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SMR.550 - 25

SPRING COLLEGE IN MATERIALS SCIENCE ON
"NUCLEATION, GROWTH AND SEGREGATION IN MATERIALS
SCIENCE AND ENGINEERING"
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TRANSPORT PROCESSES
(INCLUDING RADIATION ENHANCED DIFFUSION)
Part III

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These are preliminary lecture notes, intended only for distribution to participants.

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The Interplay of Solute- and Self-Diffusion – a Key for Revealing Diffusion Mechanisms in Si and Ge

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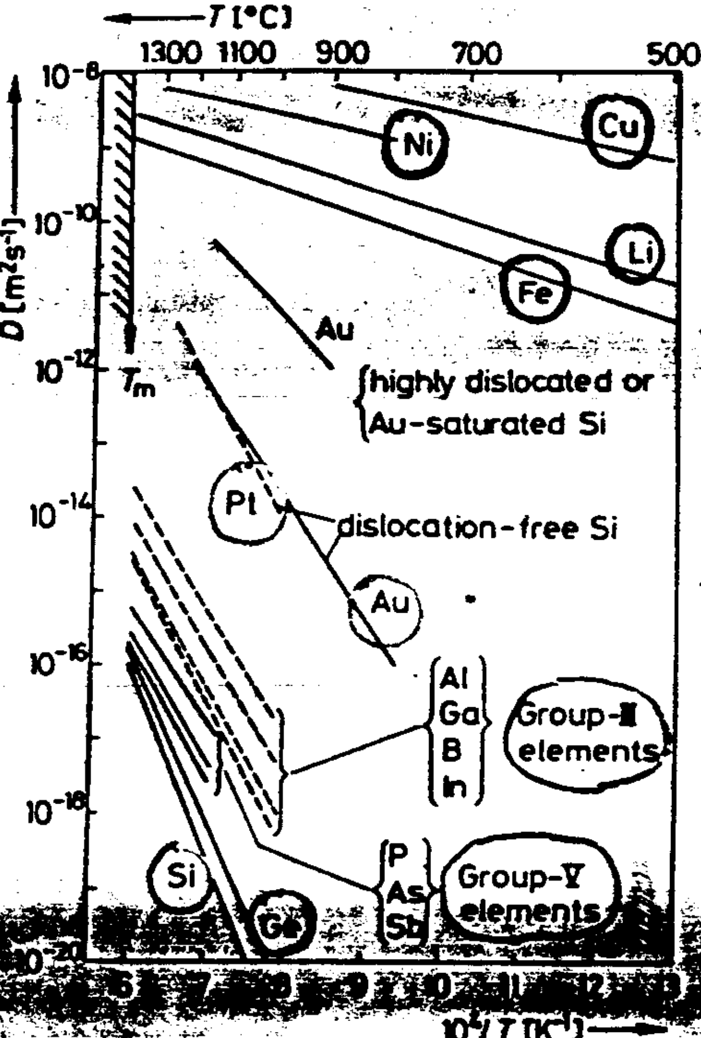
Diffusion in Si



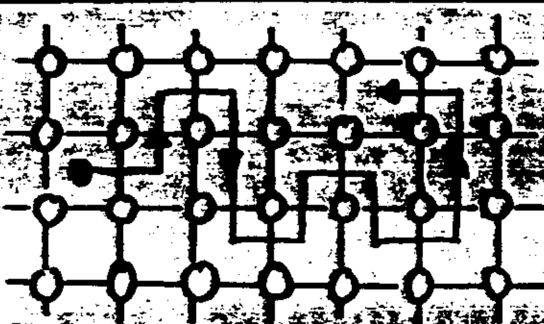
fast interstitials

hybrids

slow substi= tutional solutes & self-diffusion

Nature of diffusion mechanisms[2]

fast interstitials



direct interstitial diffusion (decoupled)

hybrids
substitutional solutes
self-diffusion

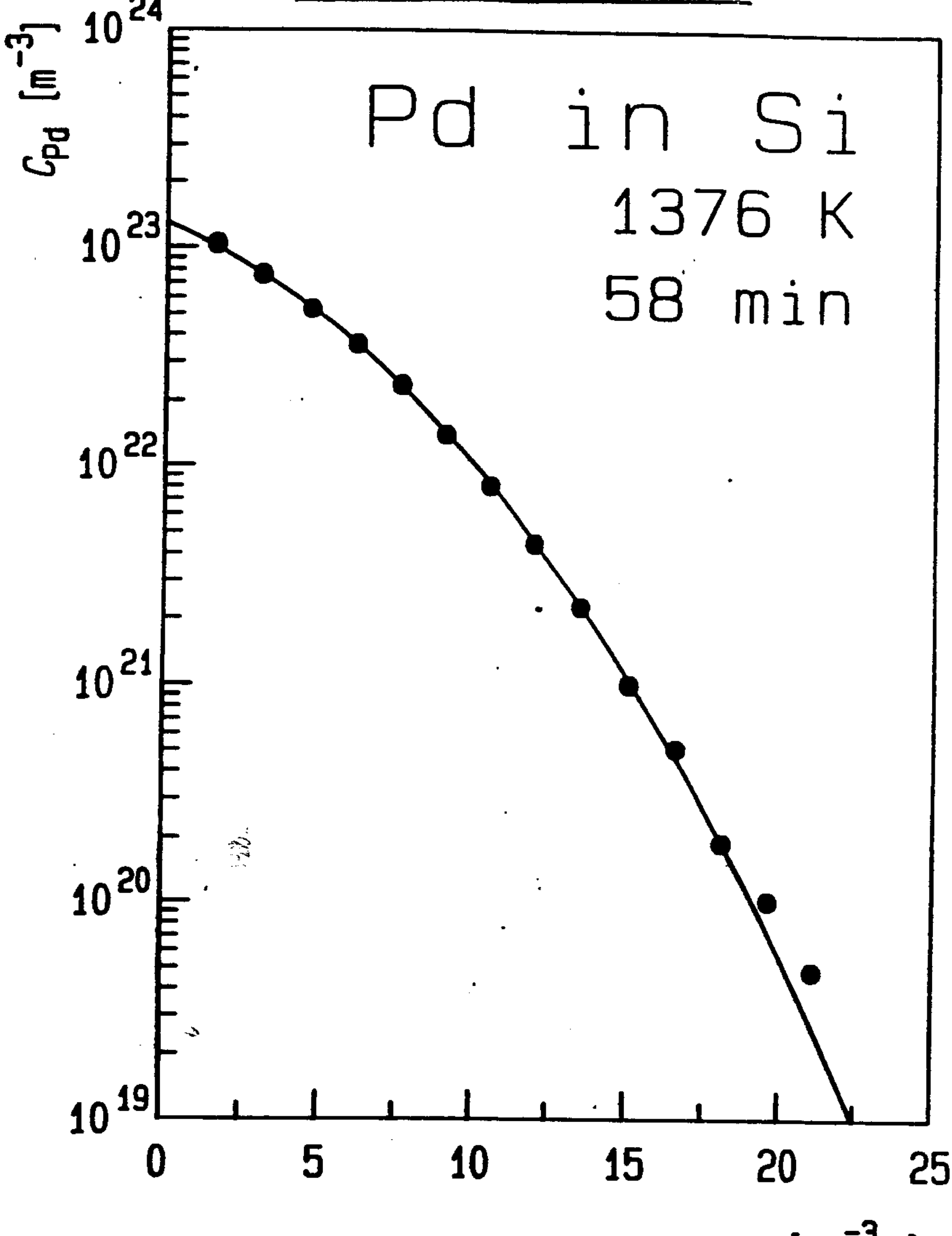
indirect diffusion mechanisms coupled via vacancies (V) & self interstitials (I)

