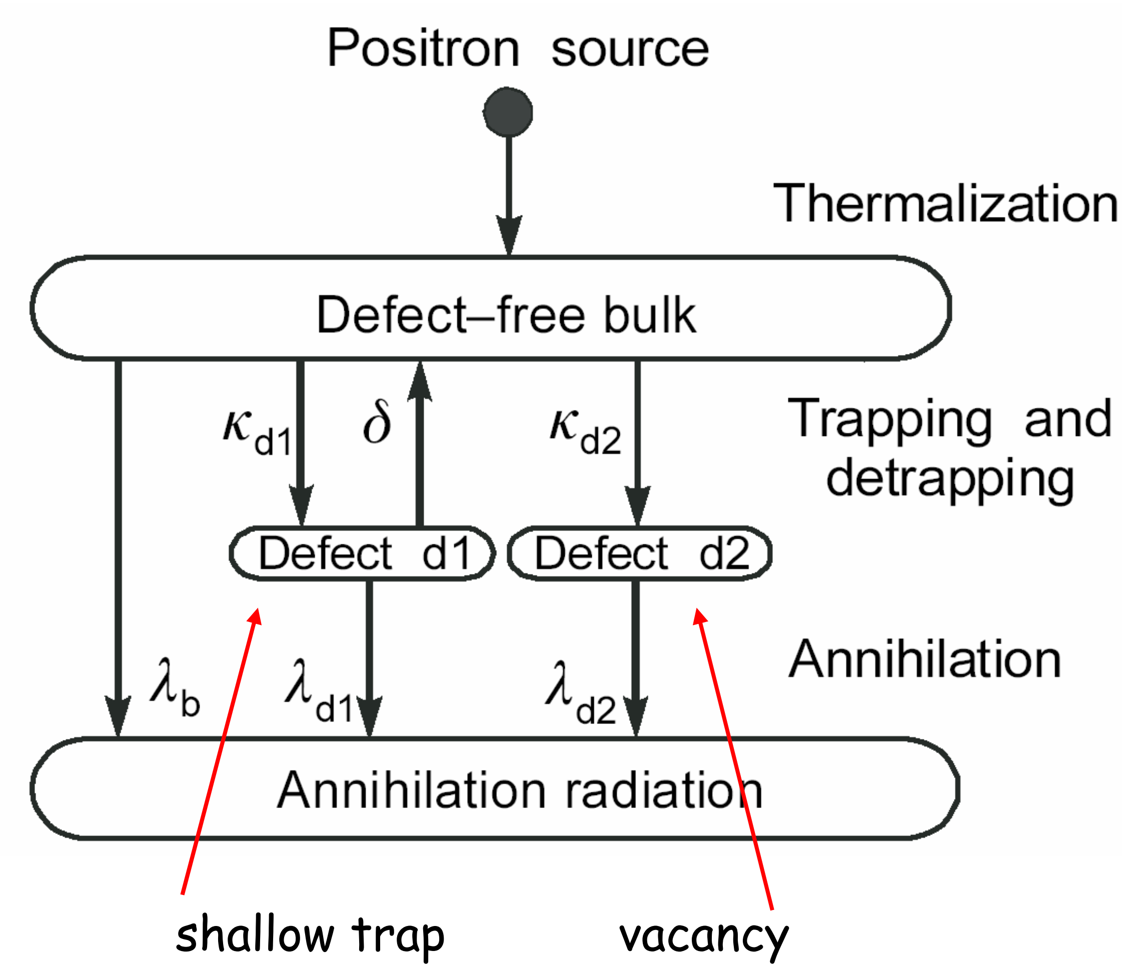


- at low T: negatively charged defects without open volume may trap positrons
- "shallow" due to small positron binding energy
- annihilation parameters close to bulk parameters
- acceptor-type impurities, dopants, negative antisite defects
- thermally stimulated detrapping can be described by:

$$\delta = \frac{\kappa}{\rho_{st}} \left(\frac{m^* k_B T}{2\pi\hbar^2} \right)^{3/2} \exp\left(-\frac{E_{st}}{k_B T} \right)$$

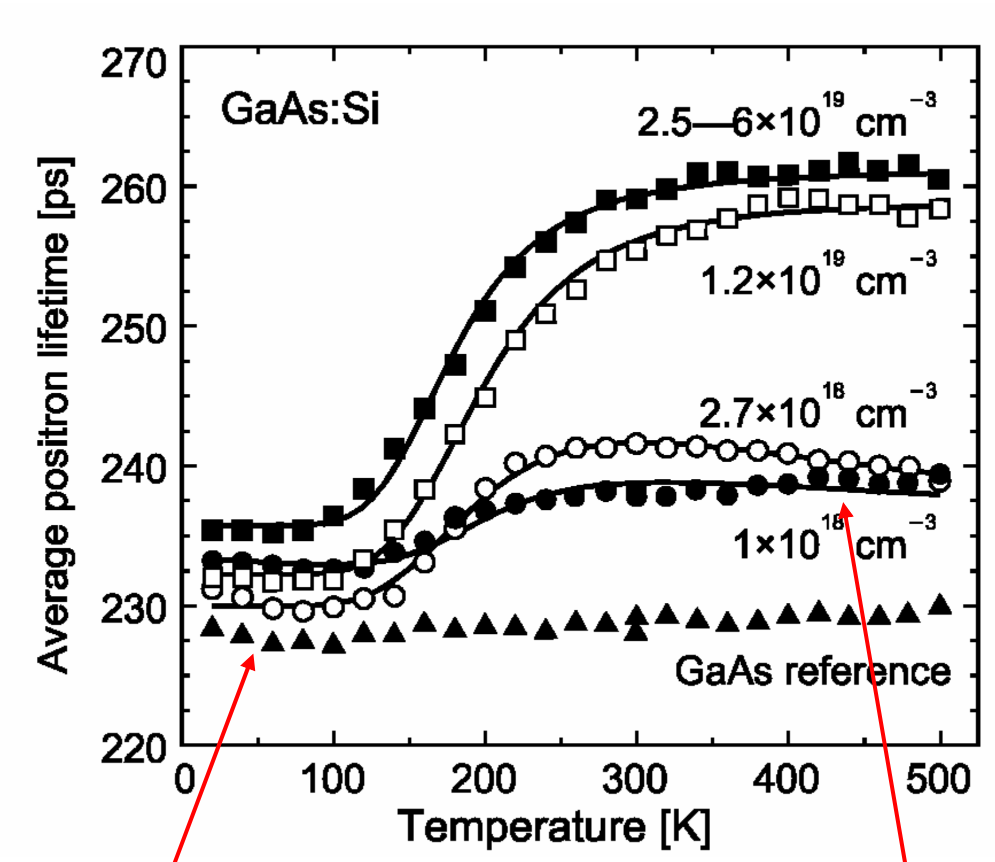
Saarinen et al., 1989

Shallow positron traps



- positron trapping model gets more complex
- however: trapping at shallow traps can be avoided at high temperatures

Effect of shallow positron traps



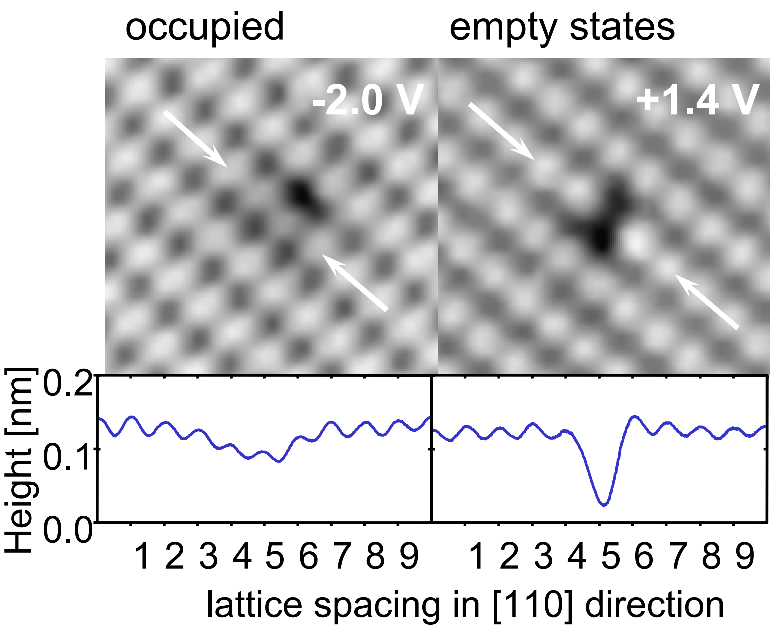
- temperature dependence is characterized by competing trapping by vacancies and shallow traps
- in GaAs:Si we observe V_{Ga}-Si_{Ga} complexes at high temperatures
- and Si_{Ga}^{-} donors at low T in addition (shallow traps)

