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SPRING COLLEGE IN MATERIALS SCIENCE ON
"NUCLEATION, GROWTH AND SEGREGATION IN MATERIALS SCIENCE AND ENGINEERING"
(6 May - 7 June 1991)

TRANSPORT PROCESSES (INCLUDING RADIATION ENHANCED DIFFUSION)

Part IV

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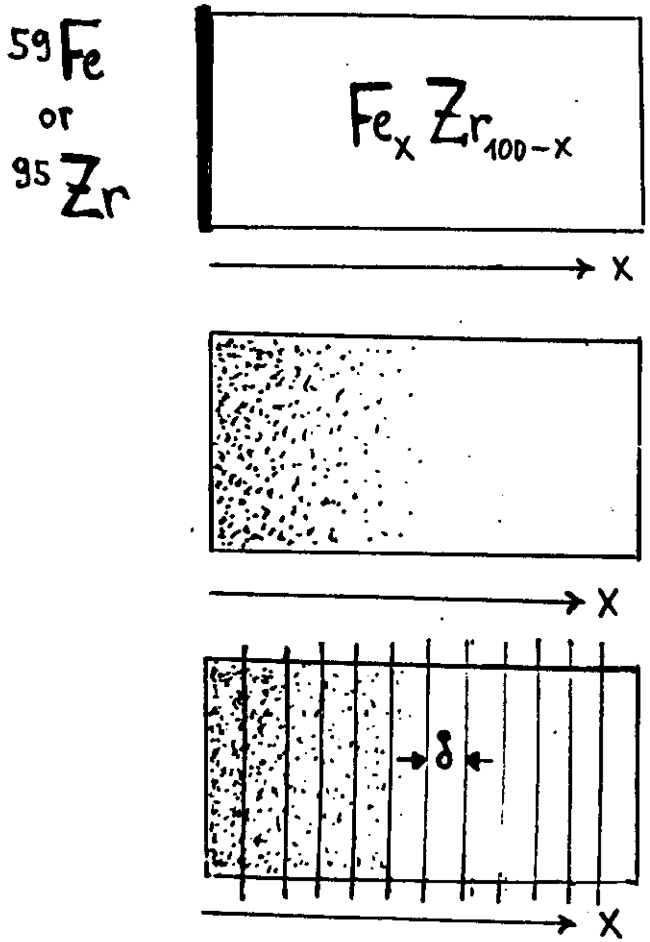
Diffusion in Amorphous Metallic Alloys

Motivation

- Example of diffusion in disordered solid media
- Metastability of amorphous state
- Crystallization is influenced by diffusion or even diffusion-controlled
  (practical significance for thermal stability of amorphous materials)

Diffusion experiments with radioactive tracer atoms

(J. Horváth)



electro-chemical deposition of an approximately 1 nm thin tracer layer

annealing in a furnace at a temperature T for a duration t

sectioning and measurement of radioactivity of the individual Sections

This talk is confined to

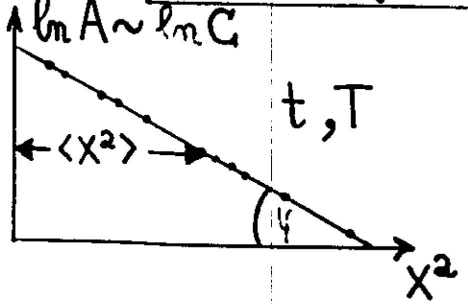
1) self-diffusion,

Determination of diffusion coefficients from penetration profiles

Diffusion equation: $\frac{\partial C}{\partial t} = D \nabla^2 C$

Thin-film solution $(d_T \ll \langle x \rangle)$:

