Vacancy-like defects in undoped annealed GaAs

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Defect chemistry in undoped GaAs: *introduction*

Physical background of positron annihilation

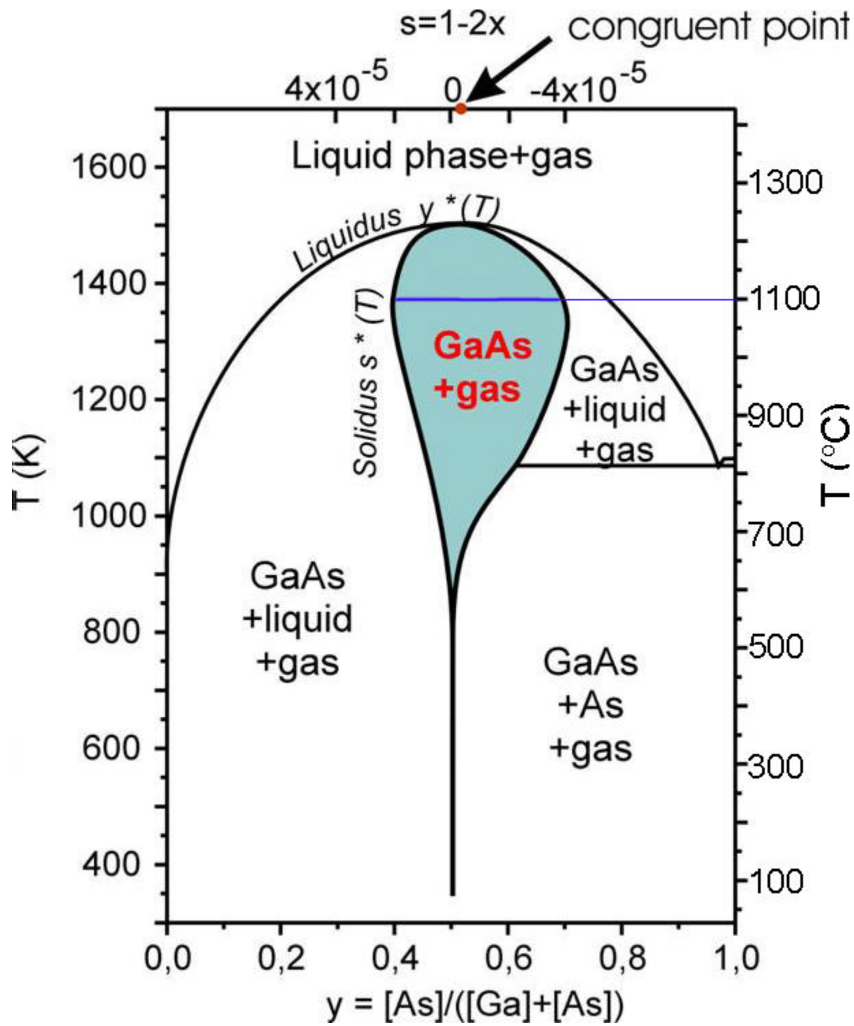
- Positron lifetime spectroscopy
- Doppler coincidence spectroscopy
- Defects identification in doped GaAs

Results of positron annihilation

Defects identification

Defect chemistry in undoped GaAs

- **Idea**: investigation of the native point defects configuration in different equilibrium states
- **Material**: semi-insulating GaAs
- Continuation of the work done on n-type GaAs: **GaAs:Si, GaAs:Te**



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

Native point defects in GaAs

GaAs Vapor – Solid system has F = C – P + 2 = 2 degrees of freedom

Six native point defects demand six reactions:

$$\frac{1}{4} As_{4,vap} \leftrightarrow I_{As} \Rightarrow K_1(T) = \frac{[I_{As}]}{P_{As_4}^{1/4}}$$

$$Ga_{vap} \leftrightarrow I_{Ga} \Rightarrow K_2(T) = \frac{I_{Ga}}{P_{Ga}}$$

$$As_{As} \leftrightarrow I_{As} + V_{As} \Rightarrow K_3(T) = [I_{As}][V_{As}]$$

$$Ga_{Ga} \leftrightarrow I_{Ga} + V_{Ga} \Rightarrow K_4(T) = [I_{Ga}][V_{Ga}]$$

$$Ga_{Ga} + I_{As} \leftrightarrow As_{Ga} + I_{Ga} \Rightarrow K_5(T) = \frac{[As_{Ga}][I_{Ga}]}{[I_{As}]}$$

$$As_{As} + I_{Ga} \leftrightarrow Ga_{Ga} + I_{As} \Rightarrow K_6(T) = \frac{[Ga_{As}][I_{Ga}]}{[I_{Ga}]}$$

For given T

$$[I_{As}] \propto P_{As_4}^{1/4}$$

$$[I_{Ga}] \propto P_{As_4}^{-1/4}$$

$$[V_{As}] \propto P_{As_4}^{-1/4}$$

$$[V_{Ga}] \propto P_{As_4}^{1/4}$$

$$[As_{Ga}] \propto P_{As_4}^{1/2}$$

$$[Ga_{As}] \propto P_{As_4}^{-1/2}$$

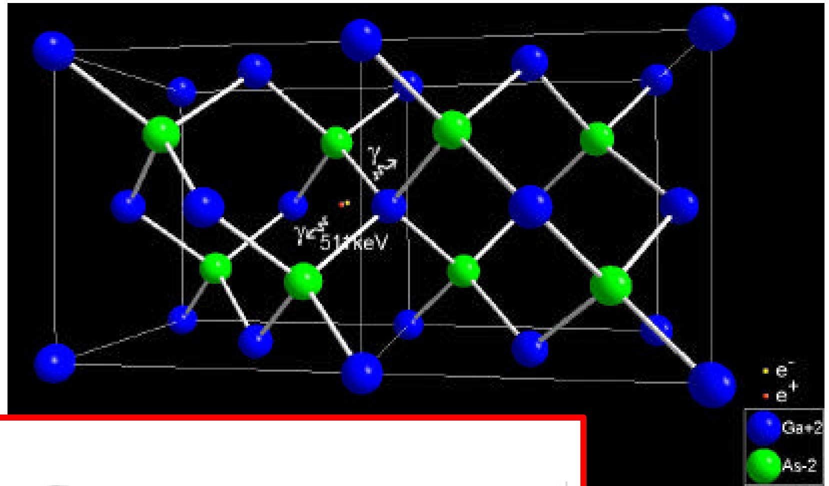
Positron lifetime spectoscopy

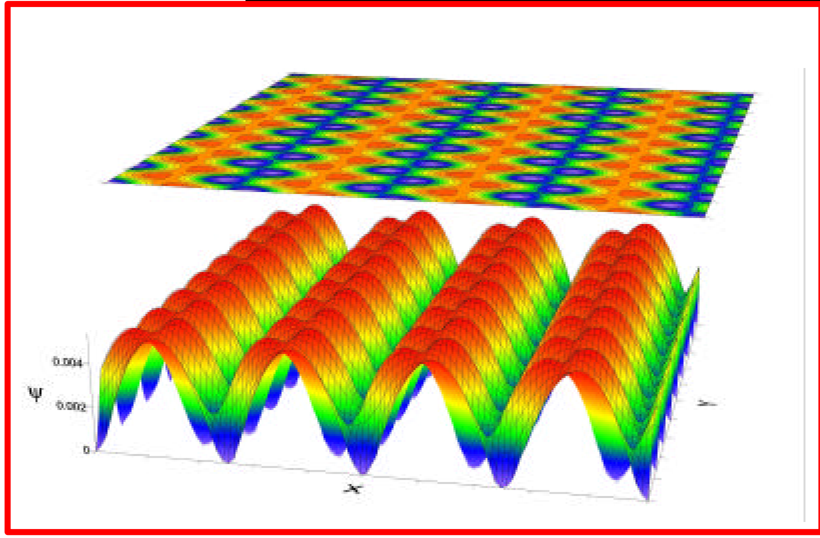
Annihilation in a perfect crystal

1) Thermalization
$t \approx 3$ ps
$E \approx 200 keV \rightarrow 0.026$ eV

2) Diffusion
$L_+ \approx 100$ nm

3) Annihilation with emitting of two γ-quanta
$E_\gamma = 511$ keV





Positron wave function in GaAs (110) plane

Time between positron burth and it's annihilation (positron lifetime) is measured

Positron lifetime spectroscopy

N(*t*) - probability that e⁺ is alive at time *t* : $\frac{\mathrm{dn}(t)}{\mathrm{d}t} = -l\ n(t)$ $\quad n(0) = 1$

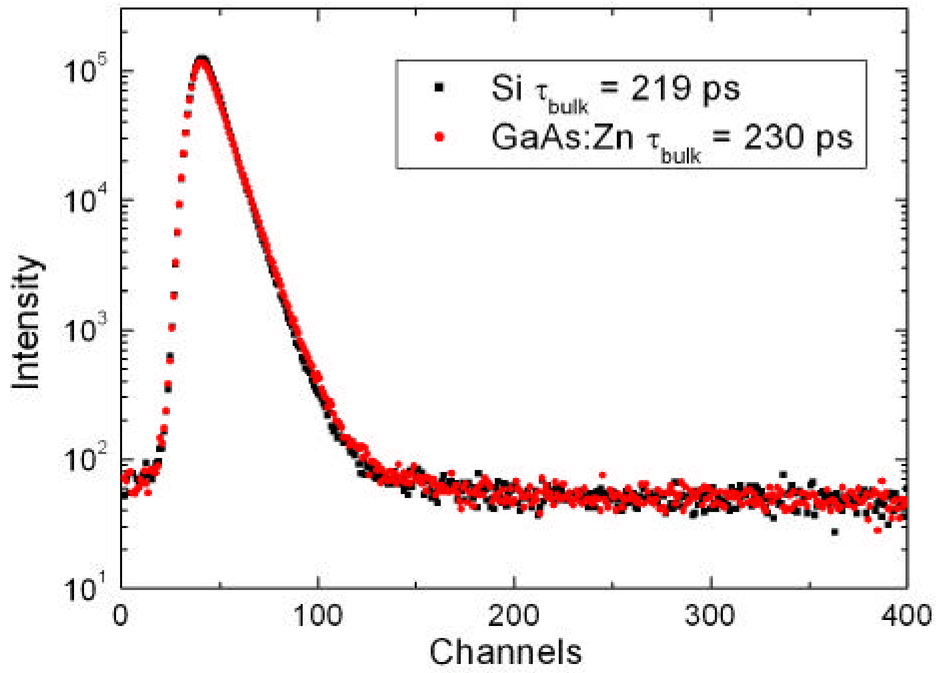
$$n(t) = e^{-l\,t}$$

positron annihilation rate: $l = p \cdot r_0 \cdot c \int y_+(\mathbf{r}) y_-(\mathbf{r}) g\ \mathrm{d}\mathbf{r}$