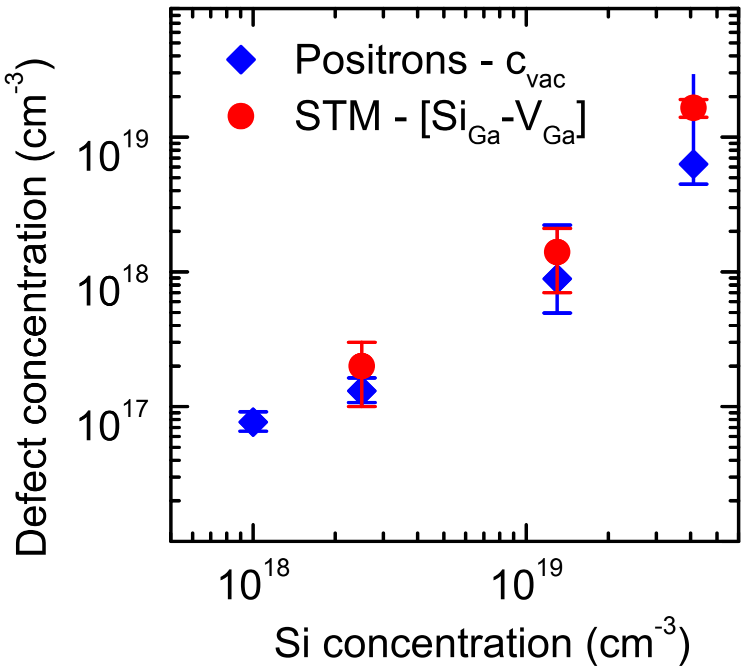
competing trapping centres at low T
shallow positron traps (Si_{Ga}^{-})

trapping by vacancies
at elevated temperatures (V_{Ga}-Si_{Ga})

J. Gebauer et al. 1997

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





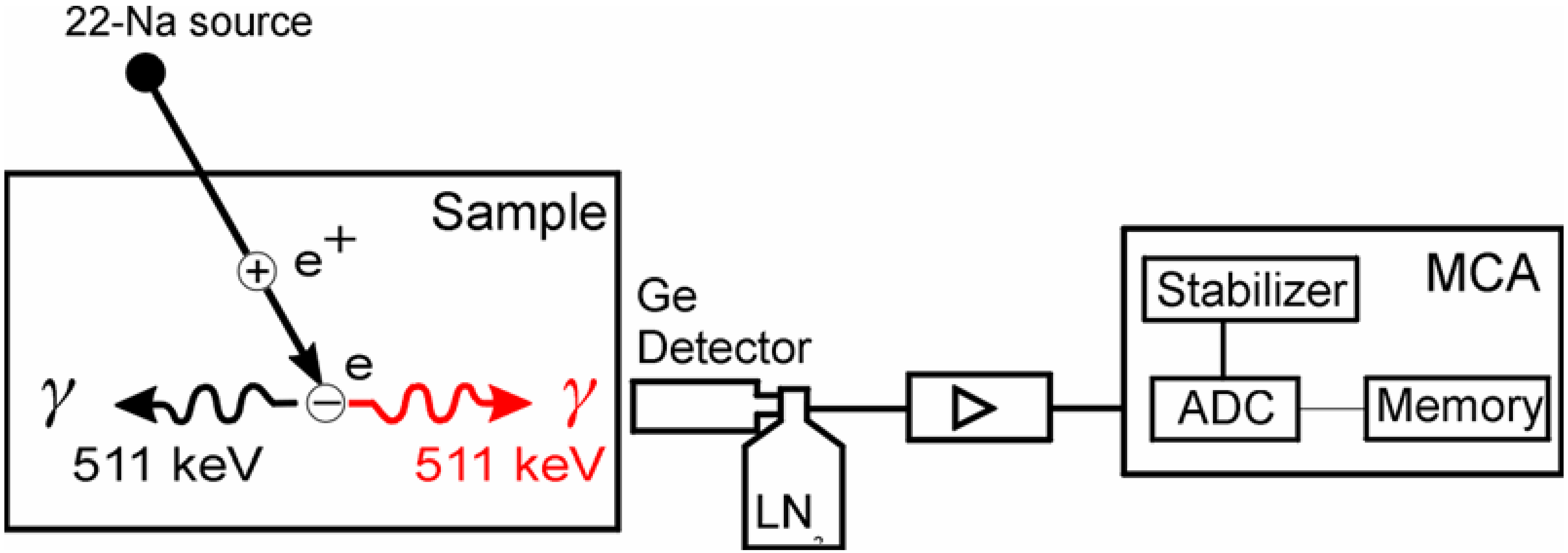
- Scanning tunneling microscopy at GaAs (110)-cleavages planes (by Ph. Ebert, Jülich)
- Defect complex identified as **V_{Ga}-Si_{Ga}**

- Quantification → Agreement

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

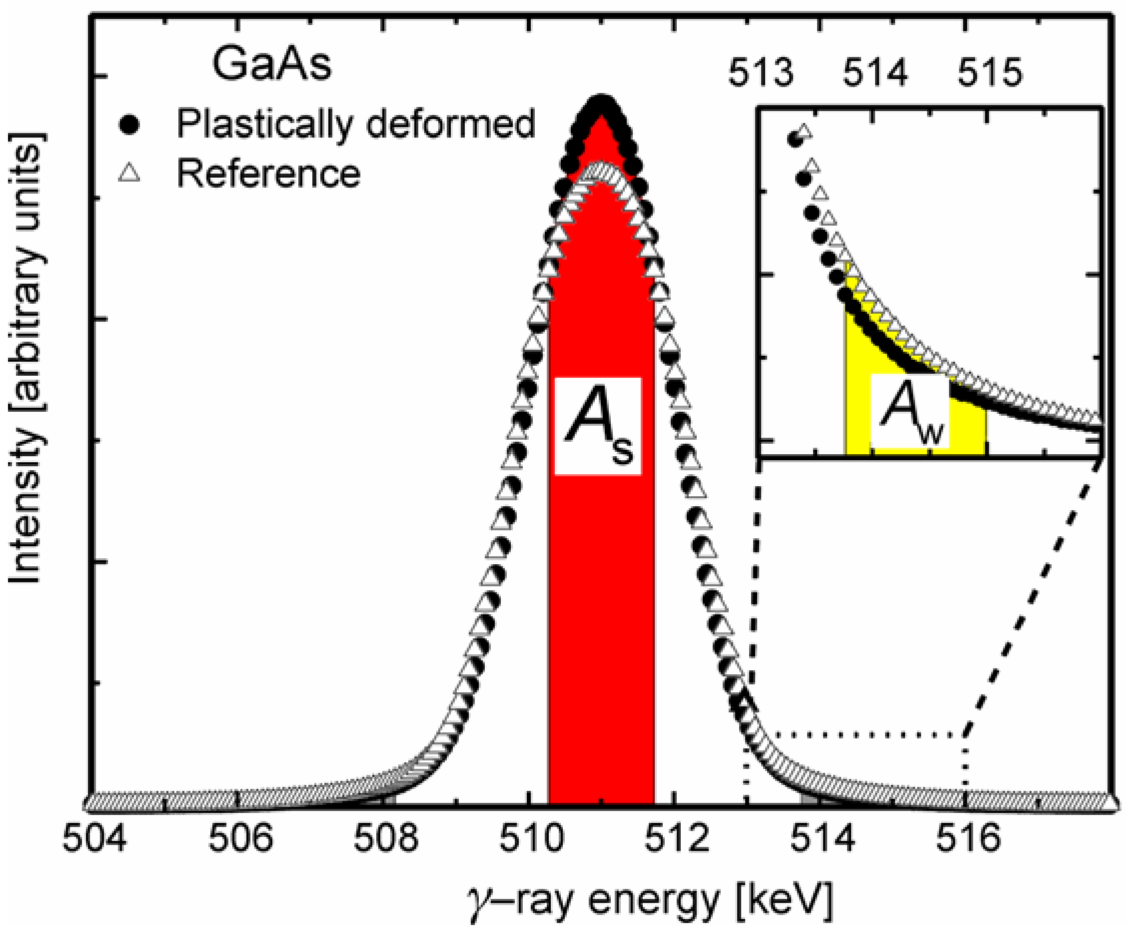
Gebauer et al., Phys. Rev. Lett. **78** (1997) 3334