$$C(x,t) = \eta_0 (\pi D t)^{-1/2} \exp(-x^2/4Dt)$$



$|\tan \psi| = 1/4Dt$

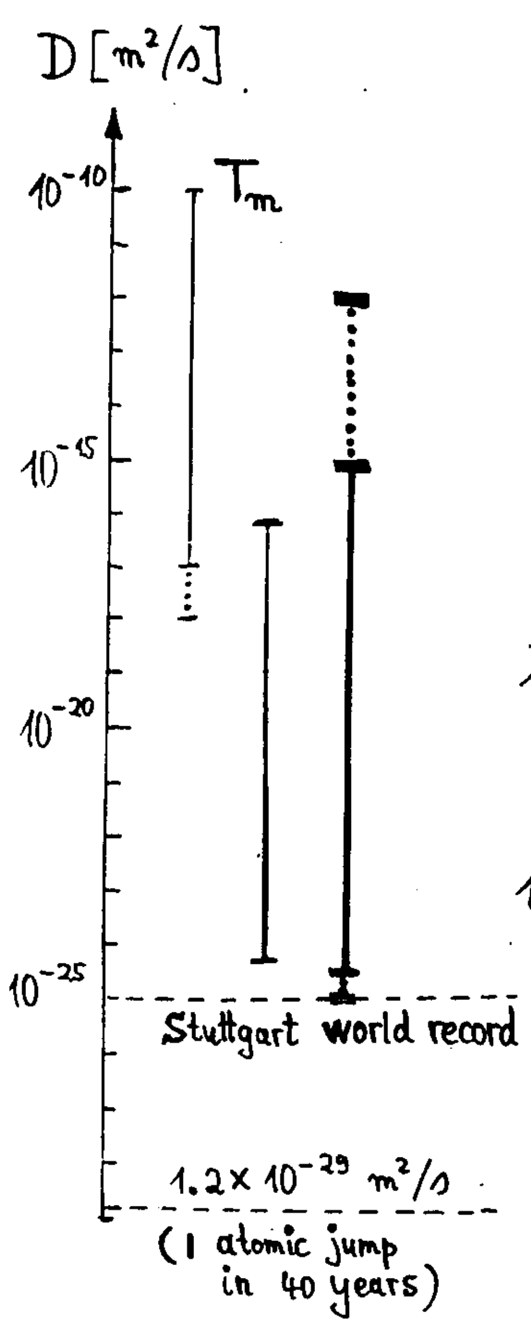
- Cross-check: Data points must lie on straight line
- Procedure remains valid if D depends on t:

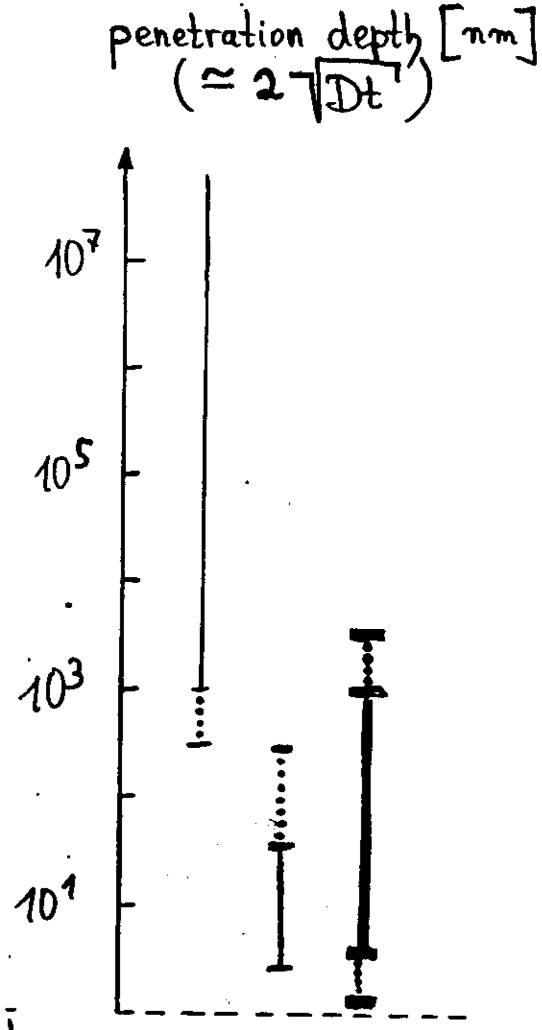
$$\langle D(t) \rangle \equiv t^{-1} \int_{t'=0}^{t} D(t')\,dt'$$

$$D(t) = \langle D(t) \rangle + t \frac{d\langle D(t) \rangle}{dt}$$

- Mean penetration depth: $\langle x \rangle \approx \sqrt{\langle x^2 \rangle} = \sqrt{2 \langle D \rangle t}$

⇒
- Measurement of small diffusion coefficients requires measurement of small penetration depths and/or long diffusion annealing times
- Duration of annealing is limited by the