Fast direct interstitial diffusion

Example: Pd in Si

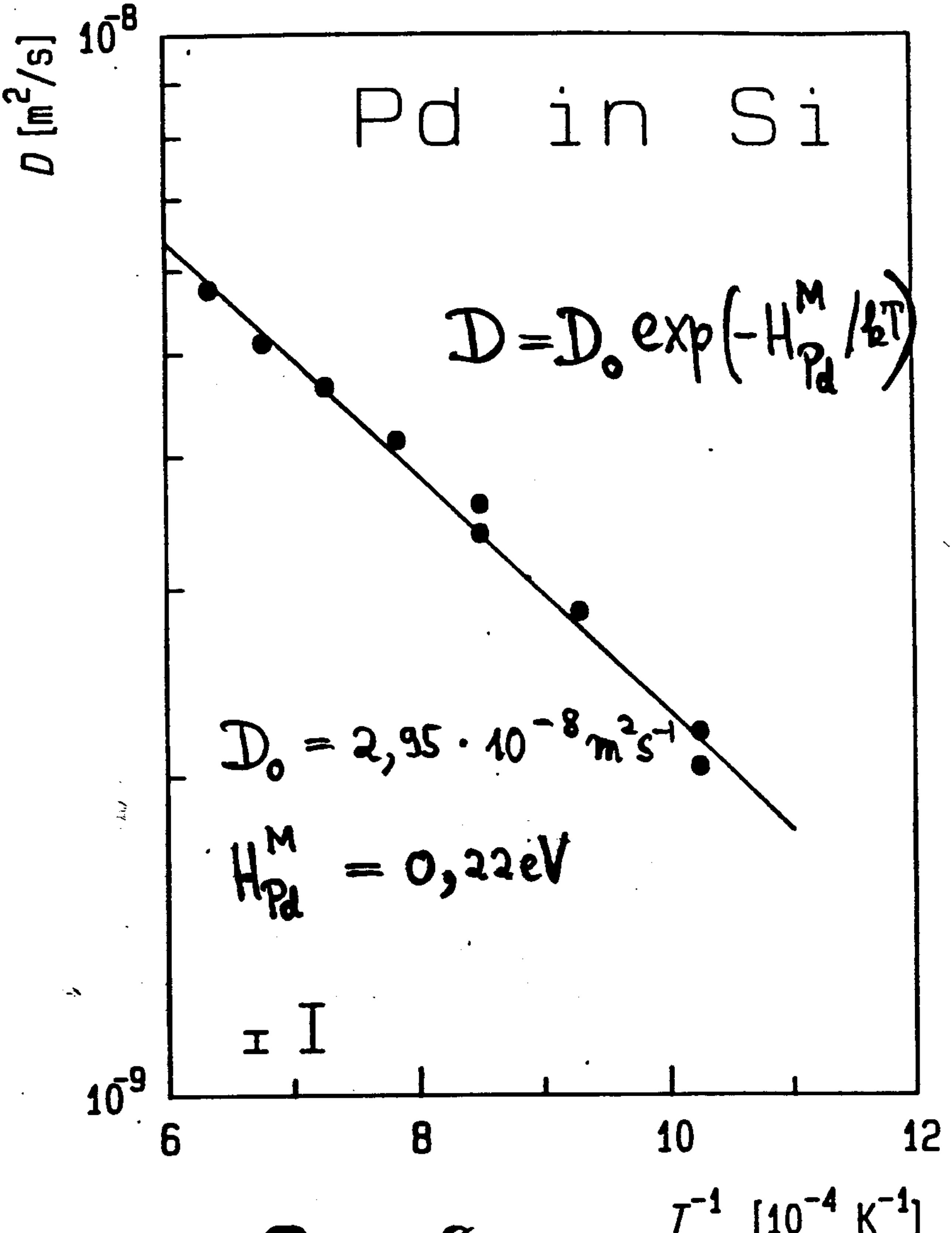
(V. Kauffmann, Th. Zerenner, J. Horváth, and W. Frank, to be published)

Diffusion profile



- neutron activation analysis + serial sectioning of 25 mm long specimen in 2 mm thick pieces
- erfc-type profile as expected for **direct interstitial diffusion**

Temperature dependence of D



Obviously **Pd in Si** is a fast diffuser like Cu, Ni, or Fe in Si!

⟹ direct interstitial diffusion

Investigations

of

fast interstitial diffusion

— yield no information on the diffusion mechanisms of other atoms !

— yield no information on intrinsic defects !

Reason:

- Direct interstitial diffusion does not involve intrinsic defects (V and/or I) as diffusion vehicles
- No coupling to diffusion of other atoms via V or I

Diffusion of substitutional dopants

under non-equilibrium conditions

(examples : B, P, Sb,... in Si)

— yields <u>qualitative information</u> on <u>diffusion mechanisms</u> and <u>intrinsic defects</u> !

Mizuo & Higuchi (≥ 1981)

Fahey & Dutton (≥ 1986)

⋮

treatment	interstitial-type dislocation loops (TEM)	diffusion	
		B	Sb
surface oxidation (SO)	grow	enhanced	retarded
surface nitridation (SN)	shrink	retarded	enhanced

Requirements for compatibility of observations

- SO injects I
- SN injects V
- B diffuses via I
- Sb diffuses via V
- V & I coexist in thermal equilibrium

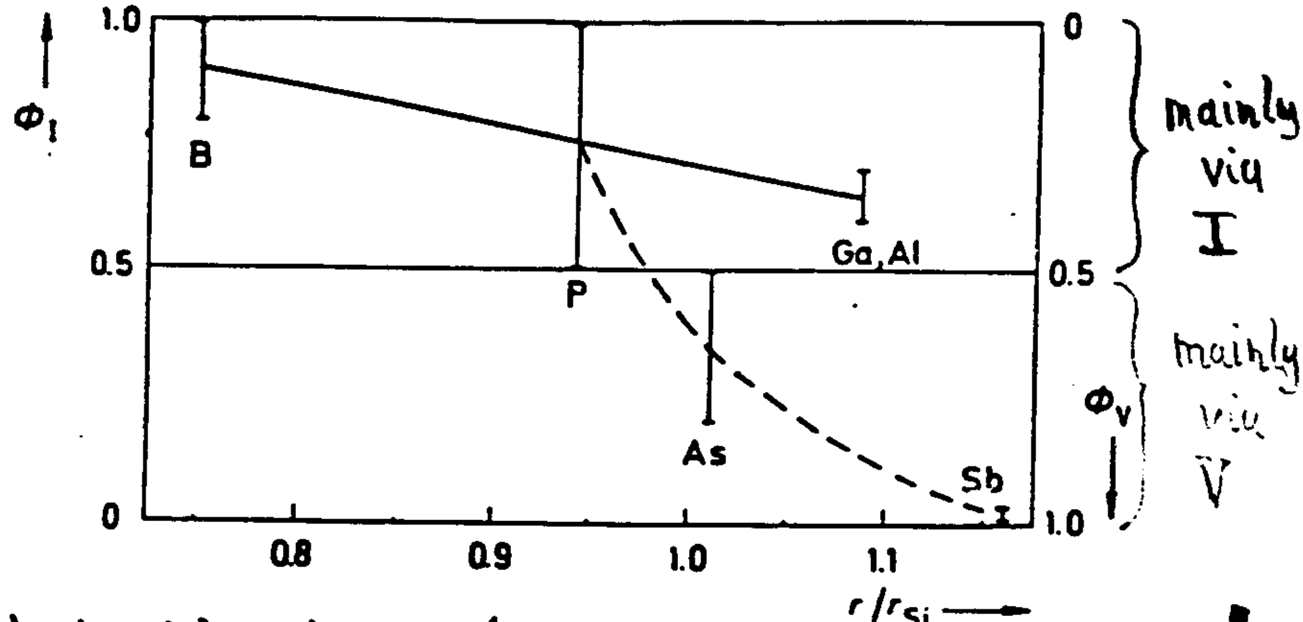
- $C_V C_I = C_V^{eq}(T) \cdot C_I^{eq}(T)$