free (bulk) positron lifetime: $t_{bulk} = \frac{1}{l_{bulk}}$

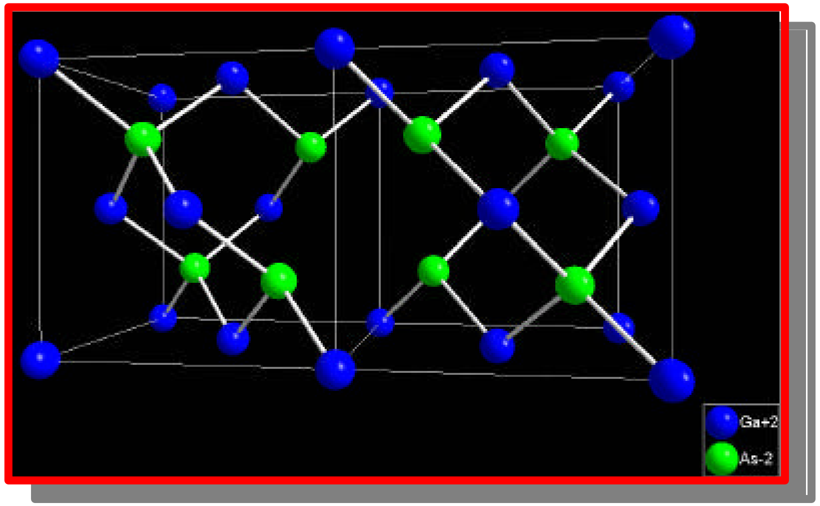
positron lifetime spectrum:

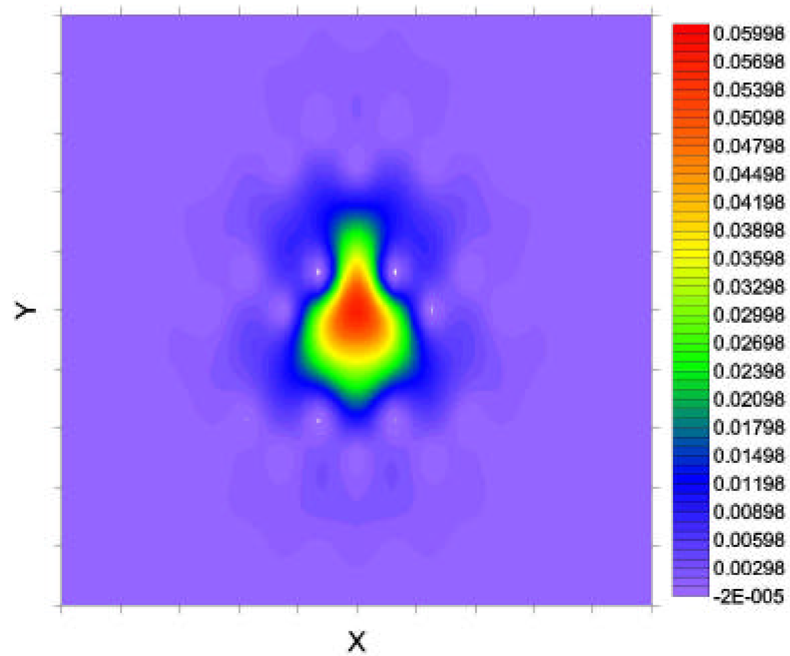
$$-\frac{\mathrm{dn}(t)}{\mathrm{d}t} = l e^{-lt}$$

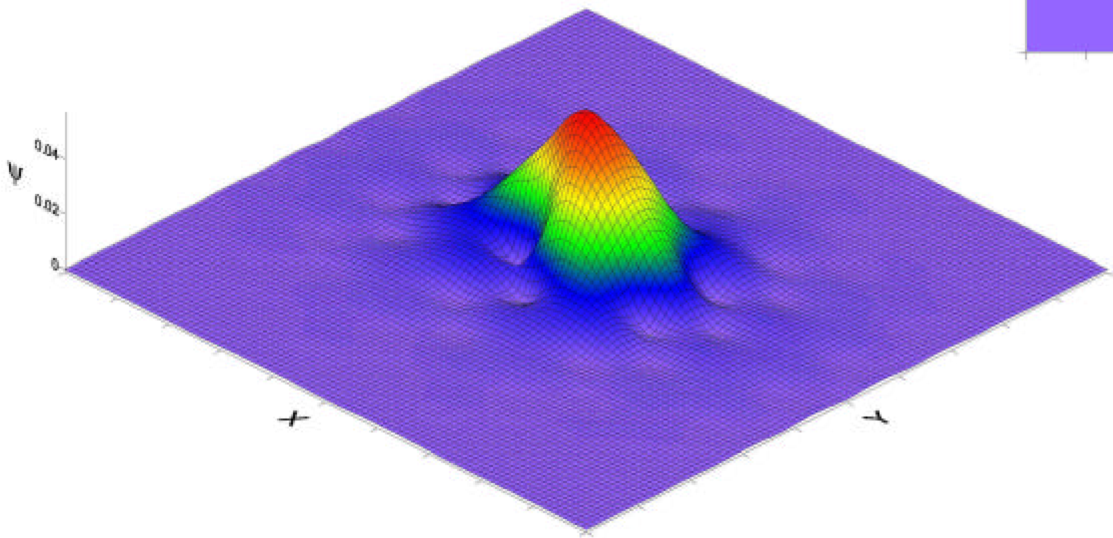


Positron lifetime spectroscopy

Trapping into a vacancy







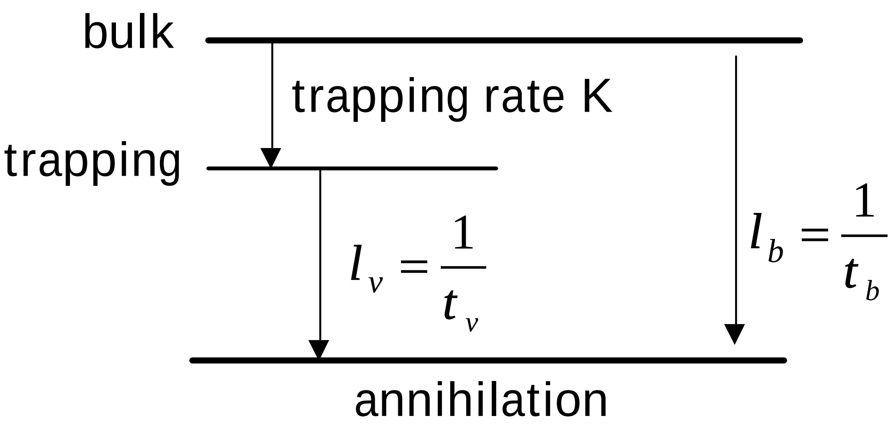
Positron wave function for V_{Ga} in GaAs in (110) plane

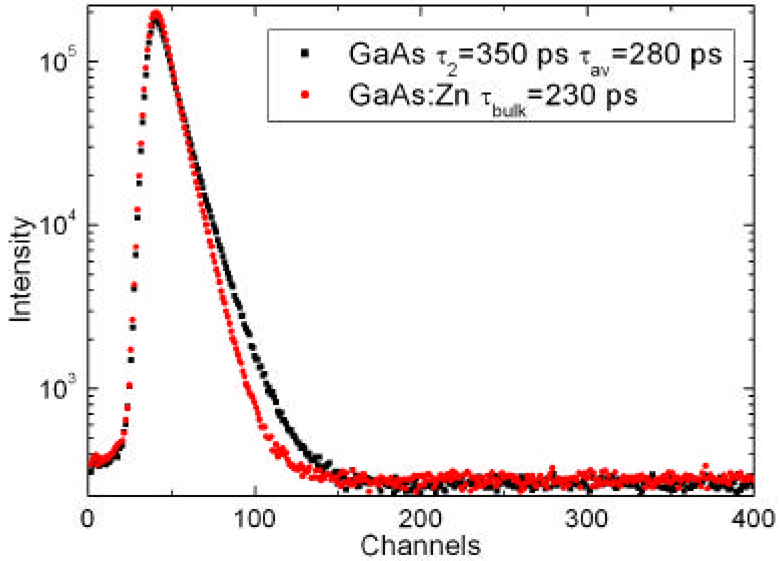
$$\lambda_v = \pi r_0 c \int \psi_+(r)\psi_-(r)\gamma\, dr$$

$$\lambda_v < \lambda_b \Rightarrow \tau_v = \frac{1}{\lambda_v} > \tau_b$$

Positron lifetime spectroscopy

two-component trapping model





lifetime spectrum $N(t) = I_1 / t_1 \exp(-t/t_1) + I_2 / t_2 \exp(-t/t_2)$

average lifetime $t_{av} = \sum_i I_i t_i$

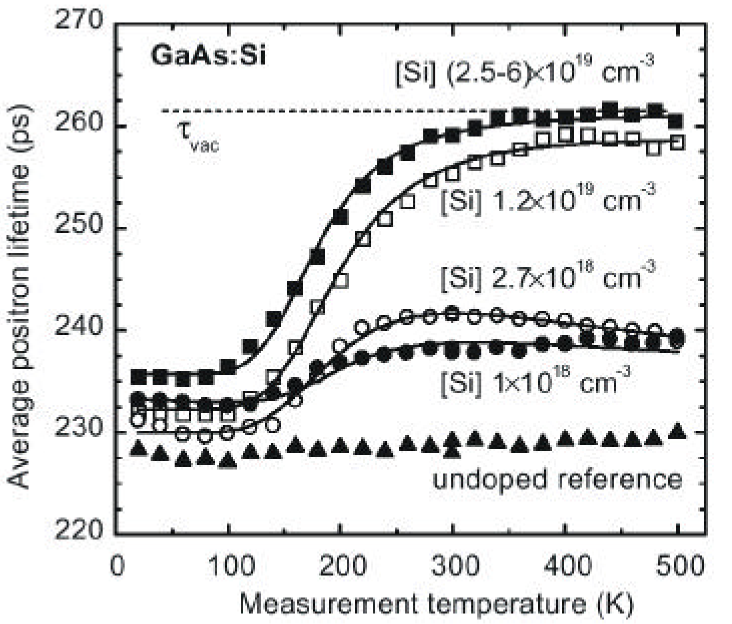
trapping rate K – proportional to the concentration of the trapping centers
defect-related lifetime (t_v) – depends on the electron density
i.e. size of the open-volume of the defect