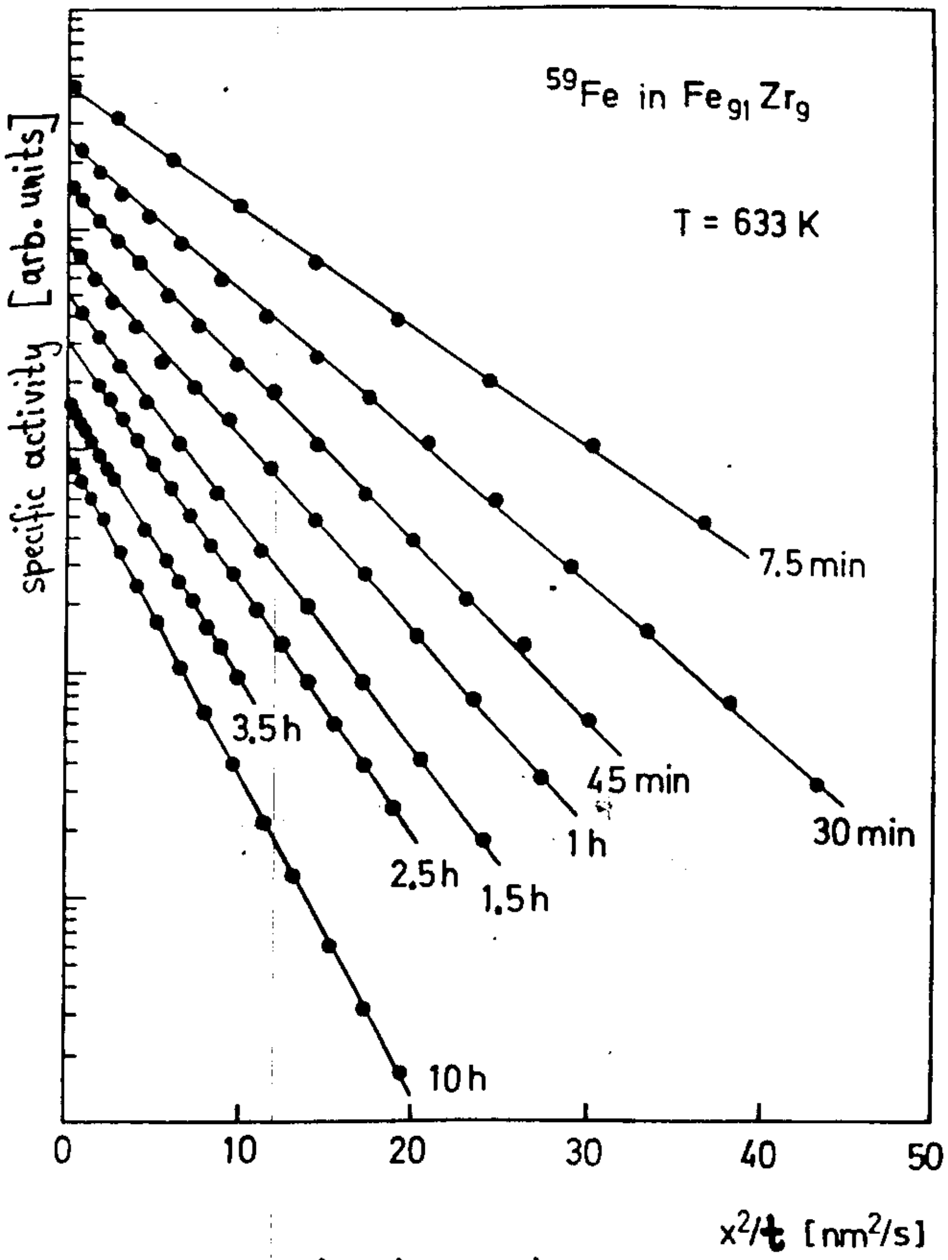


I conventional sectioning techniques

I amorphous alloys

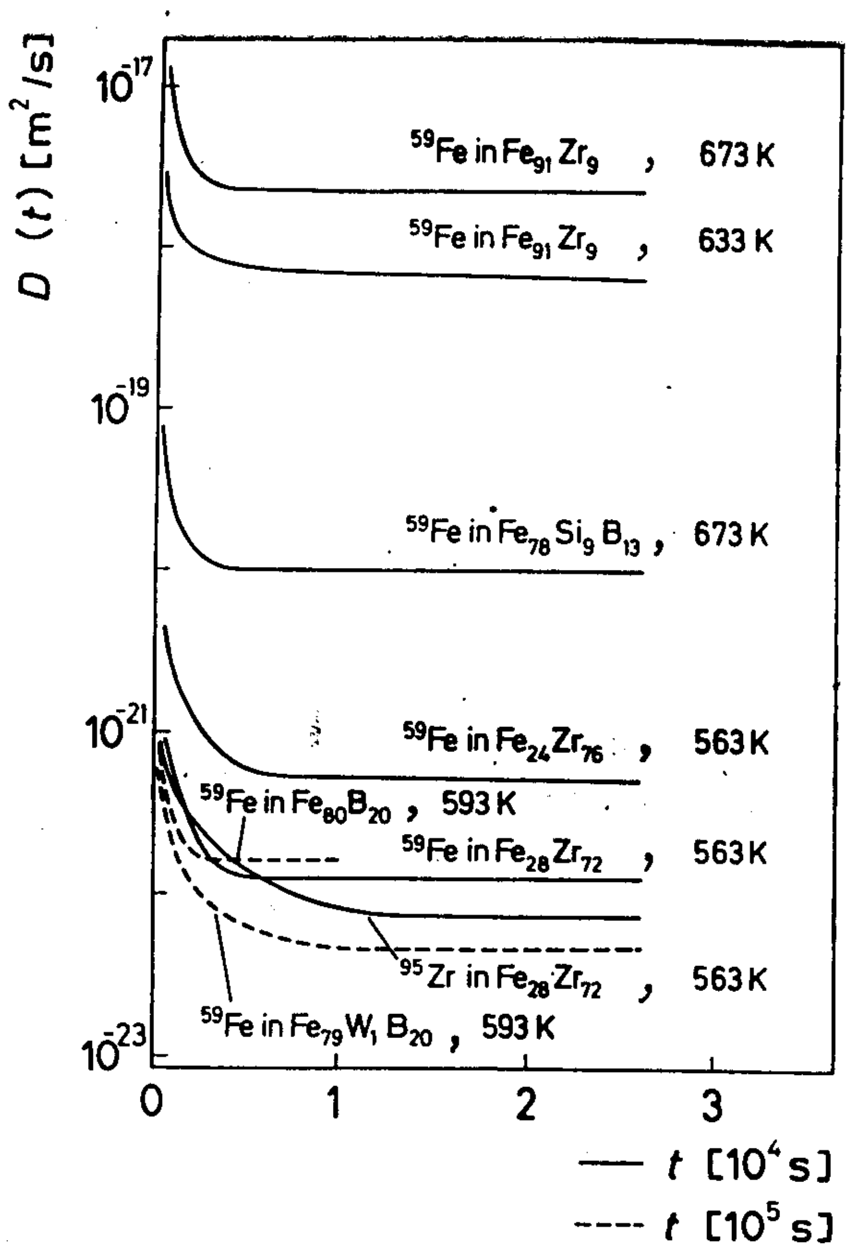
I ion-beam sputtering (K. Maier)

Diffusion profile

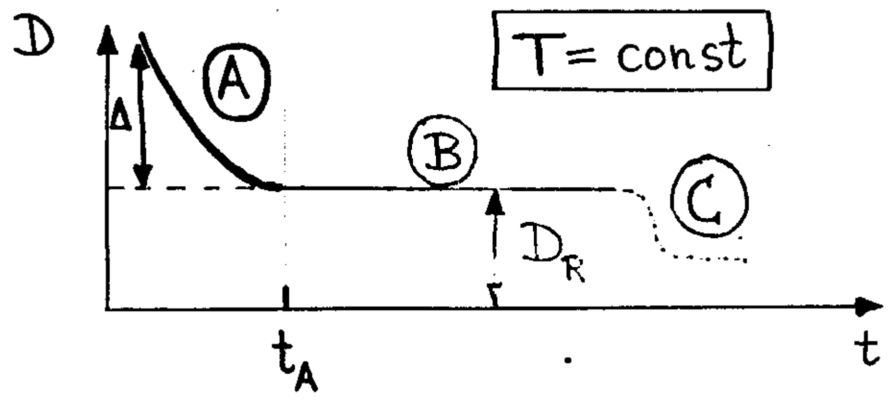


- Data points lie nicely on straight lines
- Diffusion coefficient decreases in the

Isothermal decrease of diffusion coefficients



Schematic illustration and description of the isothermal change of the diffusivities in amorphous alloys



Ⓐ **Initial decrease** (Δ, t_A)
depends on prehistory of specimen;
may be eliminated by pre-annealing