$\longrightarrow V + I \rightleftarrows 0$

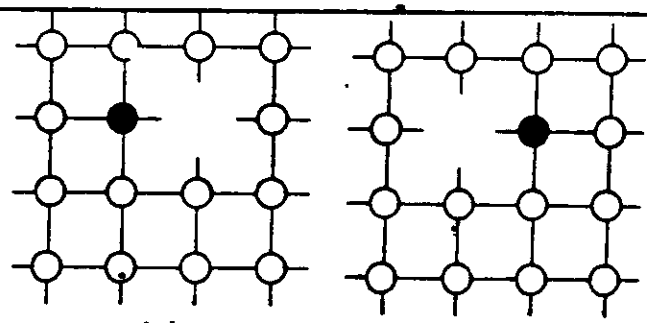
(spontaneous formation & annihilation of Frenkel pairs

Qualitative information

1) subst. dopant diffusion
2) intrinsic point defects
3) self-diffusion

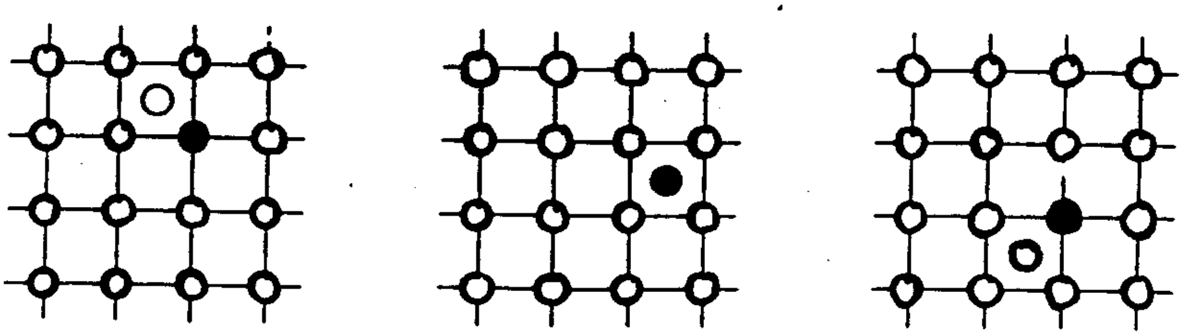


- elastic interaction (large dopants prefer V, ...)
- Coulomb interaction (donor dopants attract V [= acceptors], ...)



(a) (b)

(indirect) vacancy mechanism



(a) (b) (c)

indirect interstitial mechanism (= interstitialcy mechanism)

Diffusion of Hybrid Solutes in Si and Ge

(a) will give us information on the self-diffusion mechanism in both Si and Ge

(b) will enable us to calculate D^{SD} from hybrid-solute diffusion

Hybrid solutes (A_s & A_i)

Au or Pt in Si

Cu in Ge

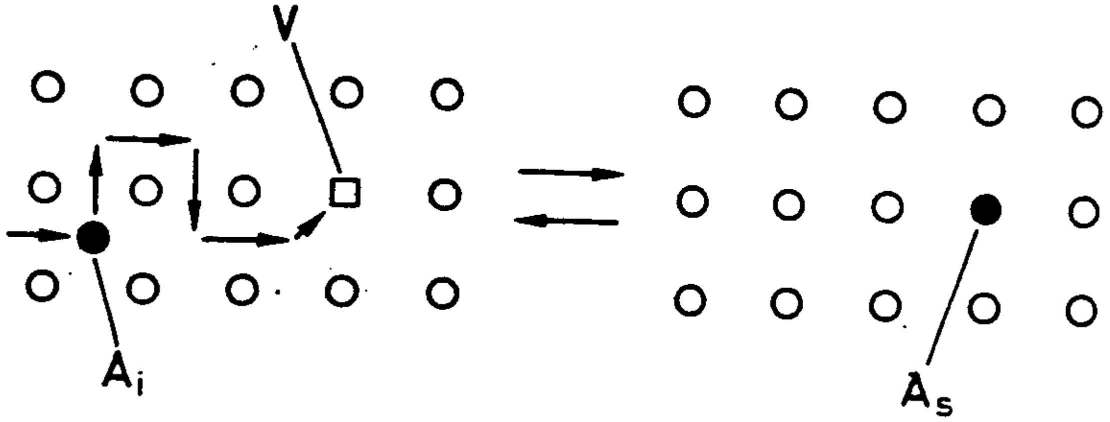
Common properties :

(i) $C_s^{eq} \gg C_i^{eq}$

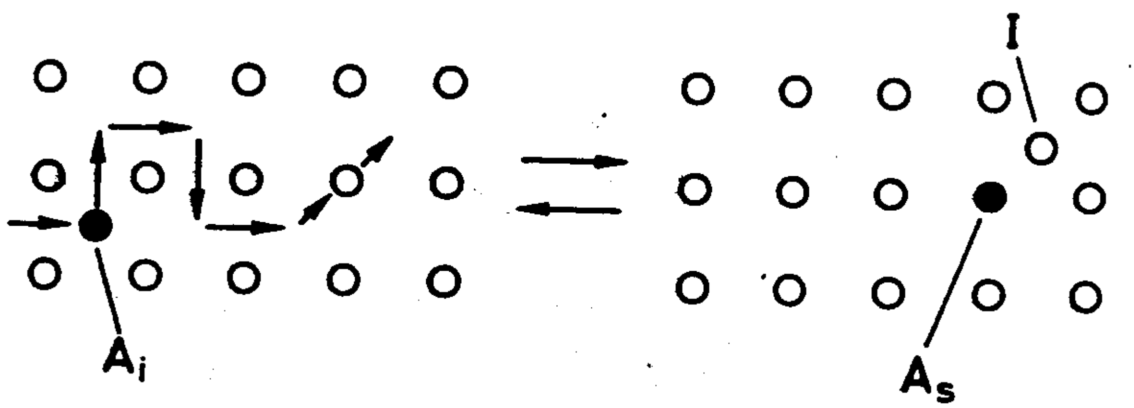
(ii) $D_s \ll D_i$

(iii) $A_s \rightleftarrows A_i$ interchanges during diffusion

Interstitial – Substitutional Diffusion Mechanisms



Dissociative mechanism (Frank & Turnbull 1956)



Kick-out mechanism (Gösele, Frank & Seeger 1980)

Dissociative Mechanism

$$A_i + V \rightleftharpoons A_s$$

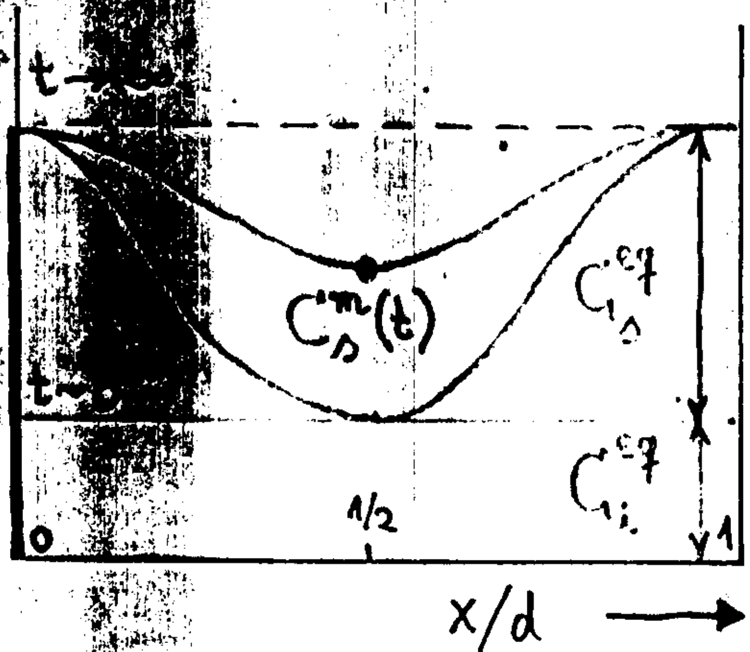
$$D_{eff}^{V} = \underbrace{\frac{C_V^{eq} D_V}{C_s^{eq}}}_{D_V^*} = \text{const}$$