Positron lifetime spectroscopy

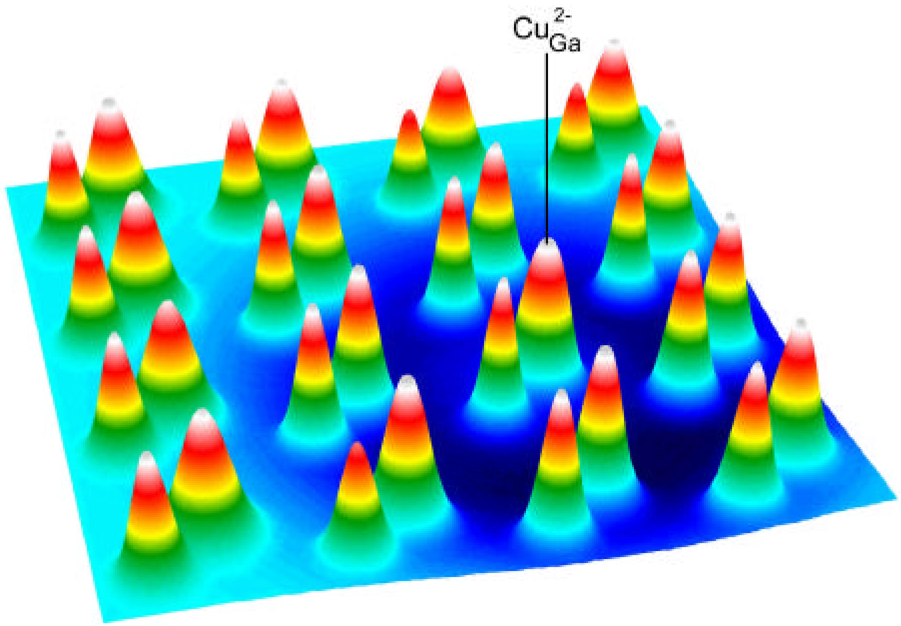
shallow positron traps

not only vacancies can trap positrons

negative ions are positron trapping centers as well due to small negative Coulomb potential



(J. Gebauer et al. 1997)

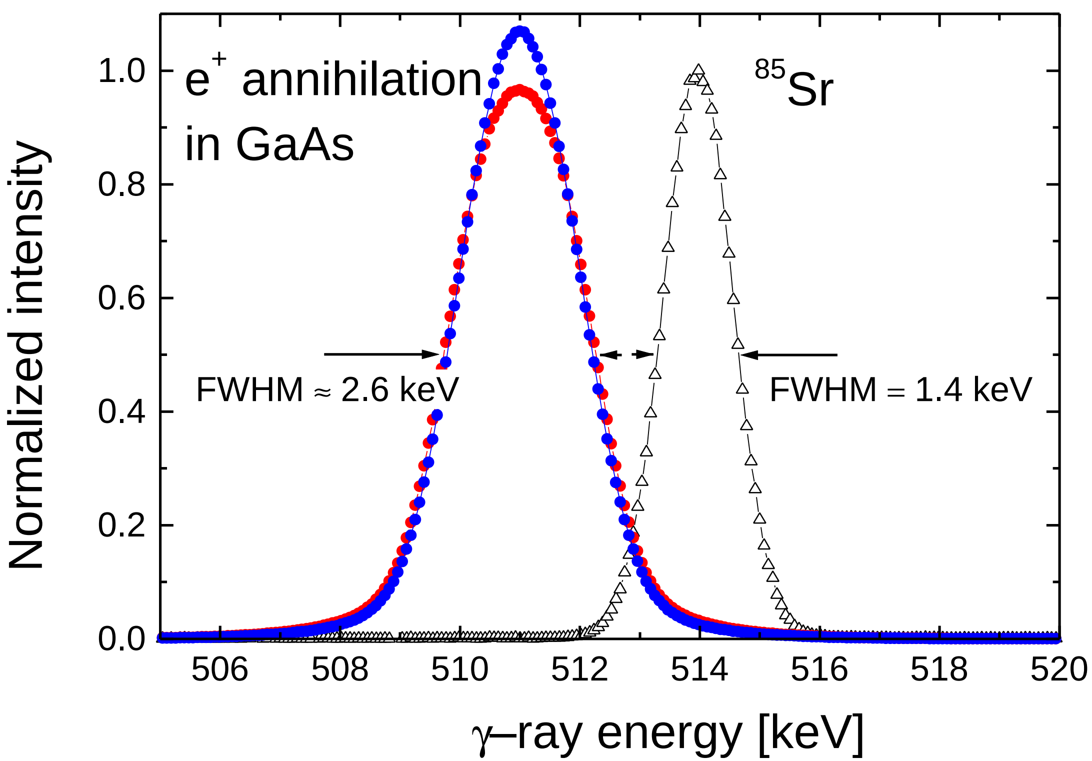


term shallow relates to the positron binding energy (few meV).
Therefore the trapping occurs at low temperatures only

$$t_{st} = t_b$$

Doppler coincidence spectroscopy

Doppler effect

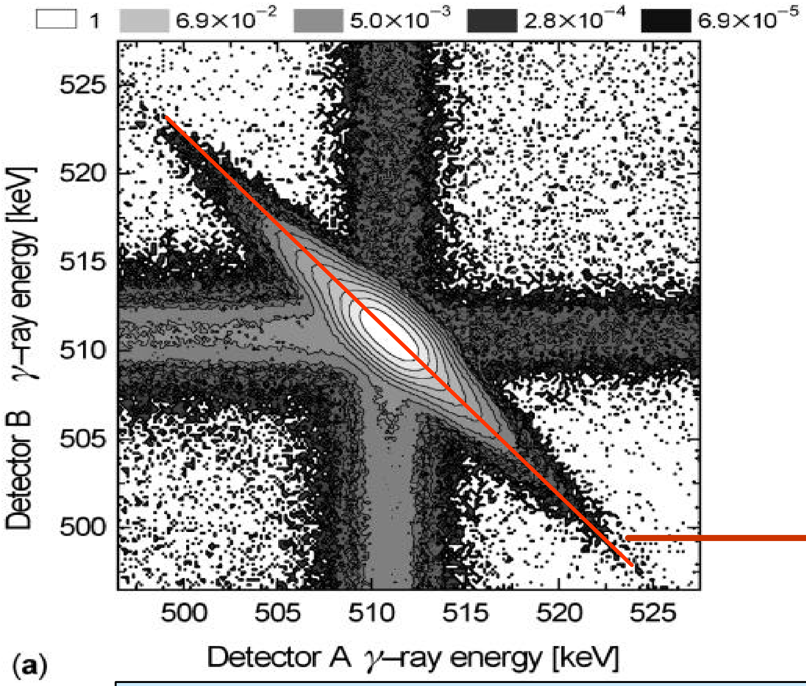


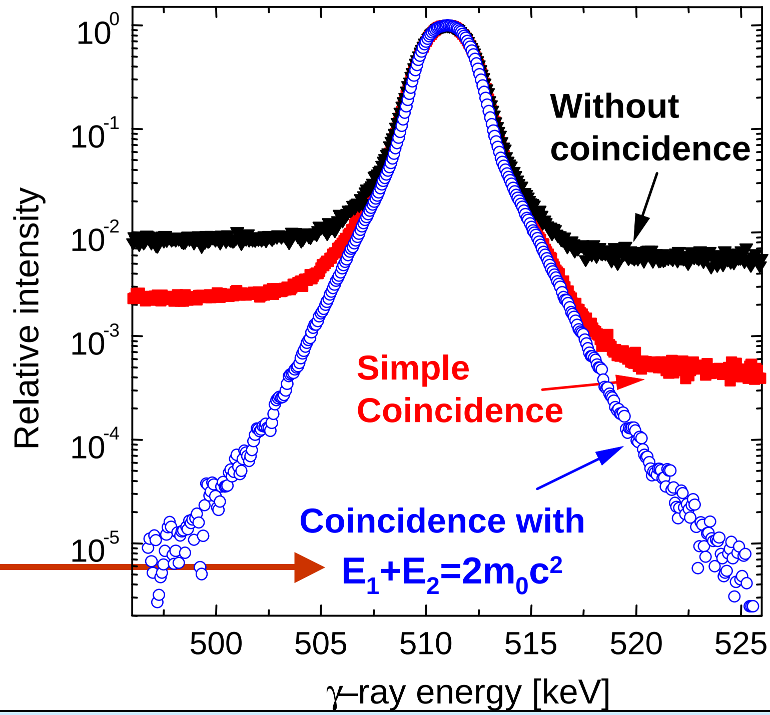
$E_1 - E_2 = p_L c$ E_1, E_2 – energy of γ quanta