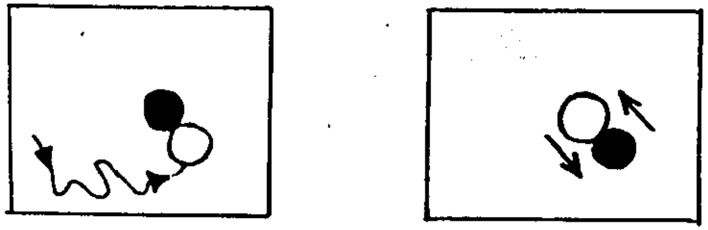
Ⓑ Plateau value D_R
is independent of prehistory;
depends on diffusion temperature in a unique way

➡ relaxed amorphous state
≡ thermodynamically (fairly stable) metastable state

Ⓒ Decrease due to crystallization
(crystallized state ≡ stable equilibrium)

Interpretation of initial decrease of D from $D_R + \Delta$ to D_R (regime Ⓐ)

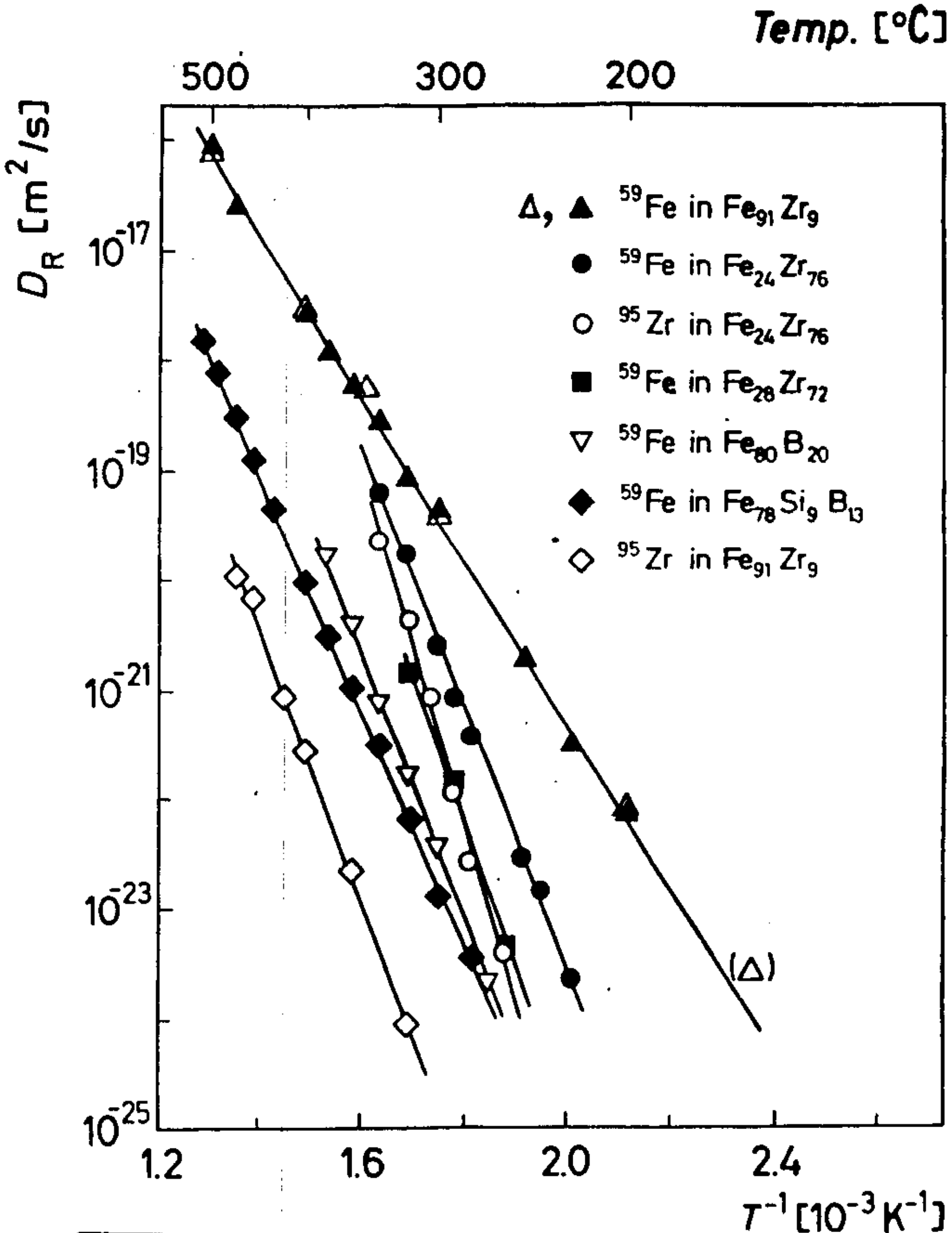
- Relaxation of as-quenched state by elimination of excess free volume (increase of density)
- Excess free volume, originally present in homogeneously distributed small units (quasi-vacancies), migrates to surface and/or forms larger agglomerates
- Tracer atoms experience diffusion enhancement Δ by indirect diffusion via quasi-vacancies:



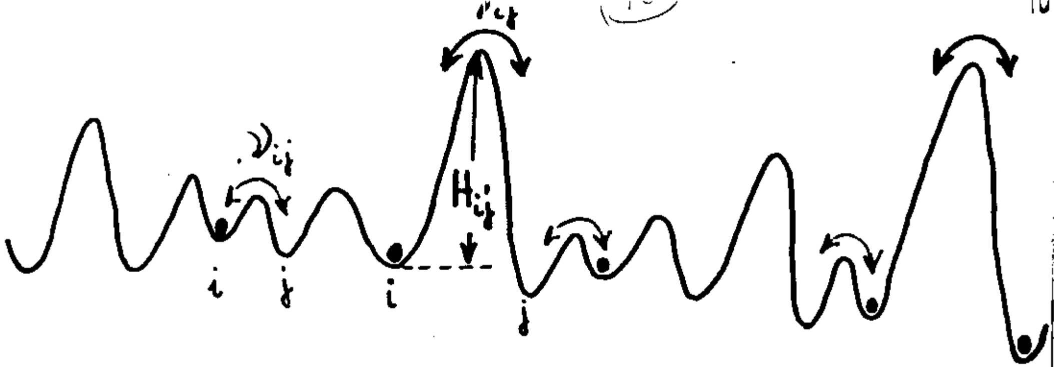
- After the supersaturation of quasi-vacancies have annealed out, D has dropped by Δ to D_R

- What happens in the relaxed amorphous state?
- Which mechanisms determine D_0?

T dependence of D_R



Arrhenius laws: $D_R = D_0 \exp(-Q/kT)$



Short t (low T):

- low barriers $H_{ij} \rightsquigarrow$ high jump frequencies ν_{ij}
- local, independent processes : $\overline{\nu} \equiv \langle \nu_{ij} \rangle$
- effective activation enthalpy:

$$\boxed{Q^s \equiv -\frac{d}{d(1/kT)} \ln D^s = H_0 - H_m^2/kT}$$

- two-level systems (magnetic after-effect)

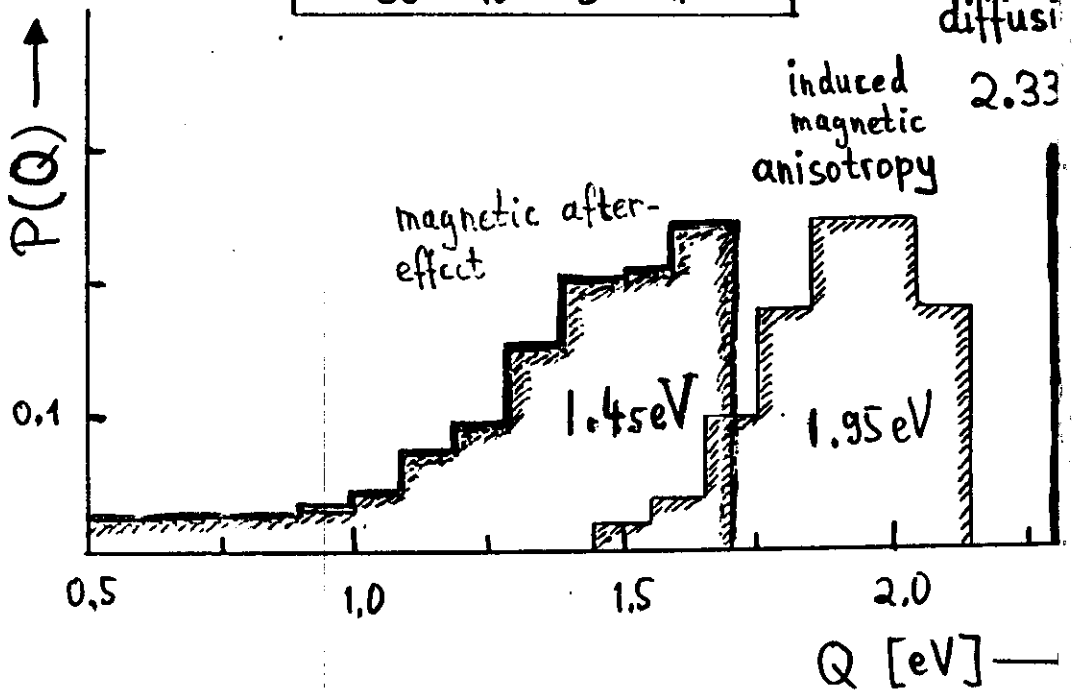
Long t (high T):