Kick-Out Mechanism

$$A_i \rightleftharpoons A_s + I$$

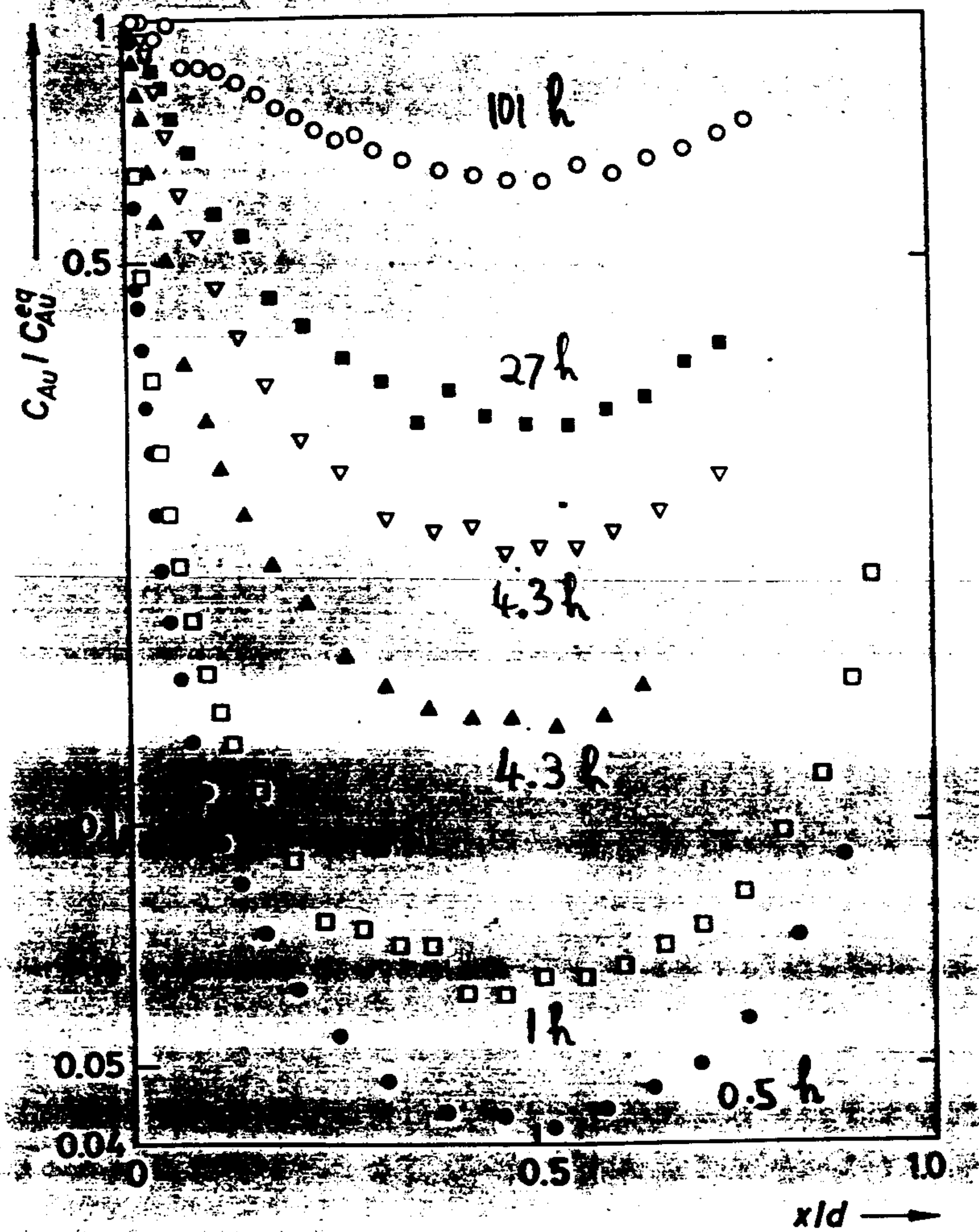
Dislocation-free crystal:

$$\frac{\partial C_s}{\partial t} = \frac{\partial}{\partial x} D_{eff} \frac{\partial C_s}{\partial x}$$



$$D_{eff}^{I}(x,t) = \underbrace{\frac{C_I^{eq} D_I}{C_s^{eq}}}_{D_I^*} \left[\frac{C_s^{eq}}{C_s(x,t)}\right.$$

Au diffusion in dislocation-free Si wafers



T = 1273 K

d ~ 300 μm (▽) and ~ 500 μm (other cases)

Measuring Techniques

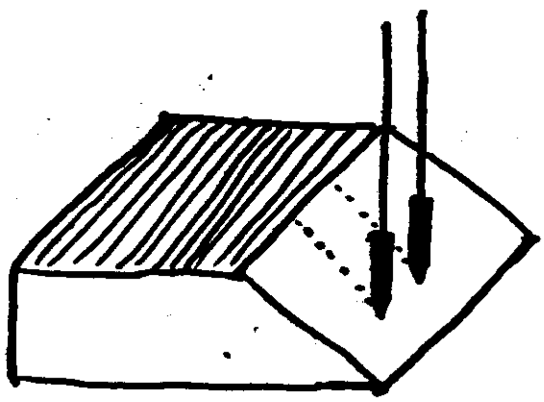
1) Neutron-activation analysis (NAA)

+

serial sectioning

$$C^{total} = C_s + C_i + \dots$$

2) Spreading resistance (R_s)



$$R_s \longrightarrow \rho \longrightarrow C_s$$

Observation : $C^{total} \sim C_s$, i.e. $C_s \gg C_i$

Theoretical Predictions

Dissociative mechanism

$$D_{eff}^{V} = \text{const} \qquad (\text{see text books})$$

Kick-out mechanism

$$D_{eff}^{I}(x,t) = D_I^{*} \left(\frac{C_s^{eq}}{C_s(x,t)} \right)^2$$

$$D_I^{*} = \frac{C_I^{eq} D_I}{C_s^{eq}}$$

Wafer (Gösele, Frank & Seeger 1980)

$$\operatorname{erf}\left[\ln \left(\frac{C_s}{C_s^{m}} \right)^{1/2} \right] = \left| \frac{d/2 - x}{d/2} \right| \qquad (1)$$

$$C_s^{m} / C_s^{eq} = \frac{2}{d} \sqrt{\pi D_I^{*} t} \qquad (2)$$

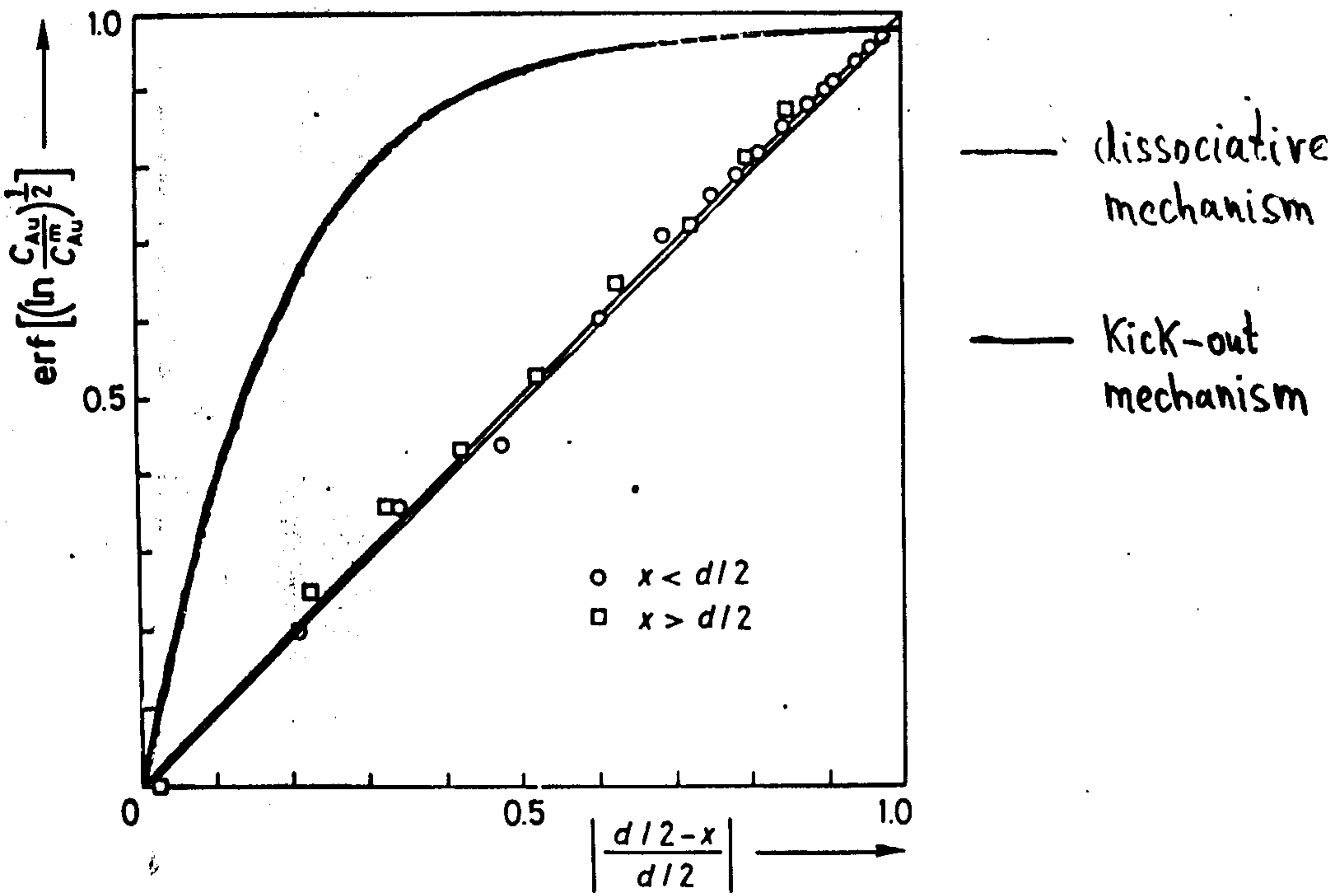
(3)