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

Doppler coincidence spectroscopy

background reduction





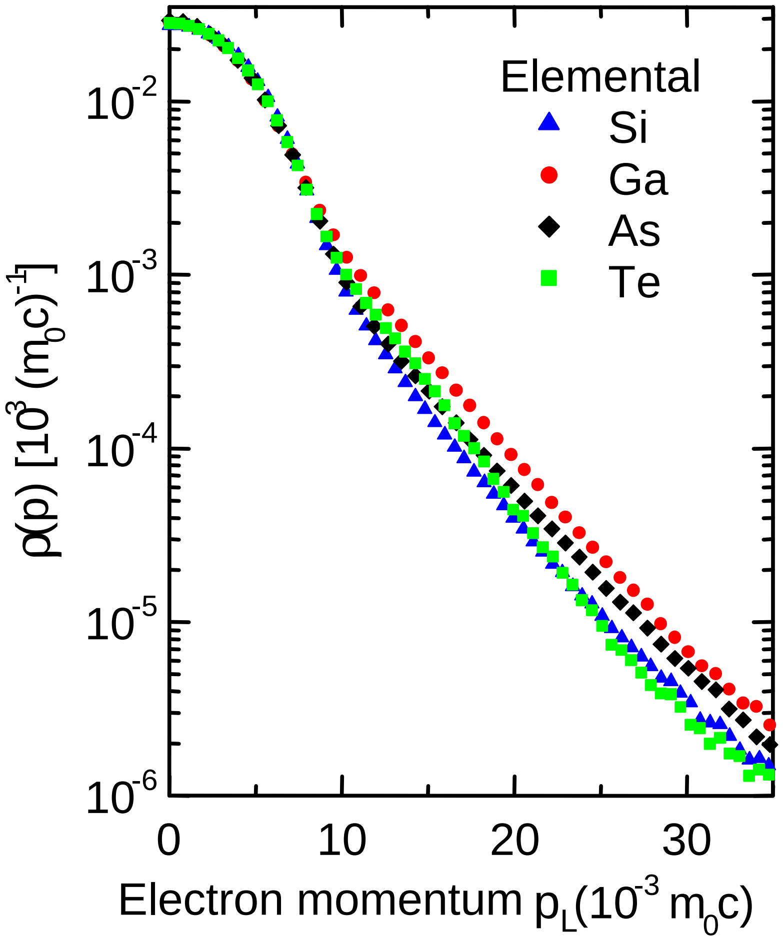
background is dramatically reduced by coincident detection of second annihilation γ-quantum

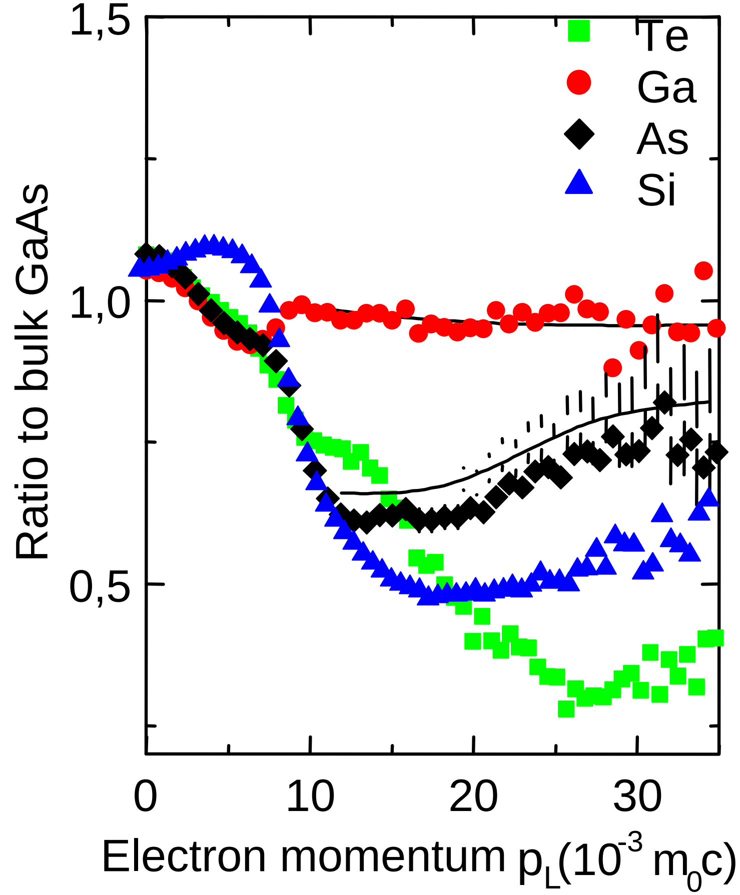
this opens a possibility to investigate the high momentum part of the energy spectrum, i.e. annihilation with core electrons the atoms