Measurement of Doppler Broadening



- electron momentum in propagation direction of 511 keV γ-ray leads to Doppler broadening of annihilation line
- can be detected by conventional energy-dispersive Ge detectors and standard electronics

Line Shape Parameters



S parameter:

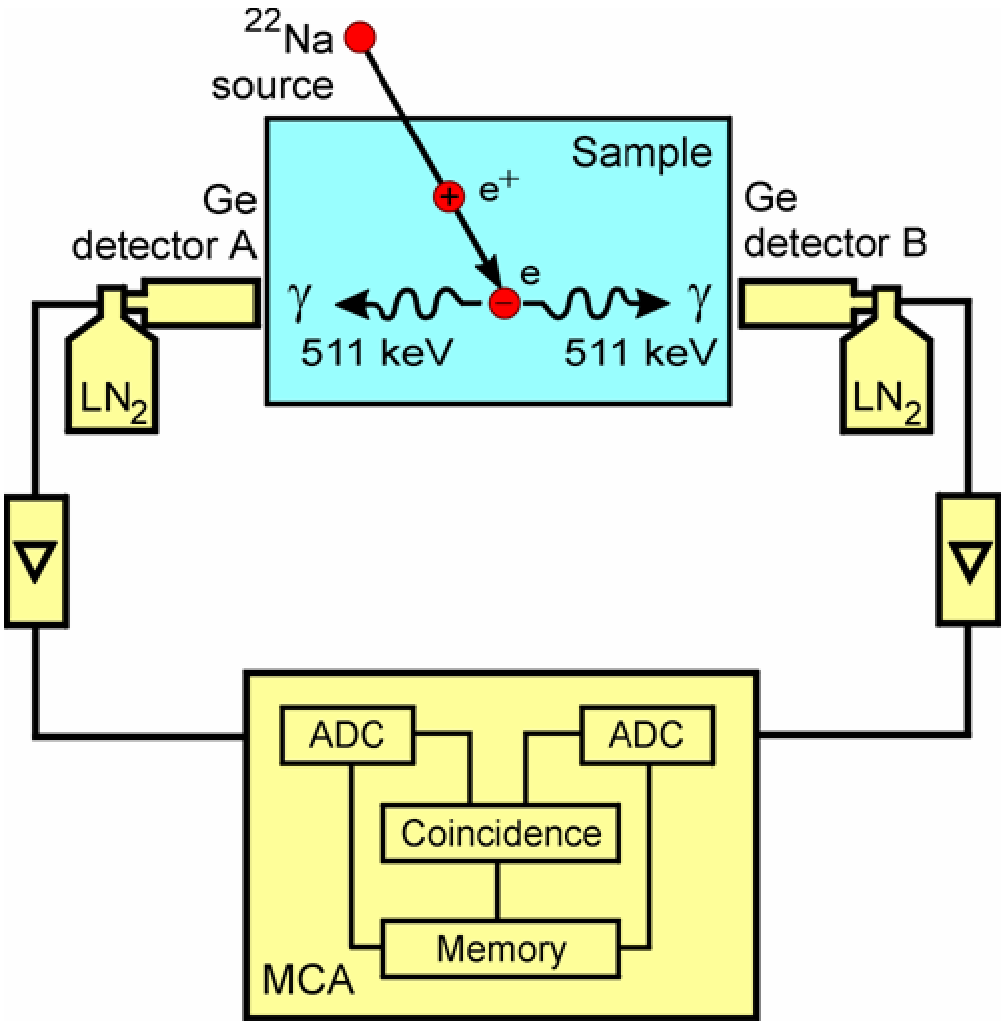
$S = A_S/A_0$

W parameter:

$W = A_W/A_0$

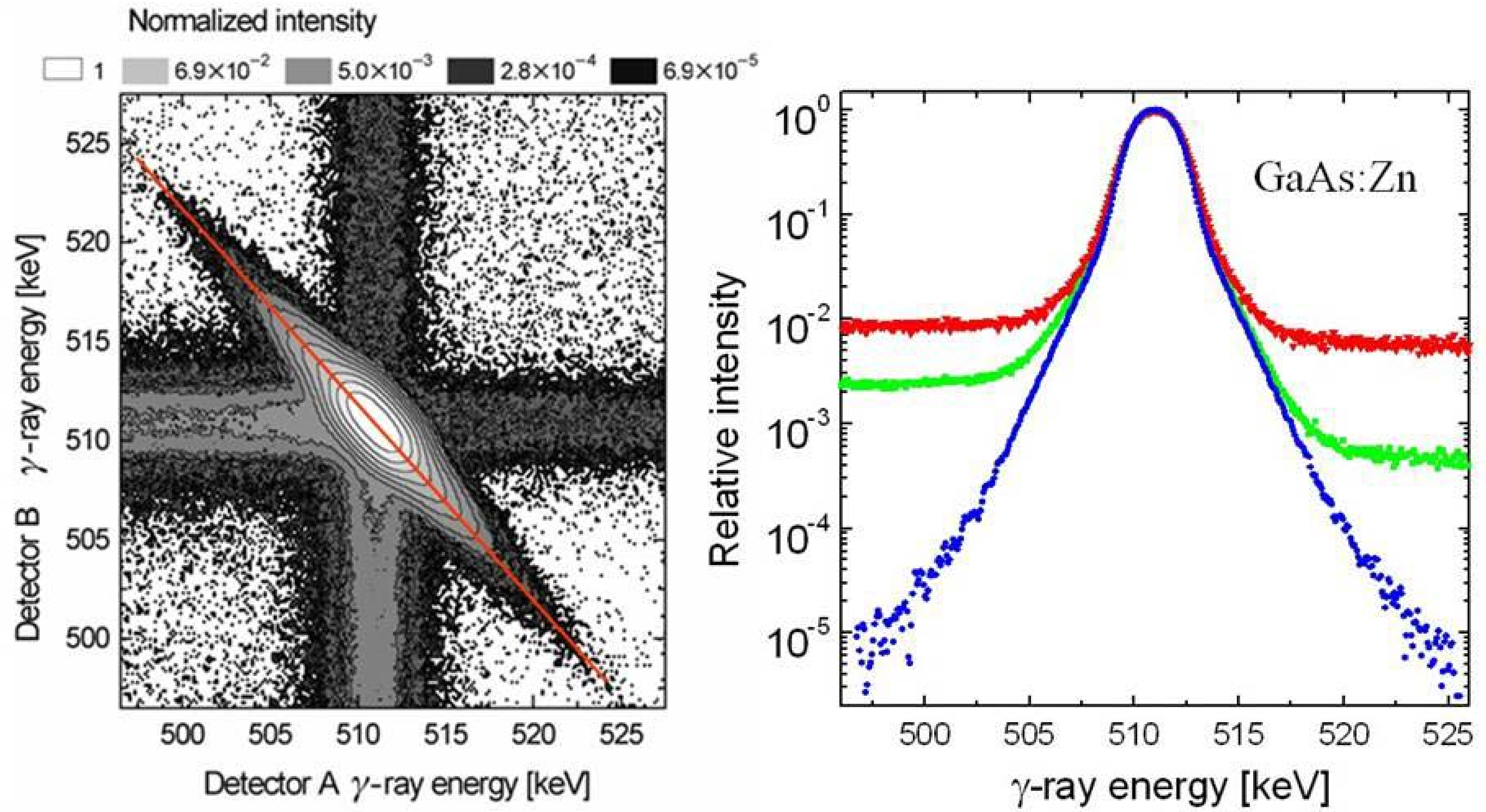
W parameter mainly determined by annihilations of core electrons (chemical information)

Doppler Coincidence Spectroscopy



- coincident detection of second annihilation γ reduces background
- use of a second Ge detector improves energy resolution of system