Thick specimens (Seeger 1980)

$$C_s(x,t) / C_s^{eq} = F(x, t; D_I^{*}) \qquad (4)$$

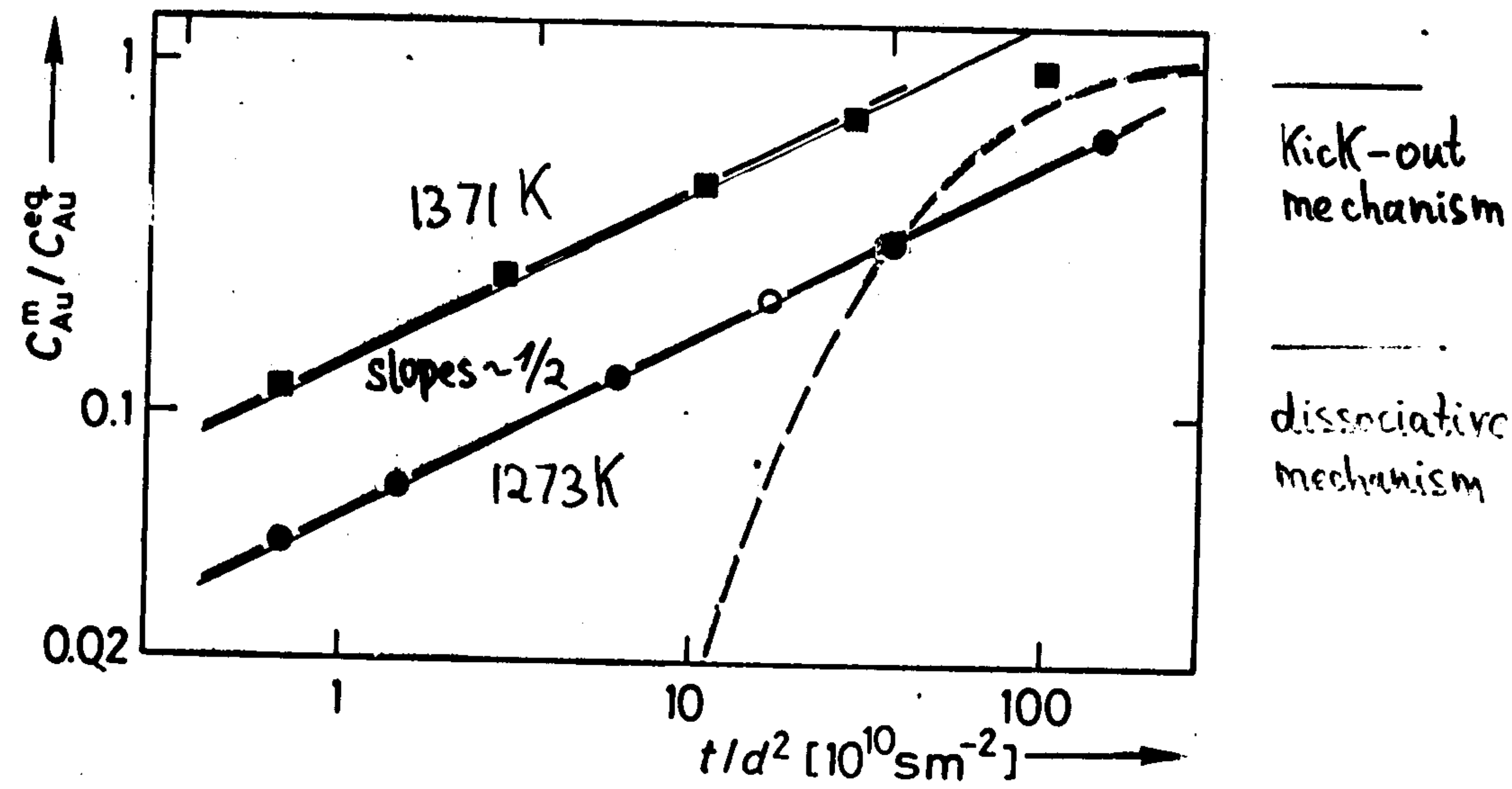
Au diffusion profile in an Si wafer (1273 K, 1 h)