thus the chemical surrounding of a positron trap can be studied

Doppler coincidence spectroscopy

chemical sensitivity of energy spectra



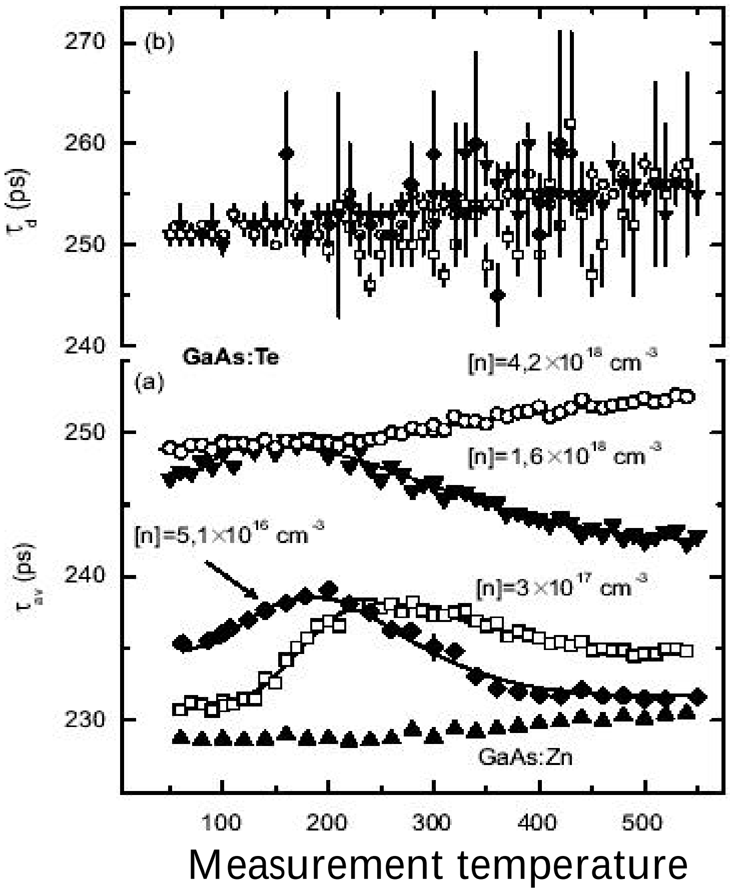


Defects identification in GaAs

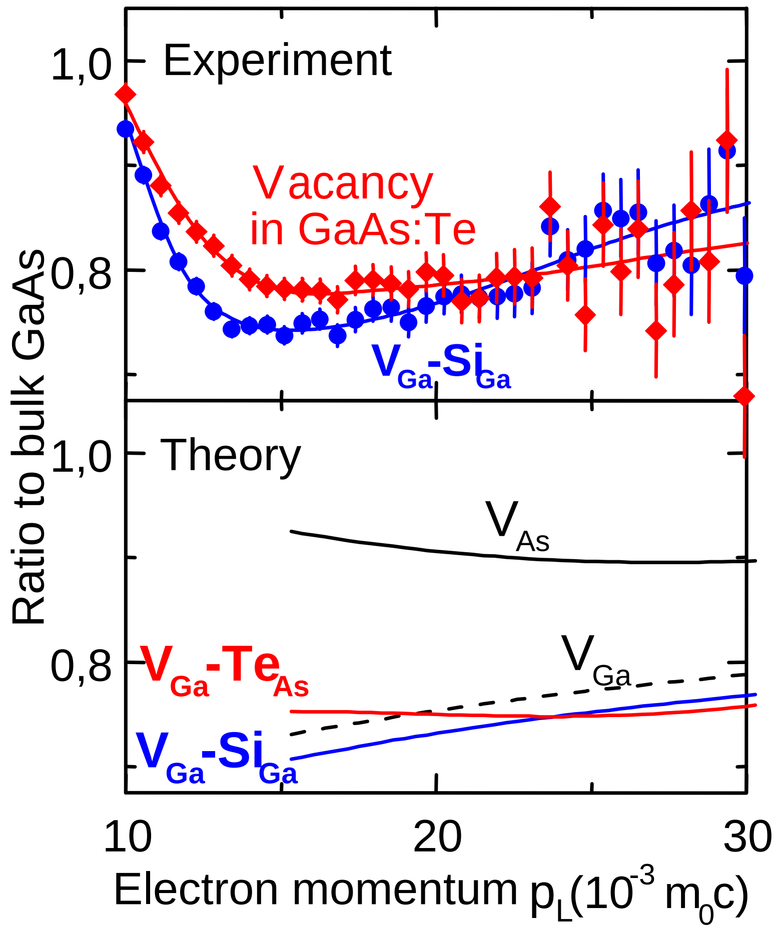
positron lifetime spectroscopy

V_{Ga}-Si_{Ga} in GaAs:Si τ_2 = 260 ps

V_{Ga}-Te_{As} in GaAs:Te τ_2 = 253 ps

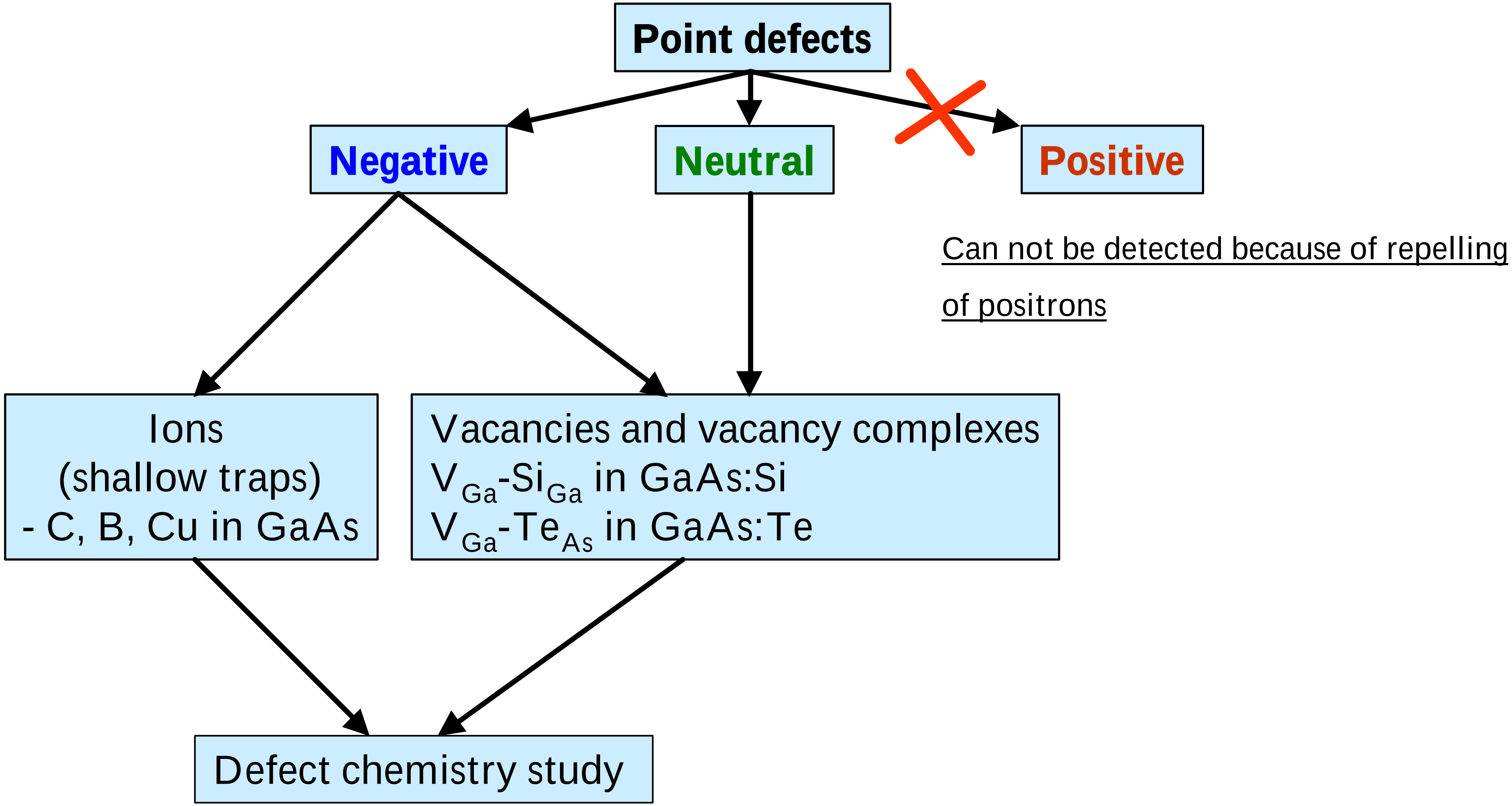


Doppler coincidence



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

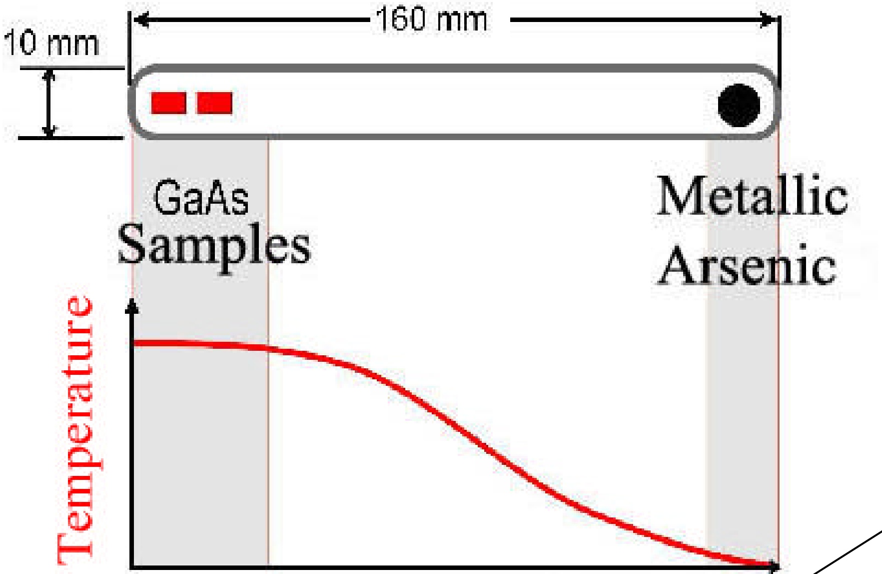
Point defects identification by positron annihilation



Scheme of the experiment

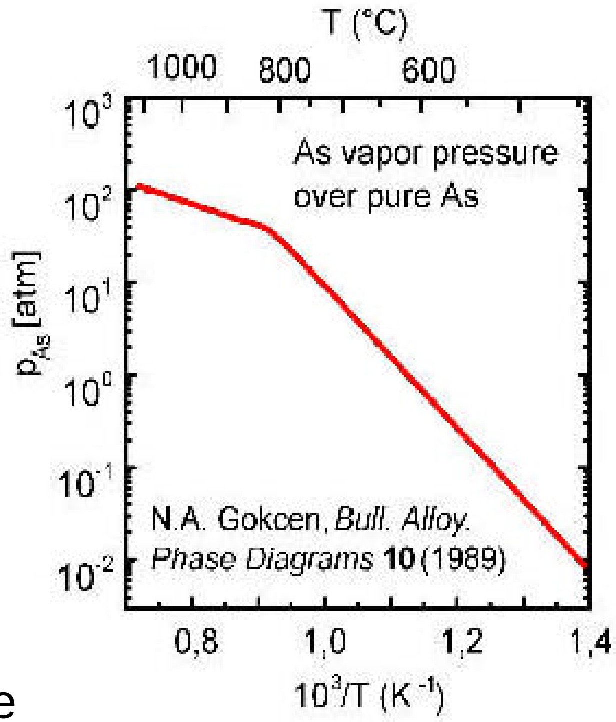
- Use of two-Zone oven to control the samples temperature and As pressure

control two necessary degrees of freedom to fix the equilibrium state (T and P_{As})



Sample T:
1100° C

T_{As}
Defines As Pressure

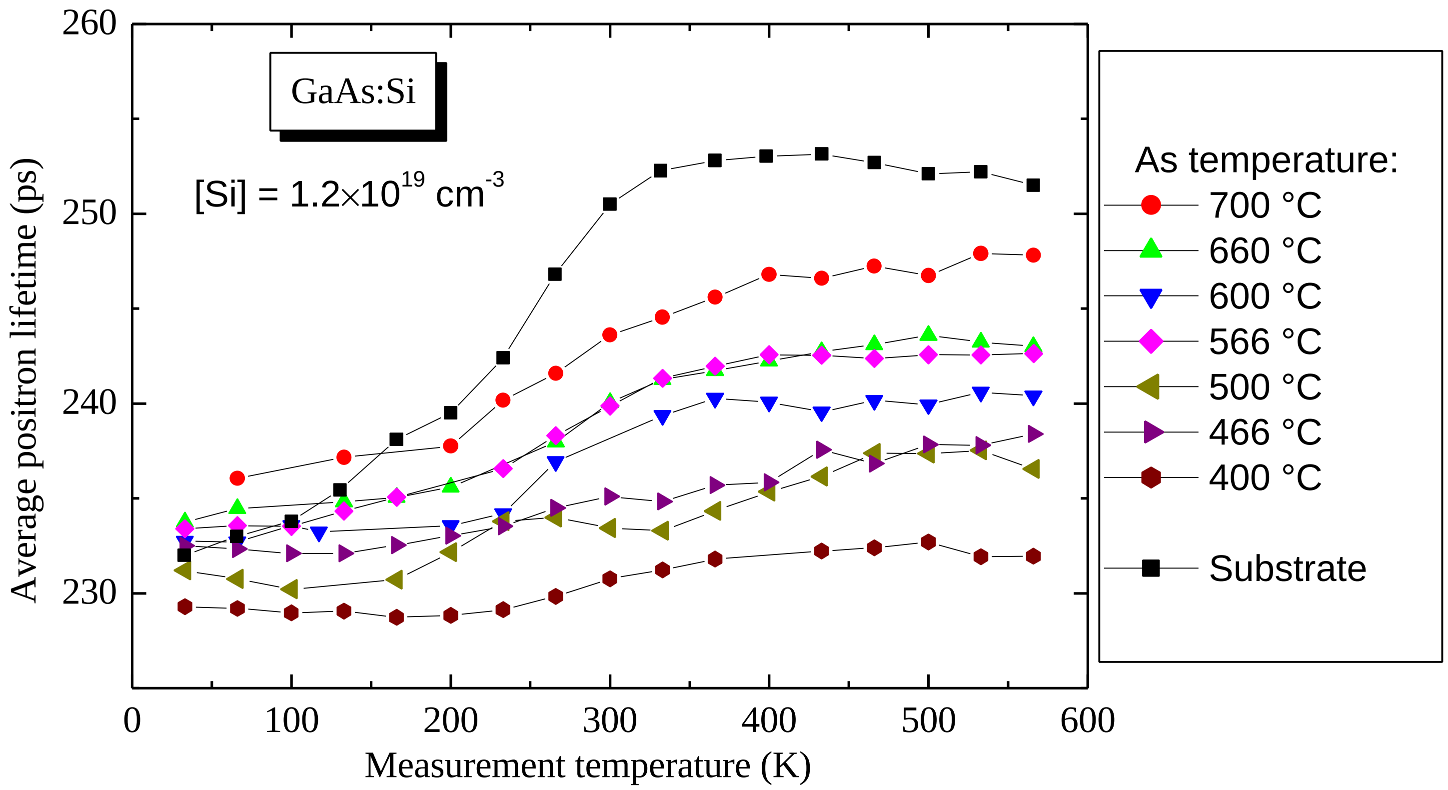


Ampoule: Cu-free quartz (*[Cu] < 0.02 ppm*)
cleaned with 3HCl:1HNO_3

Annealing during 2 hours;
Quenching into the water;
Etching in 2% Bromine Methanol