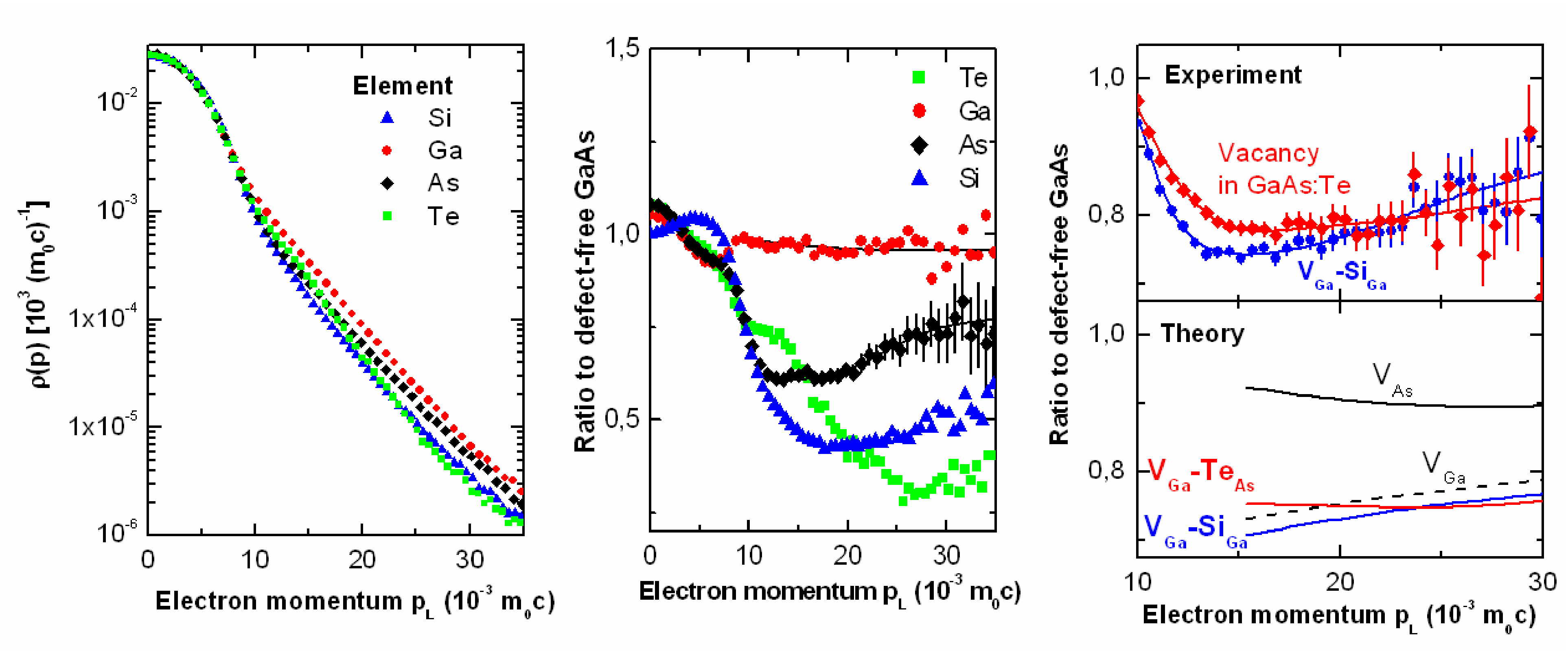
Doppler Coincidence Spectra



$$E_1+E_2= 2\ m_0\ c^2 =1022\ keV$$

Doppler-Coincidence-Spectroscopy in GaAs

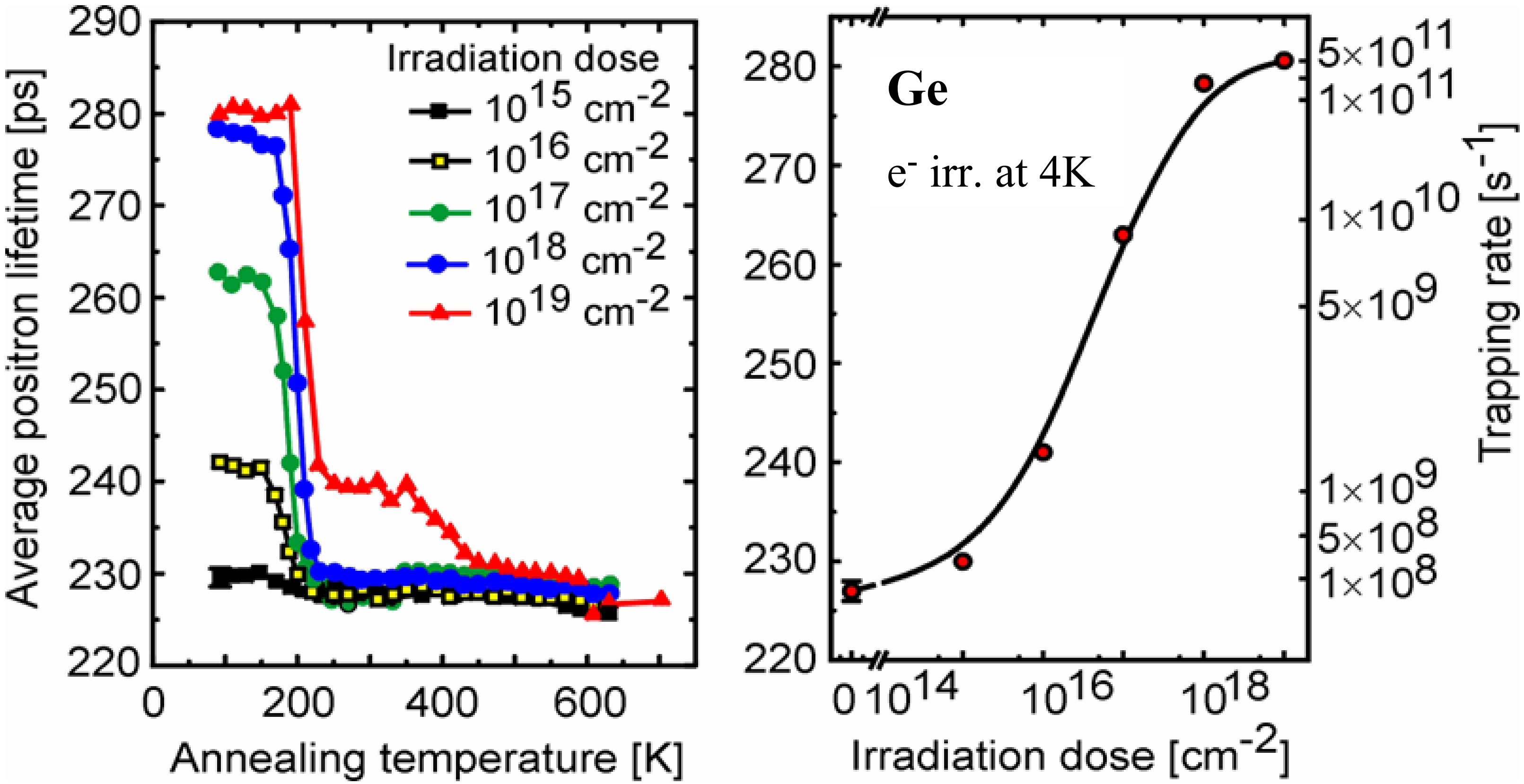
- Chemical sensitivity due to electrons at high momentum (core electrons)
- a single impurity atom aside a vacancy is detectable
- examples: V_{Ga}-Te_{As} in GaAs:Te



J. Gebauer et al., Phys. Rev. B **60** (1999) 1464

Defects in electron-irradiated Ge

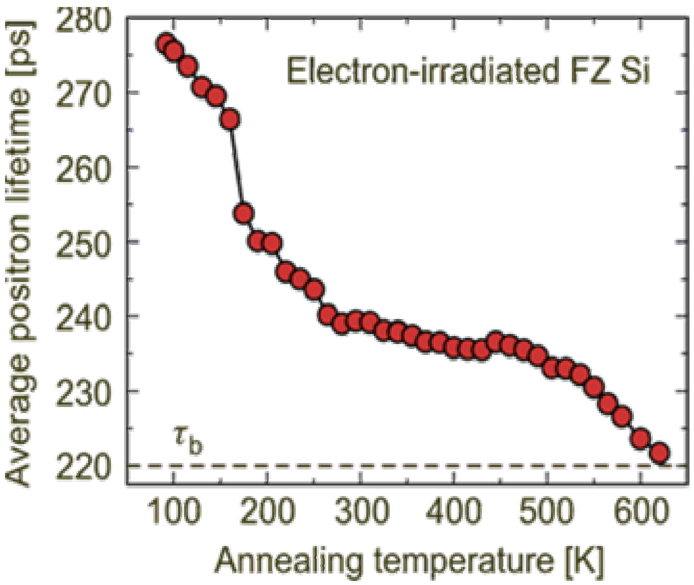
- Electron irradiation (2 MeV @ 4K) induces Frenkel pairs (vacancy - interstitial pairs)
- steep annealing stage at 200 K
- at high irradiation dose: divacancies are formed (thermally more stable)