Test (1): wafer profile shape



Increase of the Au concentration in the wafer centre in the course of time

Test (2): $C_s^m \sim \sqrt{t}$

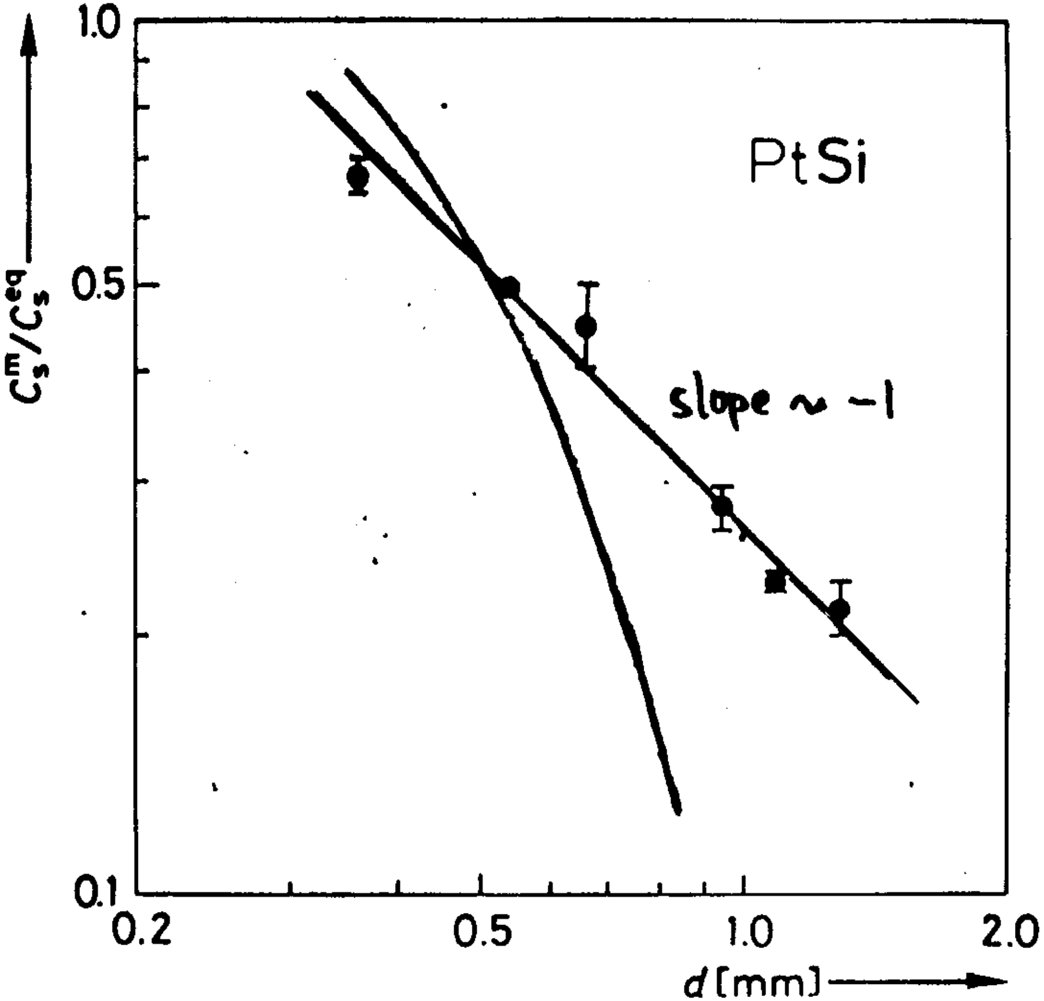


$d = 500\ \mu m$, except for O (300 μm)

Decrease of the Pt concentration in the wafer centres with increasing wafer thickness

Test (3):

$C_s^m \sim 1/d$

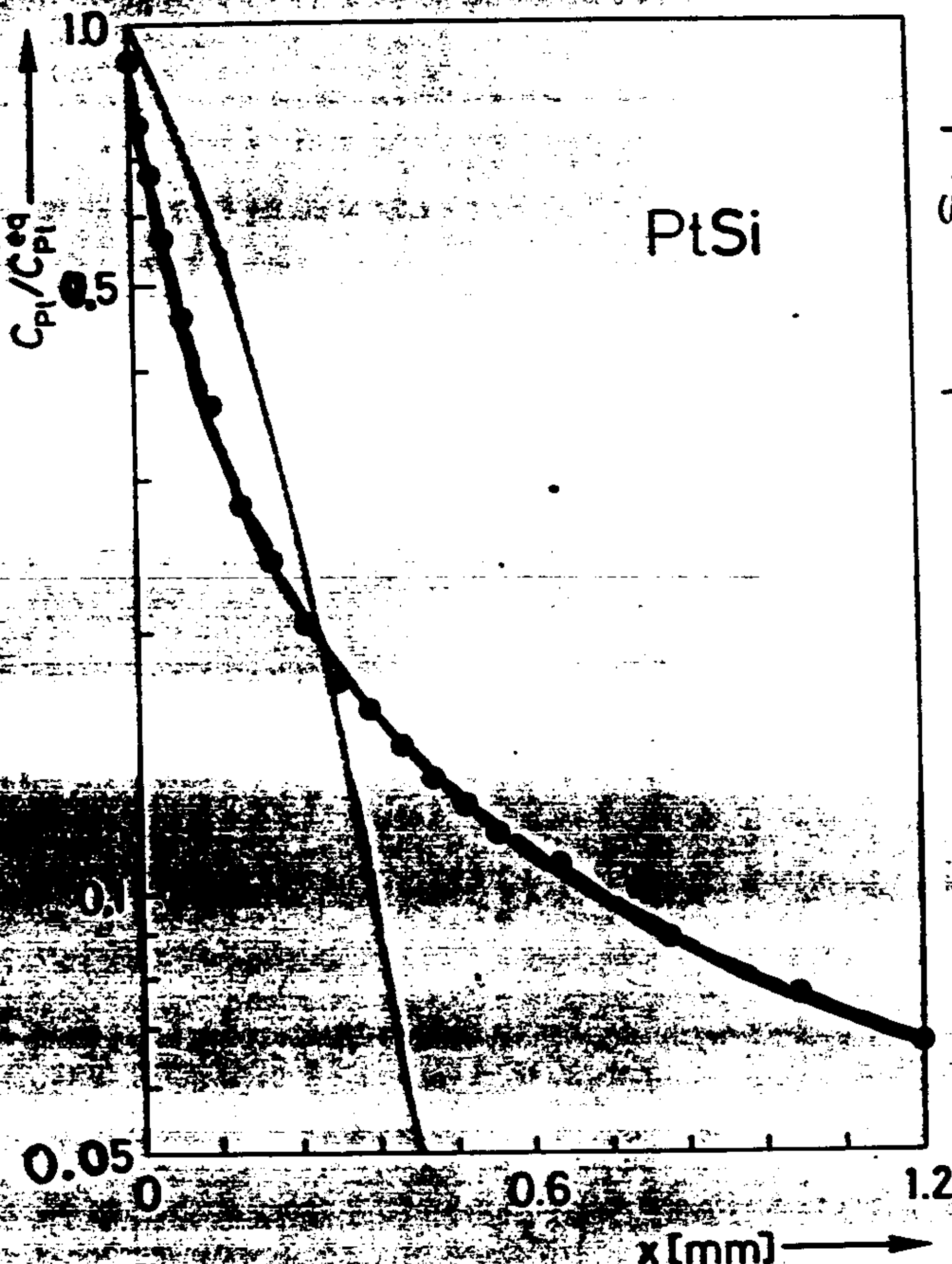


dissociative mechanism

Kick-out mechanism

1423 K , 3.5 h

Pt diffusion profile in a thick Si specimen



dissoc. mechan.

Kick-out mechan.

Test (4): thick specimen

d ~ 5 mm

1523 K, 30 min

Relation to Self-Diffusion

Tracer self-diffusion coefficient:

$$D^T = D_V^T + D_I^T$$

$$= f_V C_V^{eq} D_V + f_I C_I^{eq} D_I$$

Quantities deducible from investigations of hybrid atoms in Si:

$$D_I^* = \frac{C_I^{eq} D_I}{C_s^{eq}}$$

D_I^*: from diffusion of Au or Pt in Si

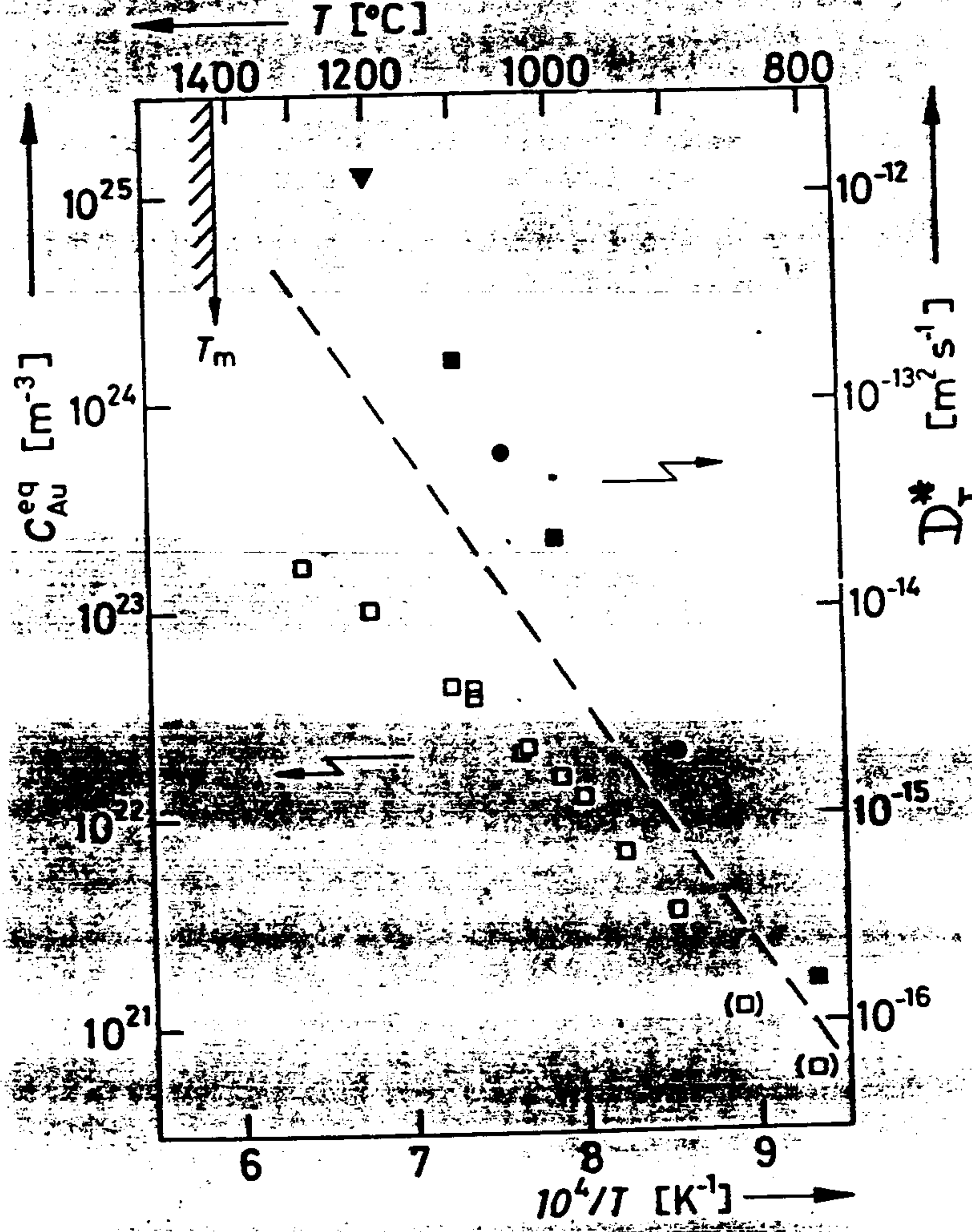
C_s^{eq}: from solubility measurements

Contribution by self-interstitials to D^T:

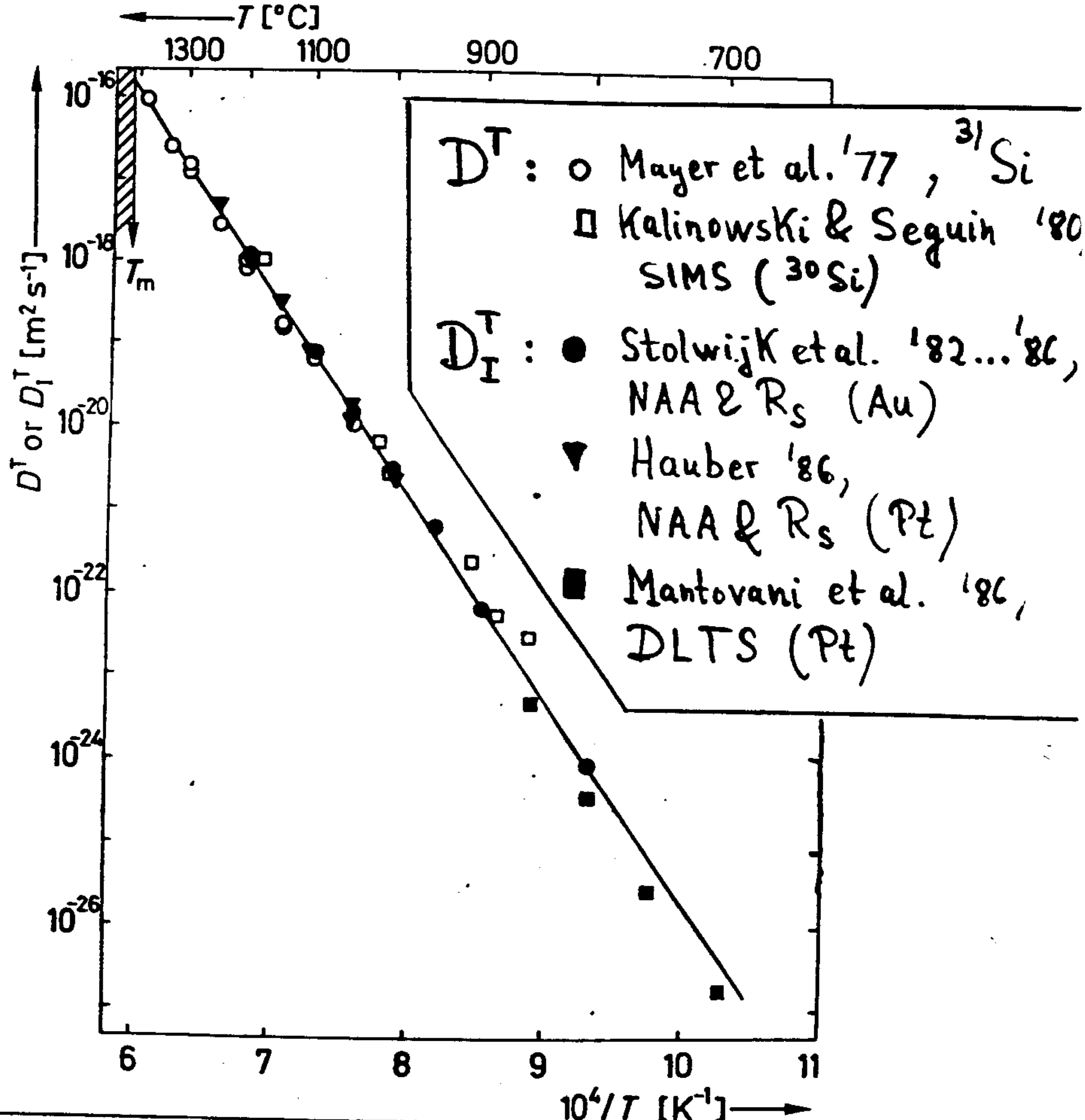
$$D_I^T = f_I \, D_I^* \, C_s^{eq}$$

f_I ($\sim \frac{1}{2}$)

Solubility and D_I^* of Au in Si



Tracer Self-Diffusion Coefficient D^T and Self-Interstitial Contribution D_I^T



$$D^T = \left(14.6 \begin{smallmatrix}+17\\-8\end{smallmatrix}\right) \times 10^{-2} \exp\left[-(5.02 \pm 0.10)\,eV/kT\right] \; m^2/s$$

$$D_I^T = \left(3.5 \begin{smallmatrix}+1.2\\-0.9\end{smallmatrix}\right) \times 10^{-2} \exp\left[-(4.81 \pm 0.04)\,eV/kT\right] \; m^2/s$$

I) $D^T \simeq D_I^T$ II) $D_0^T \simeq 10^4 D_0^T(\text{metal})$ III) D_I^T at low T