Annealing experiments in GaAs:Si

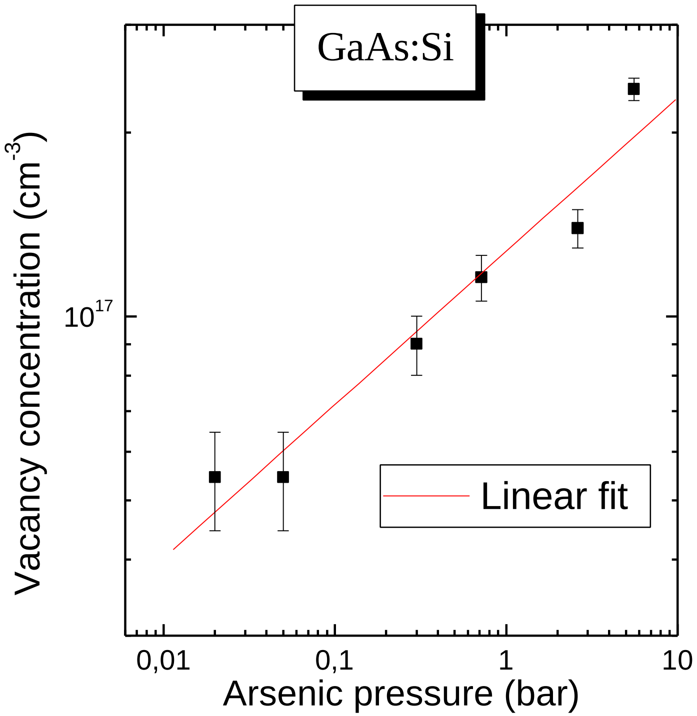
Si_{Ga} – V_{Ga} defect complex



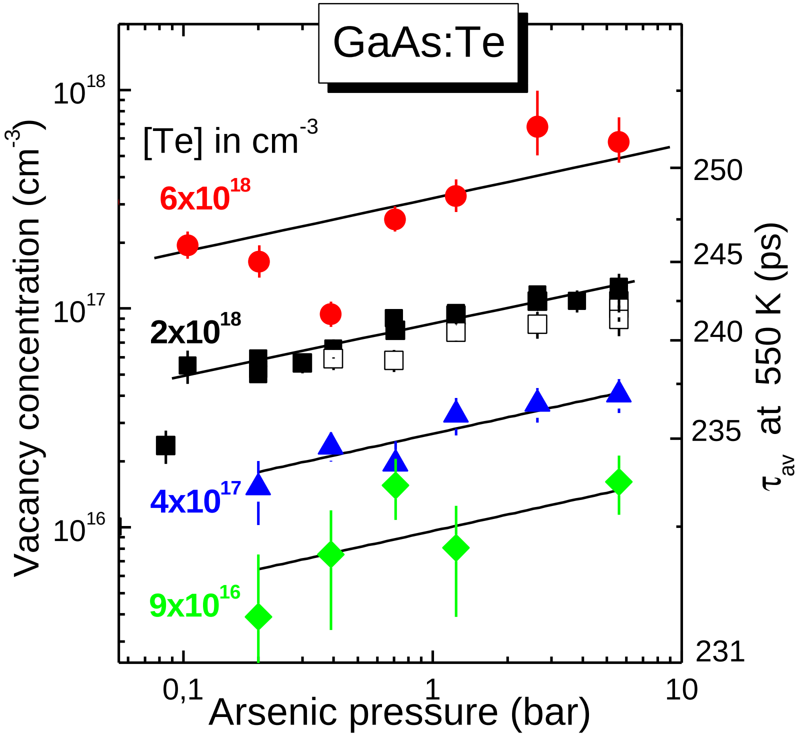
F.Redmann
degree work (1999)

Results in n-type GaAs

Si_{Ga}-V_{Ga}



Te_{As}-V_{Ga}



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

Thermodynamic reaction:

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

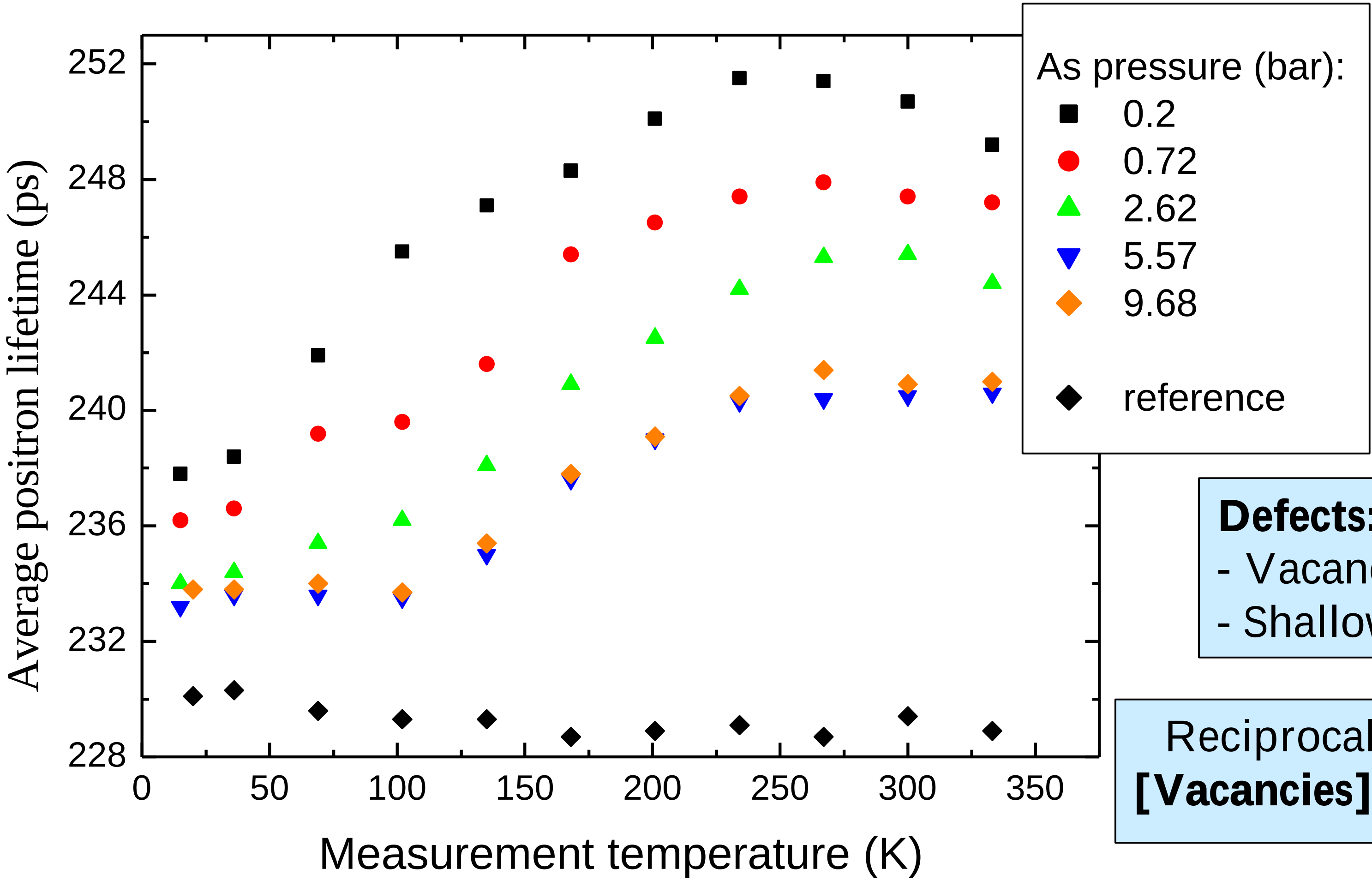
Mass action law:

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

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

$\rightarrow n = 1/4$

Undoped GaAs

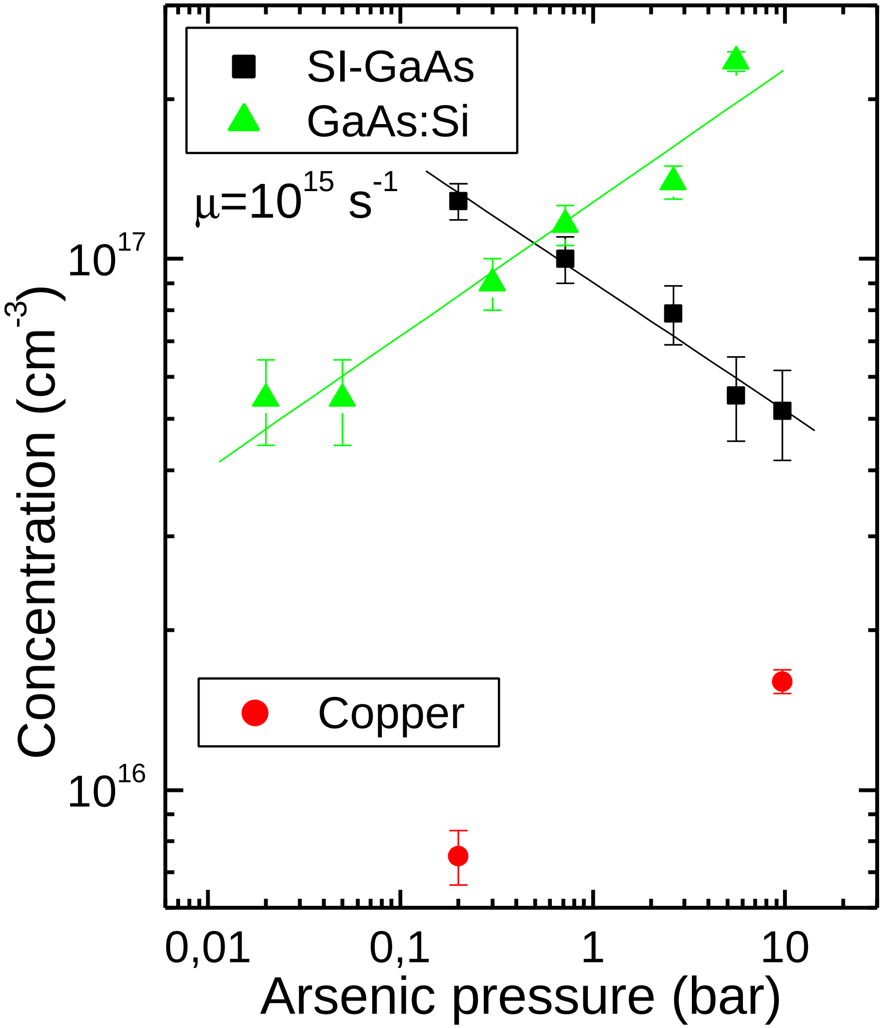


Defects:
- Vacancy complex
- Shallow traps

Reciprocal dependence
[Vacancies] – As pressure

2-component decomposition: τ_2 = 293 ± 10 ps - monovacancy
at 300 K I_2 = 40 – 70 %

Defect identification: vacancy complex



Thermodynamic reaction:

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

Mass action law:

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

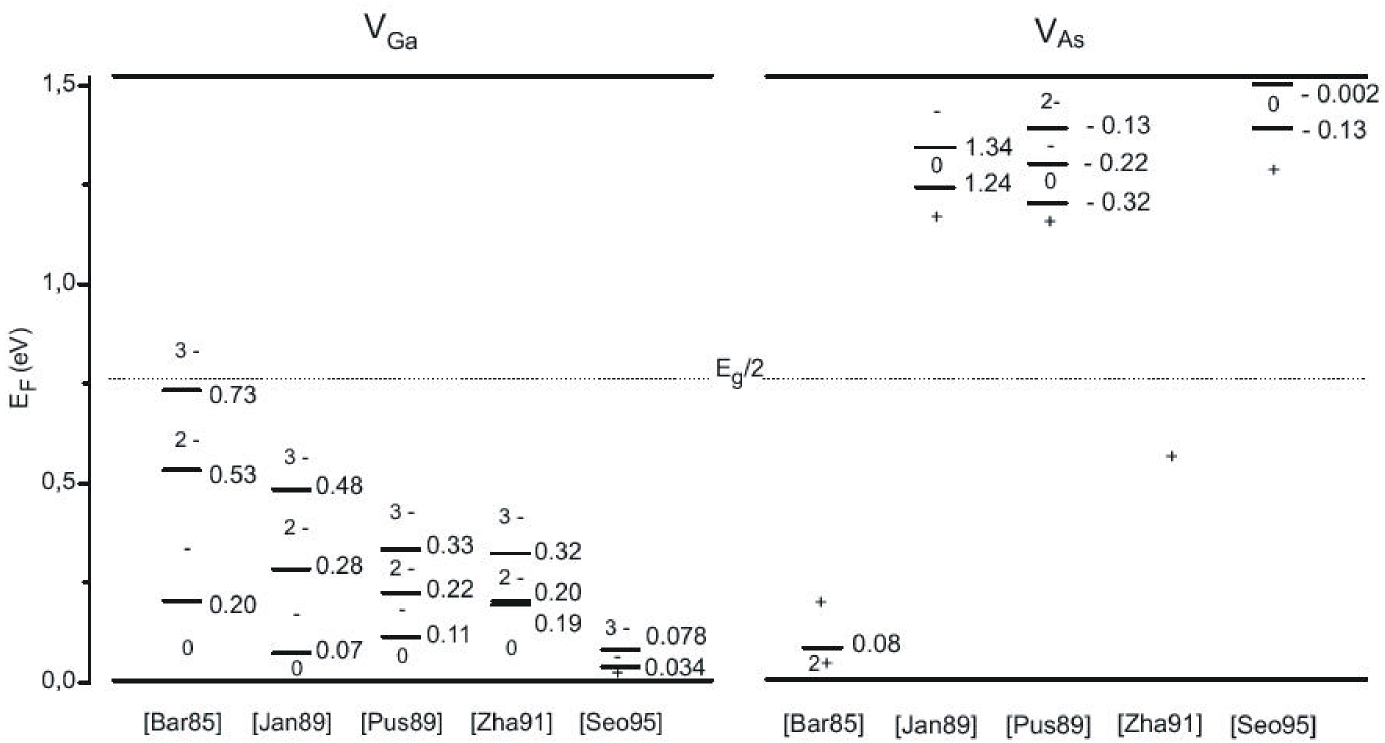
Fit: $[\text{V-complex}] \sim p_{As}^{n}$

$\rightarrow n = -1/4$

As vacancy

Cu is the first candidate for the complex, due to unavoidable contamination - confirmed by titration and photoluminescence measurements

Defect identification: V_{As}-X

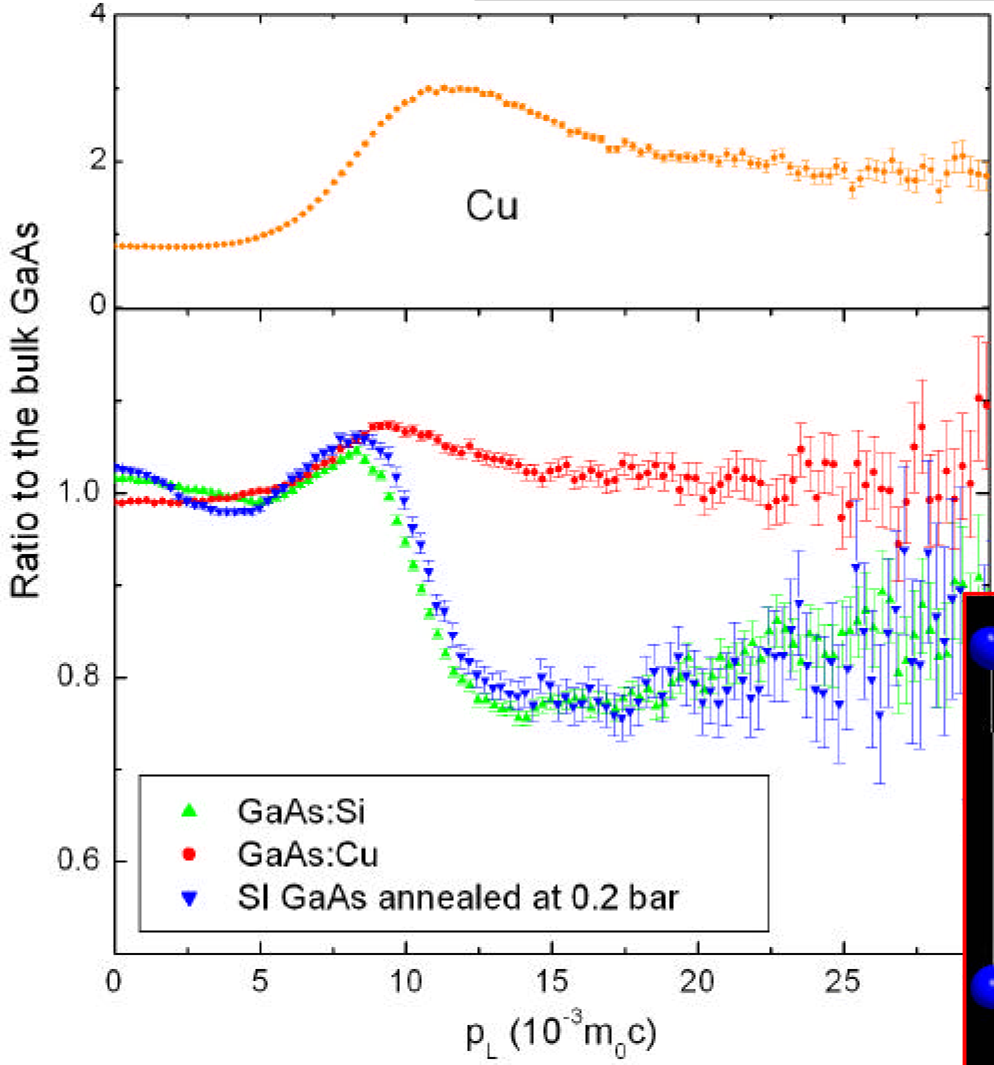


According to all theoretical calculations V_{As} are always positive in SI an p-type GaAs ⇒ not visible for positrons

⇩

V_{As}-X complex is observed

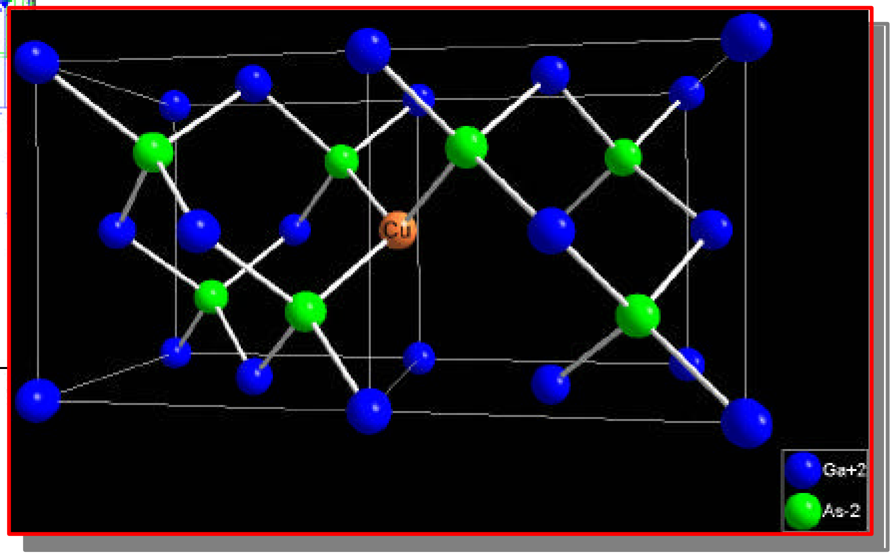
Doppler Coincidence measurements



Most popular candidates:
$V_{As}Cu_{Ga}V_{As}$
$Cu_{Ga}V_{As}$
$Cu_{Ga}V_{As}Cu_{Ga}$

but

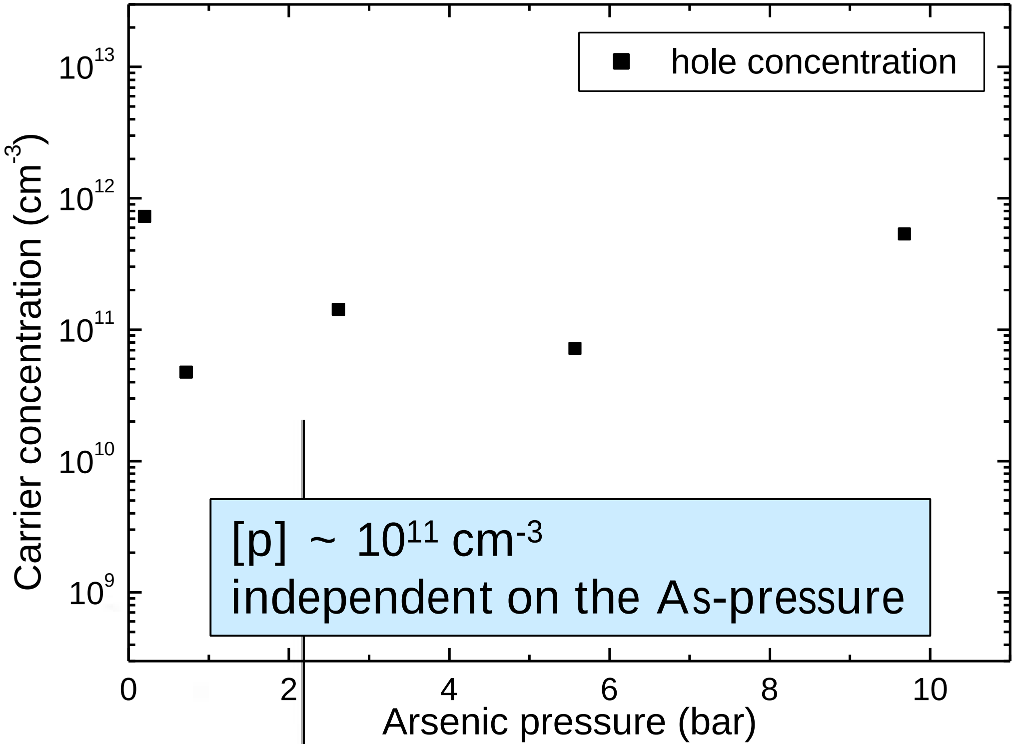
Cu cannot be the nearest neighbor in our case