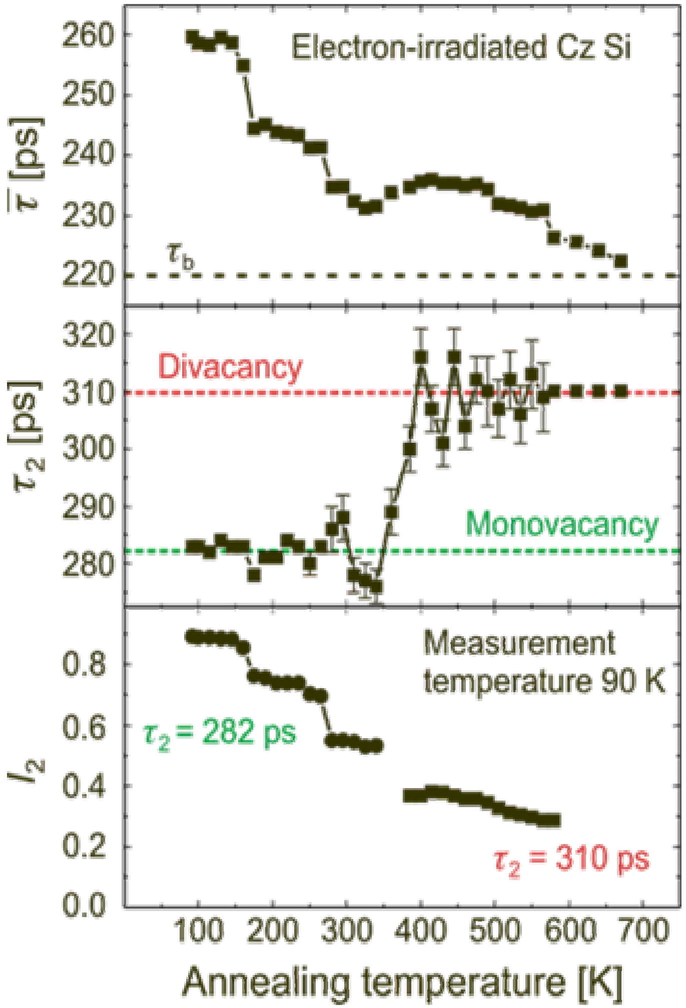


(Polity et al., 1997)

Low-temperature electron irradiation

- 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

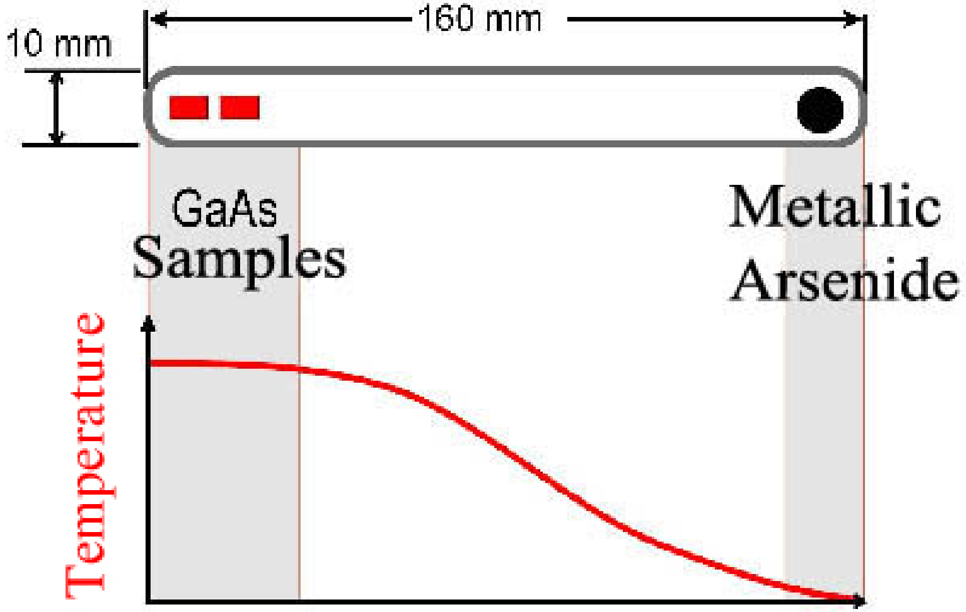




Polity et al., Phys. Rev. B **58** (1998) 10363

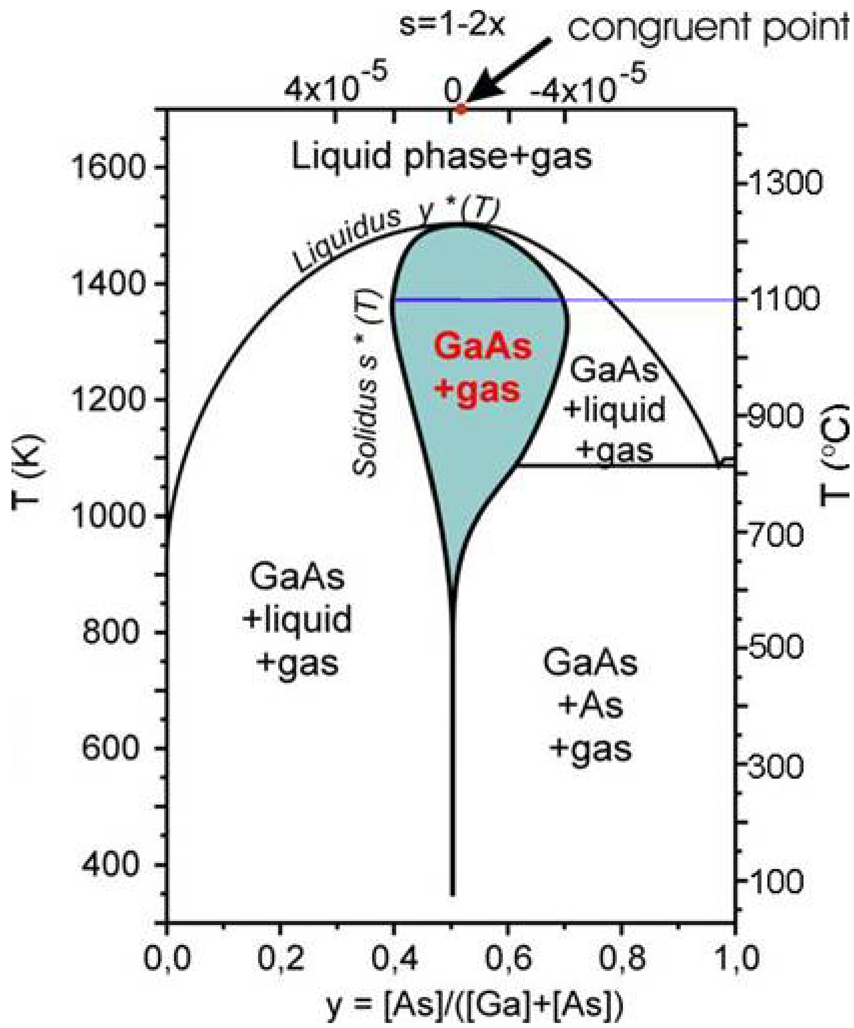
GaAs: annealing under defined As-partial pressure