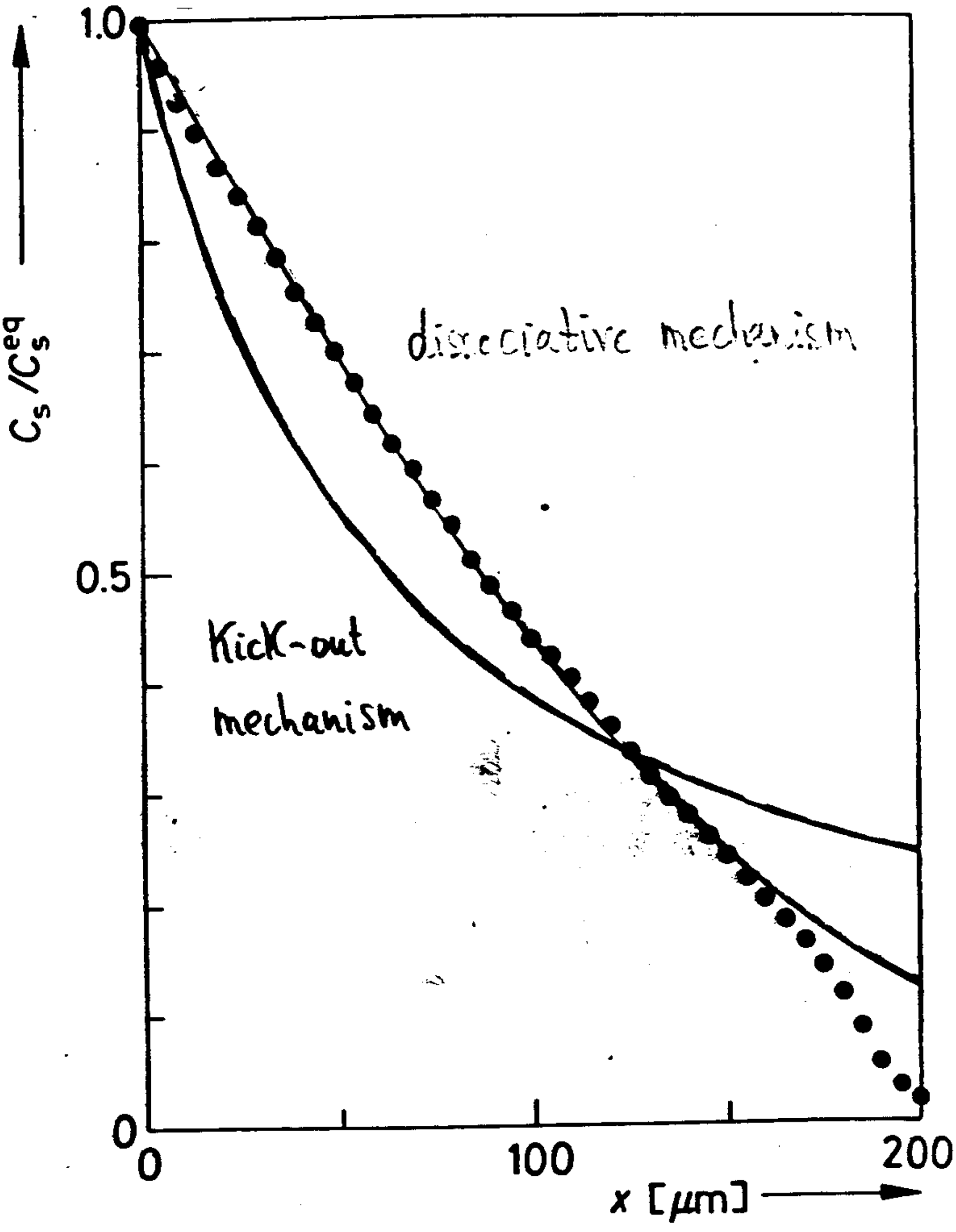
Diffusion in Ge

- Previous investigations have presented evidence for a vacancy self-diffusion mechanism in Ge

- Self-interstitial or vacancy <u>injection</u> techniques are <u>not</u> available

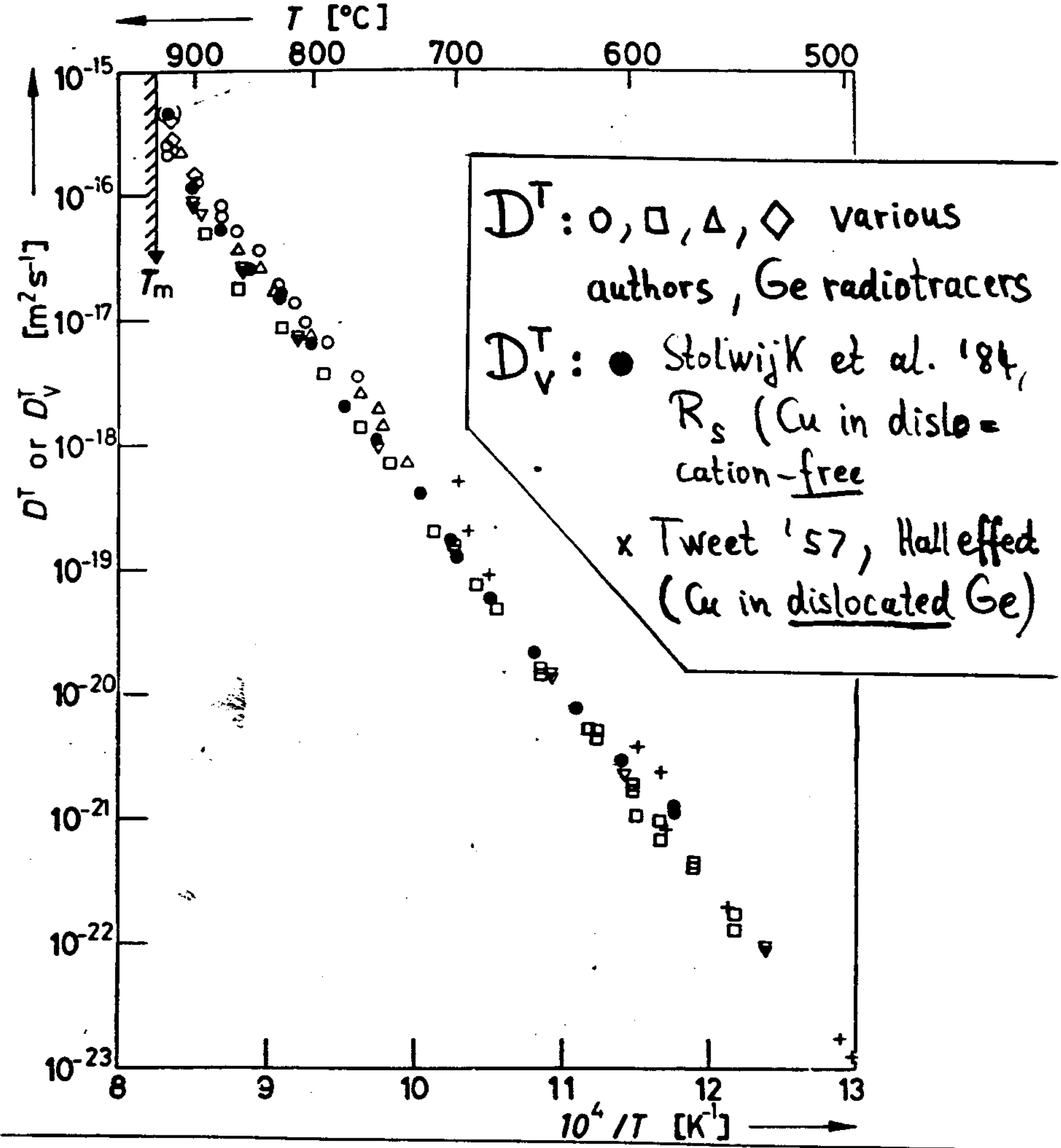
- Cross-check by means of diffusion studies of hybrid Cu in dislocation-free Ge

Cu diffusion profile in thick Ge specimen



951 K, 1 h

Tracer Self-Diffusion Coefficient D^T and Vacancy Contribution D_V^T



$$D^T = (1.36 \pm 0.15) \times 10^{-3} \exp\left[-(3.09 \pm 0.02)\,eV/kT\right]\ m^2/s$$

$$D_V^T = (2.13 \pm 1.2) \times 10^{-3} \exp\left[-(3.11 \pm 0.05)\,eV/kT\right]\ m^2/s$$

I) $D^T \simeq D_V^T$ II) $D_0^T \simeq 10^3 D_0^T$ (metals)

Summary

Si

(i) Co-existence of self-interstitials and vacancies in thermal equilibrium

(ii) Above 800°C **self-diffusion** is dominated by an **interstitialcy** mechanism. $(C_I^{eq} D_I \gg C_V^{eq} D_V)$

(iii) Self-interstitials are "**extended**" at high T.

(iv) Above 700°C **Au** and **Pt** diffuse via the **Kick-out mechanism**.

(v) **Group-III and Group-V elements** diffuse via **self-interstitials and/or vacancies.**

Ge

(i) **Self-diffusion** and **Group-III/V element diffusion** occur via **vacancies.**

(ii) **Vacancies are "extended" at high** T.

(iii) **Cu** diffuses via the **dissociative mechanism.**