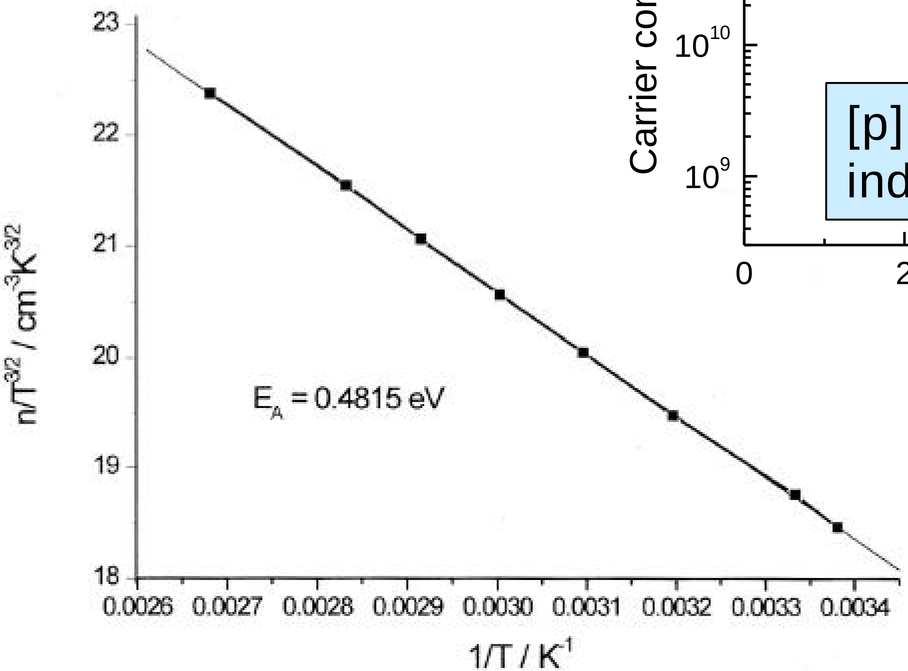
Hall measurements

Acceptor level:
$E_A = E_V + 0.48$ eV

usually attributed to copper defect complex



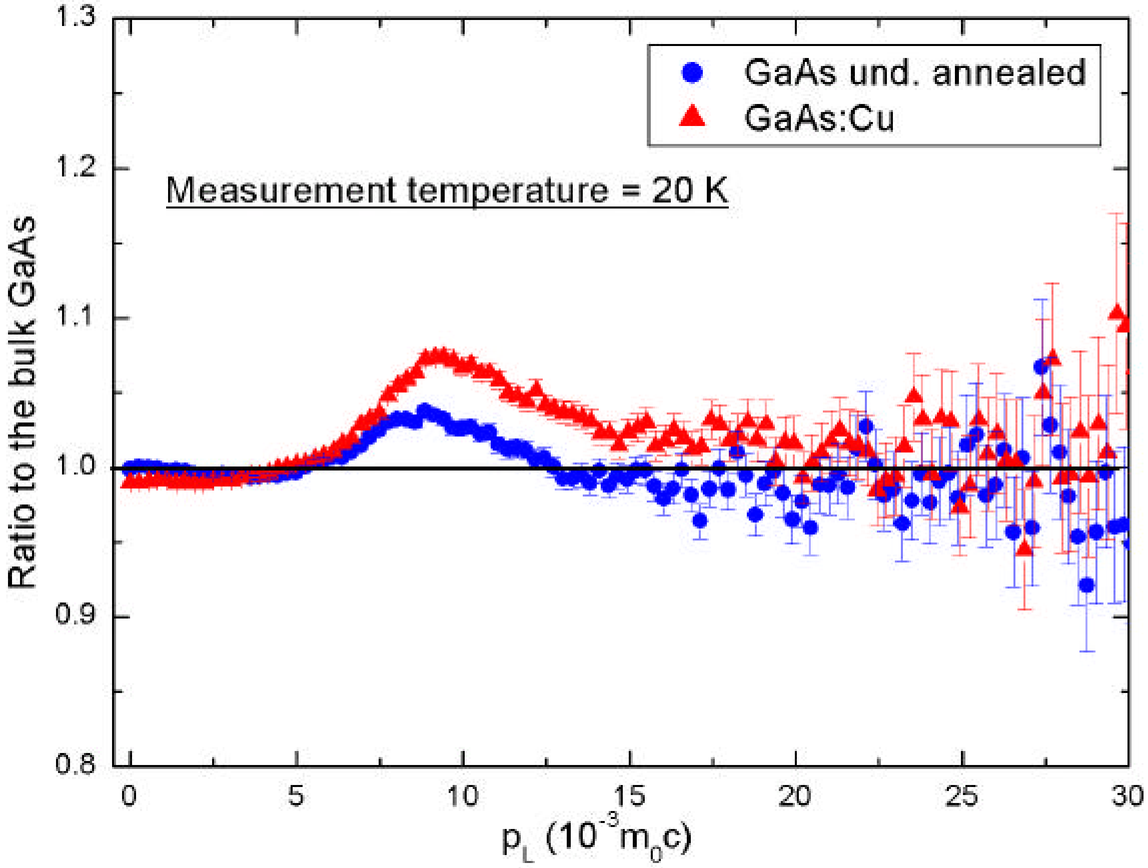
[p] ~ 10^{11} cm^{-3}
independent on the As-pressure



Cu_{Ga} acts as an acceptor and as a shallow trap for positrons

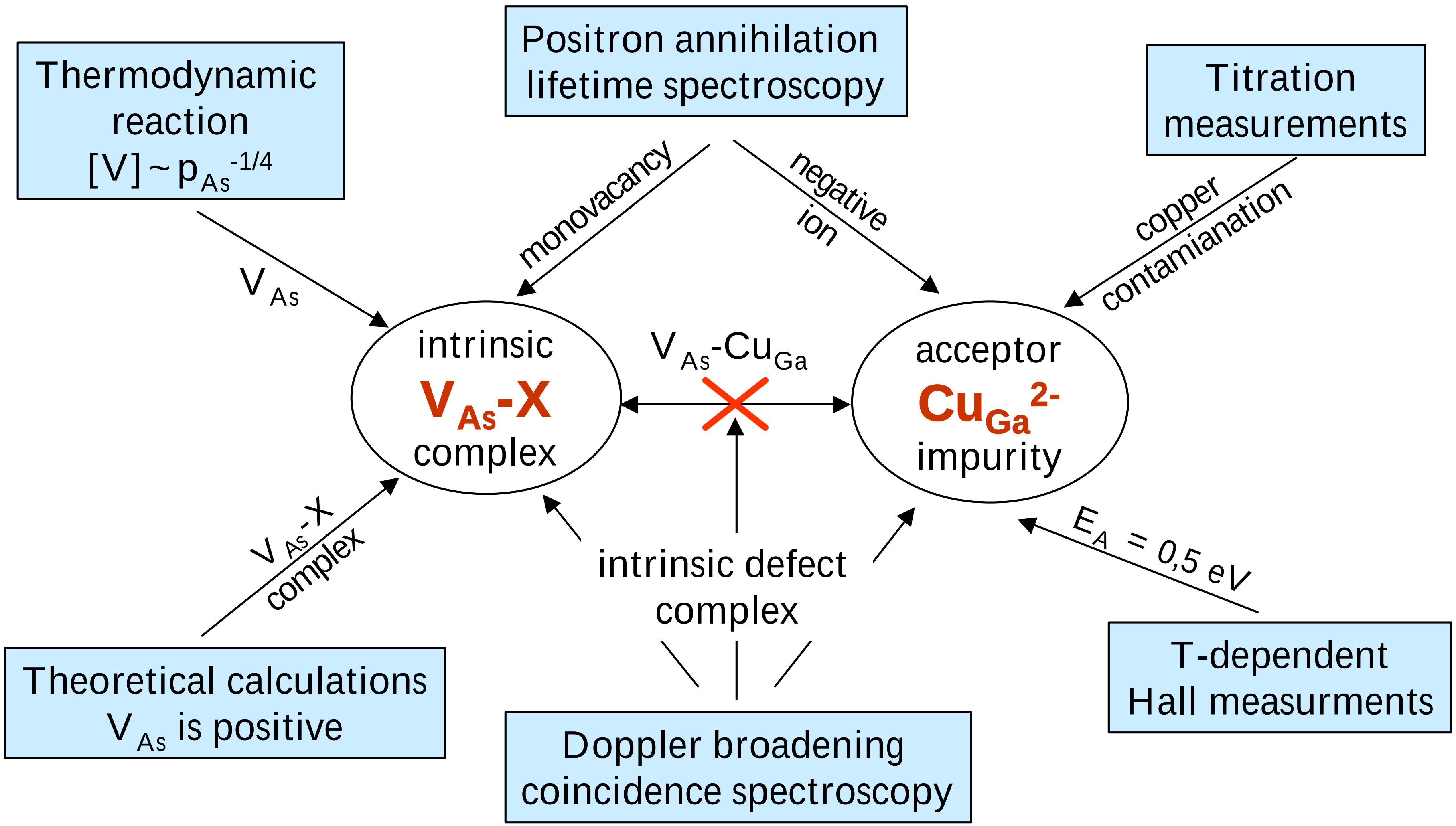
Defect identification: shallow trap

Doppler coincidence



Cu_{Ga}^{2-} acceptors are positron traps at 20 K

Defects identification – Summary



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