- 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

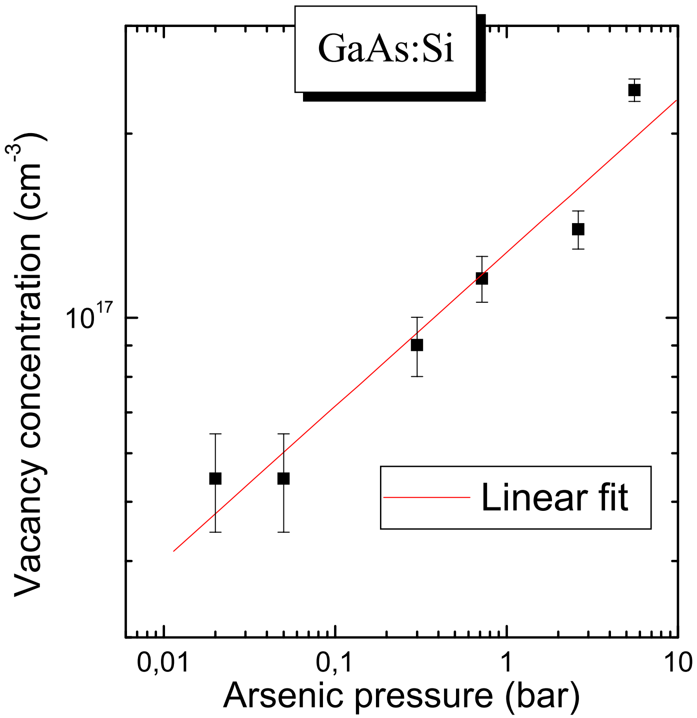
T_{As}: determines As-partial pressure



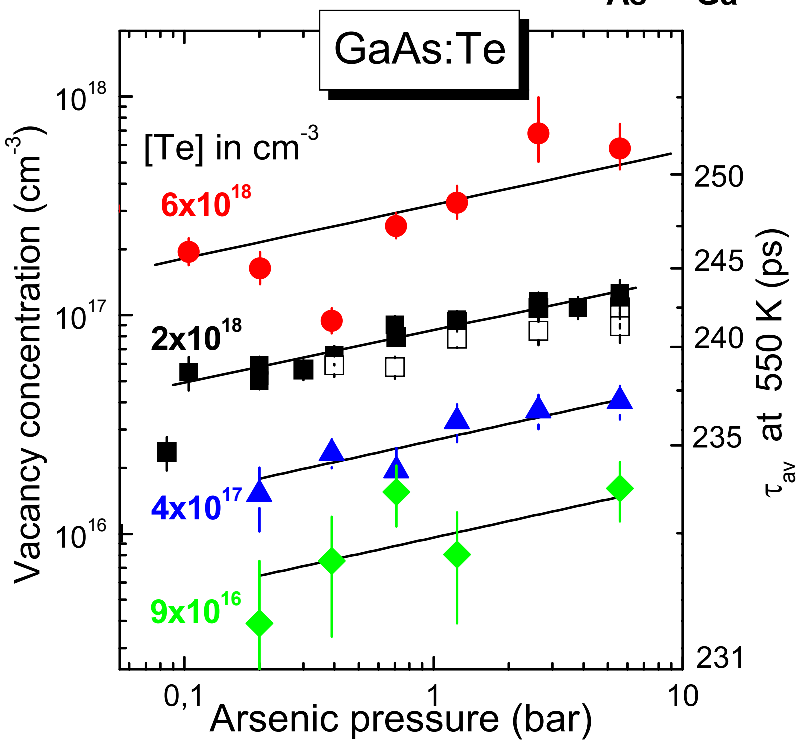
H. Wenzl et al., J. Cryst. Growth **109**, 191 (1991).

GaAs: Annealing under defined As pressure

Si_{Ga}-V_{Ga}



Te_{As}-V_{Ga}



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

Thermodynamic reaction:

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

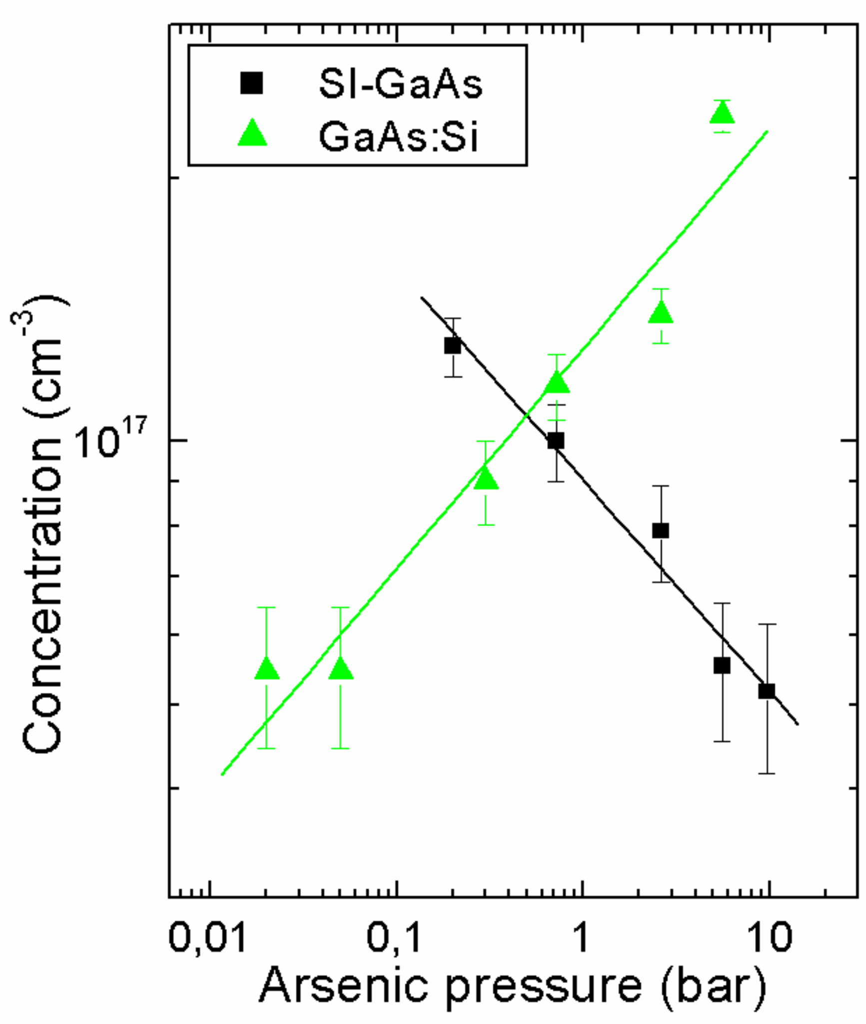
Mass action law:

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

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

$\rightarrow n = 1/4$

Comparison of doped and undoped GaAs



Bondarenko et al., 2003

Thermodynamic reaction:

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

Mass action law:

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

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

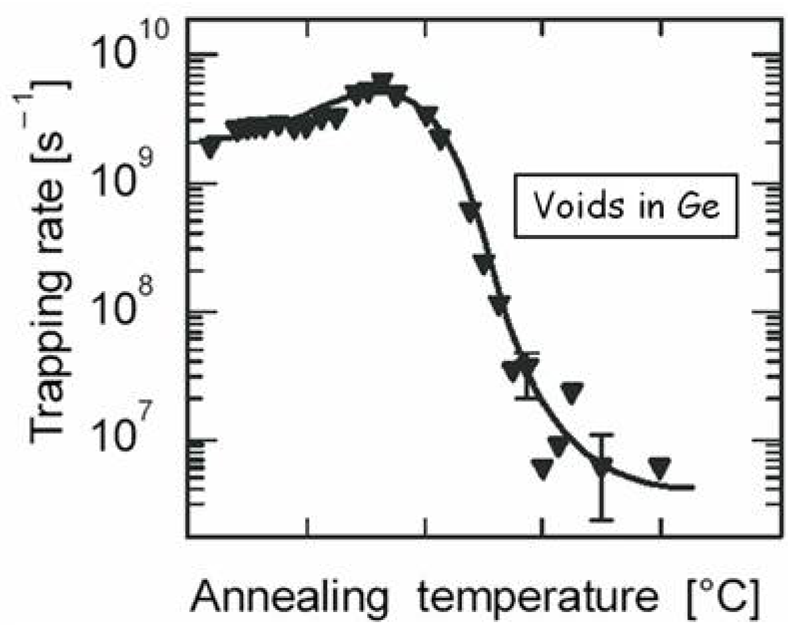
$\rightarrow n = -1/4$

↓

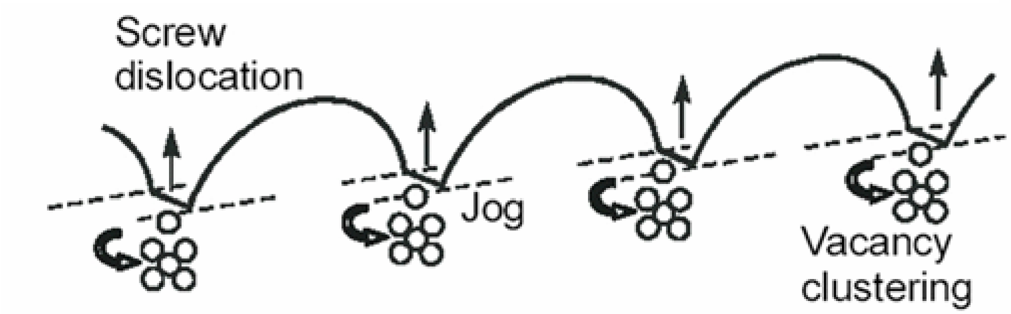
As vacancy

Vacancy clusters in semiconductors

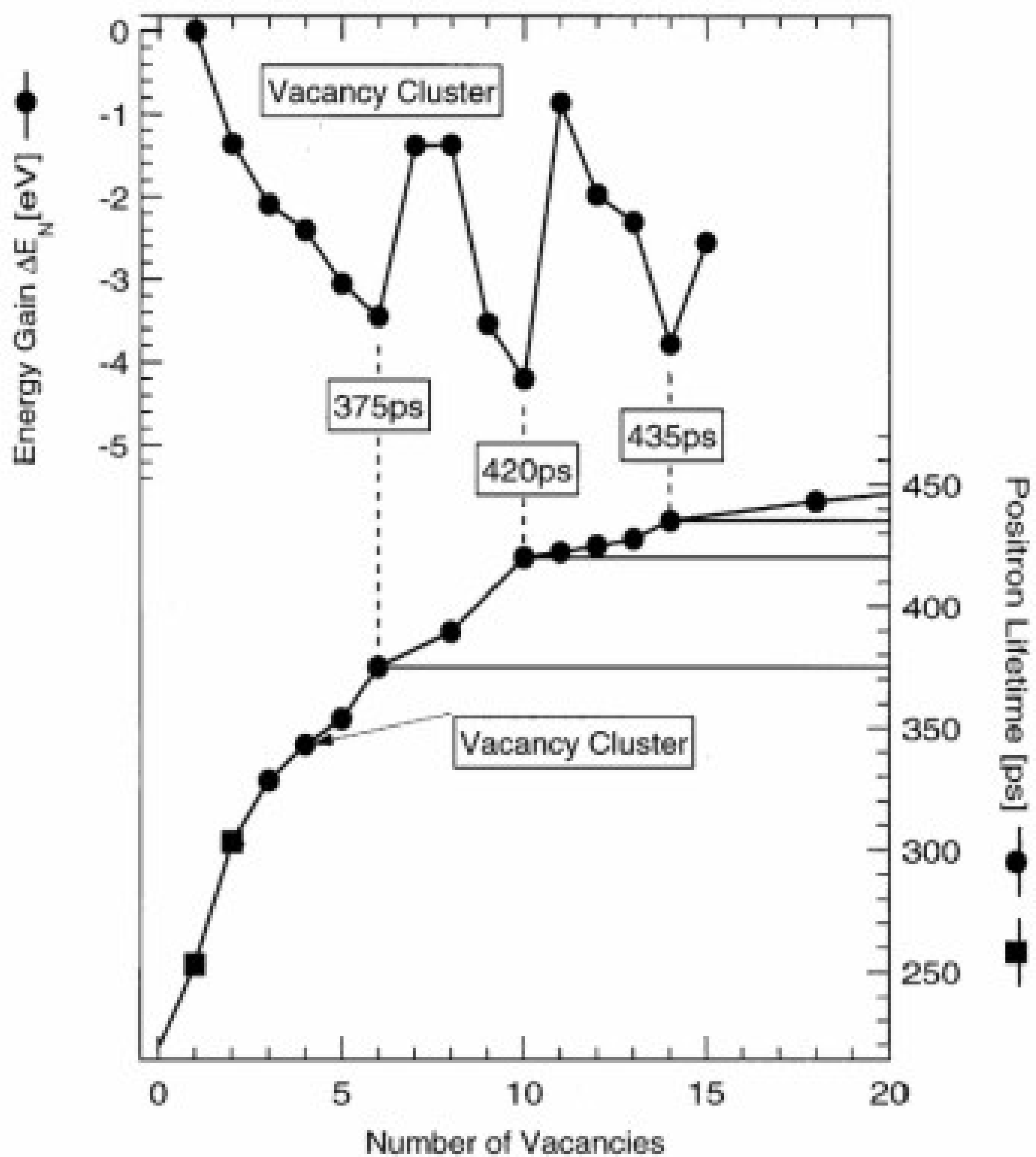
- vacancy clusters were observed after neutron irradiation, ion implantation and plastic deformation
- due to large open volume (low electron density) -> positron lifetime increases distinctly
- example: plastically deformed Ge
- lifetime: τ = 525 ps
- reason for void formation: jog dragging mechanism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



Krause-Rehberg et al., 1993



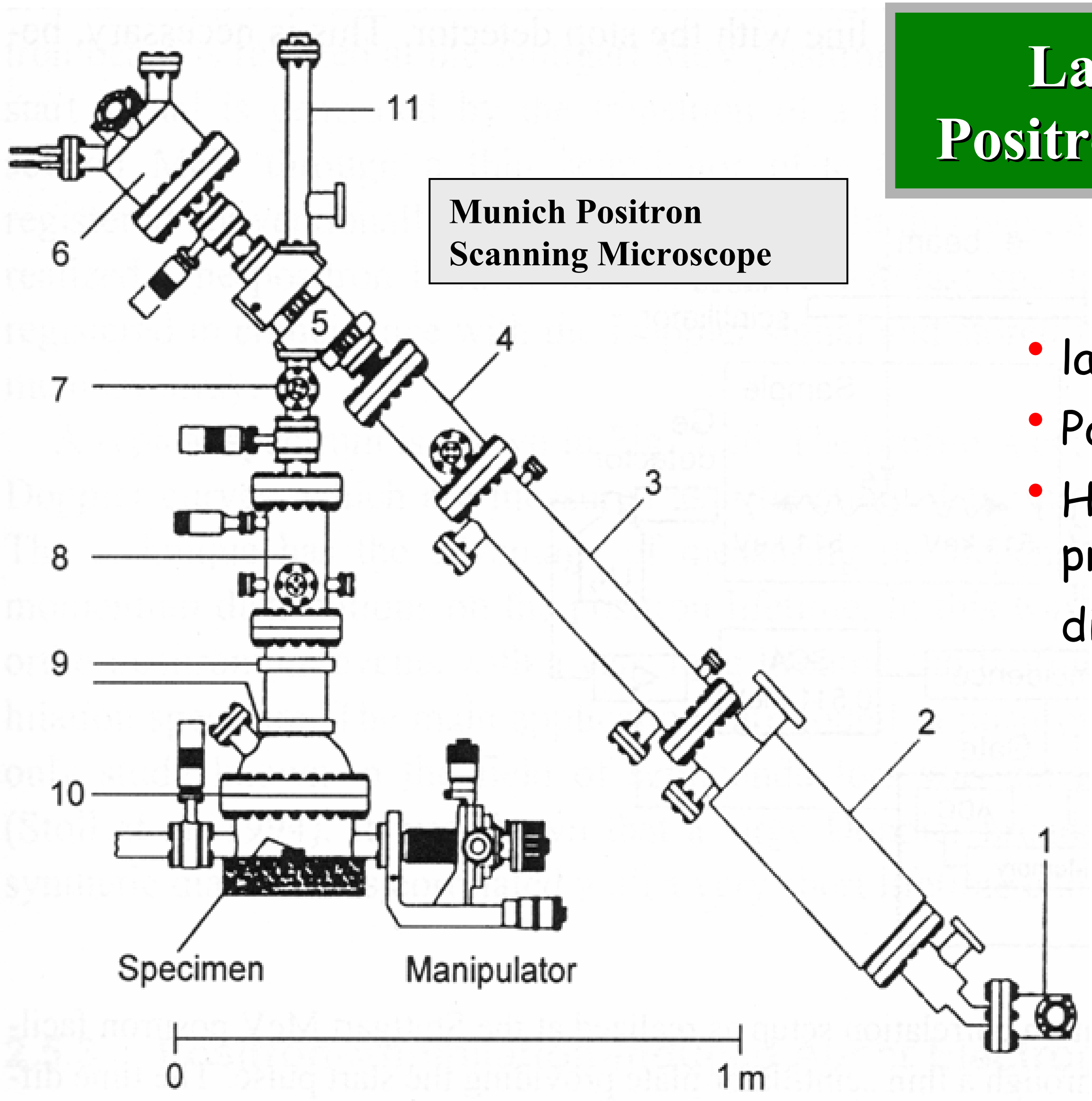
Theoretical calculation of vacancy clusters in Si



- 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

Lateral Resolution with Positron-Scanning-Microscope

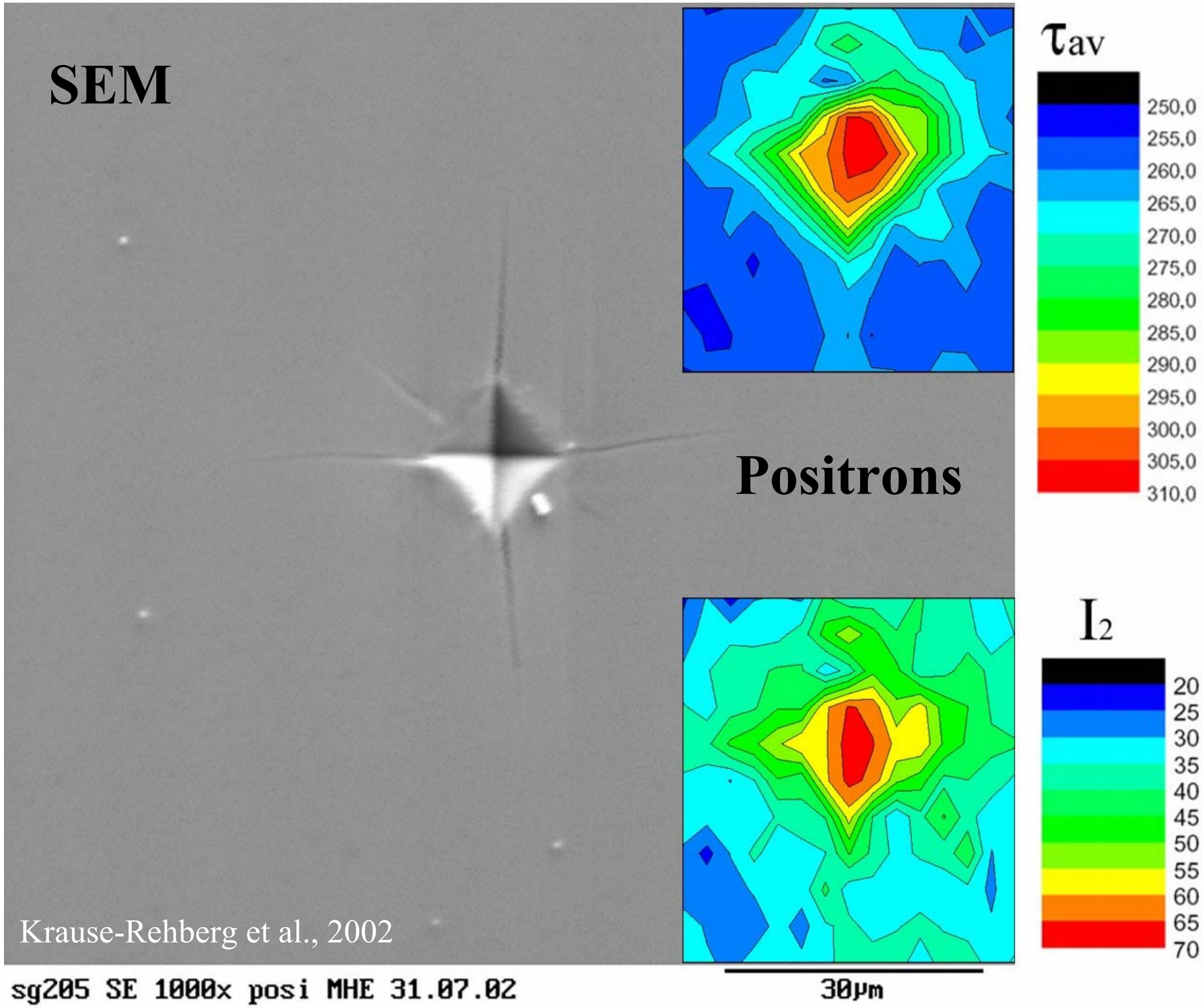


W. Triftshäuser et al., NIM B **130** (1997) 265

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

Microhardness indentation in GaAs

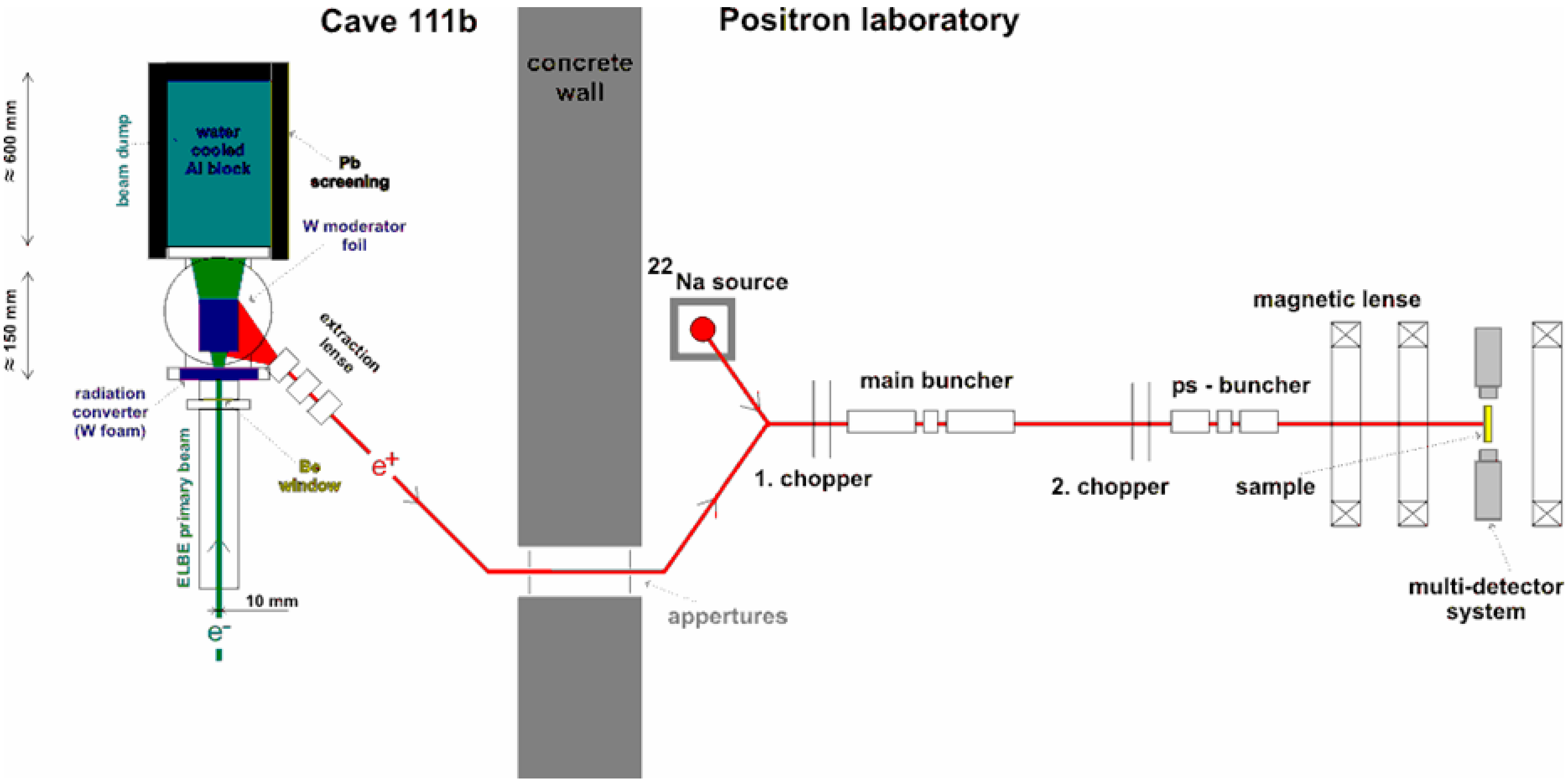
- Comparison of SEM and Munich Positron Scanning Microscope
- problem here at the moment: intensity
- hope: strong positron source at FRM-II Garching or EPOS project in Rossendorf



EPOS = ELBE Positron Source

- ELBE -> electron LINAC (40 MeV and up to 40 kW) in Research center Rossendorf (near Dresden)
- EPOS will be the combination of a positron lifetime spectrometer, Doppler coincidence, and AMOC
- User-dedicated facility
- main features:
  - ultra high-intensity bunched positron beam (E_+=1…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
  - fast lifetime mode (single detector mode) for kinetic investigations
  - very high count rate (> 10^6 s^{-1}) by multi-detector array
  - conventional source included for Doppler measurements (when primary beam is not available)
  - fully remote control via Internet by user

Schematic view of EPOS (ELBE Positron Source)



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 solids
- Positrons are sensitive for charge state of vacancies in semiconductors
- vacancy clusters can easily be observed by positron lifetime spectroscopy (appear after irradiation and plastic deformation)

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

contact: mail@KrauseRehberg.de