- high barriers $H_{ij} \rightsquigarrow$ low jump frequencies ν_{ij}
- series of dependent processes: $1/\overline{\nu} \equiv \langle 1/\nu_{ij} \rangle$
- effective activation enthalpy:

$$\boxed{Q^\ell \equiv -\frac{d}{d(1/kT)} \ln D^\ell = H_0 + H_m^2/kT}$$

- (long-range) **Diffusion**

$Co_{58}Ni_{10}Fe_5Si_{11}B_{16}$



magnetic after-effect:

$t = 180\ s$, $T \simeq 400\ K$

$Q^s \equiv \langle Q \rangle \simeq 1.45\ eV$

induced magnetic anisotropy:

$t \simeq 10^5\ s$, $T \simeq 500\ K$

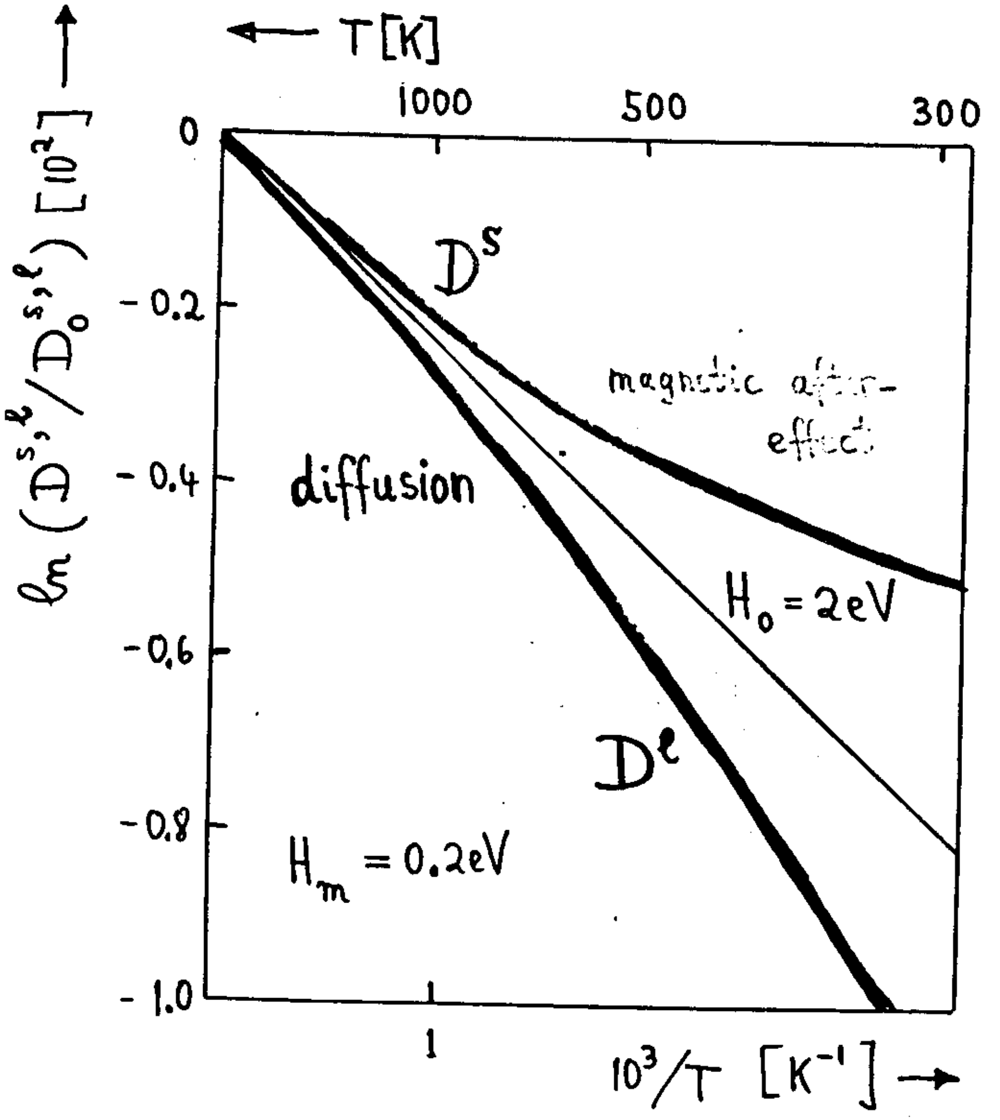
$\langle Q \rangle \simeq 1.95\ eV$

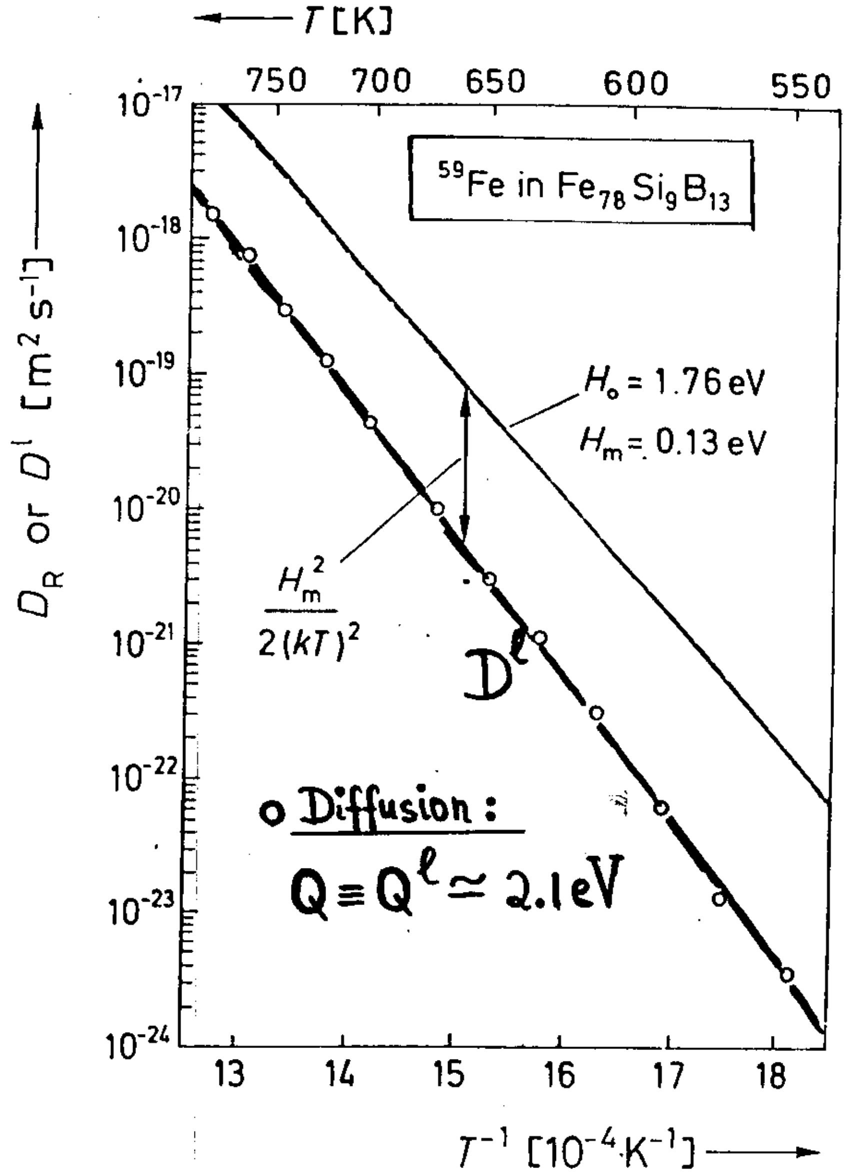
^{59}Fe diffusion

$t \simeq 10^5\ s$, $690\ K \lesssim T \lesssim 730\ K$

$Q^\ell \simeq 2.33\ eV$

Quasi-Arrhenius Laws

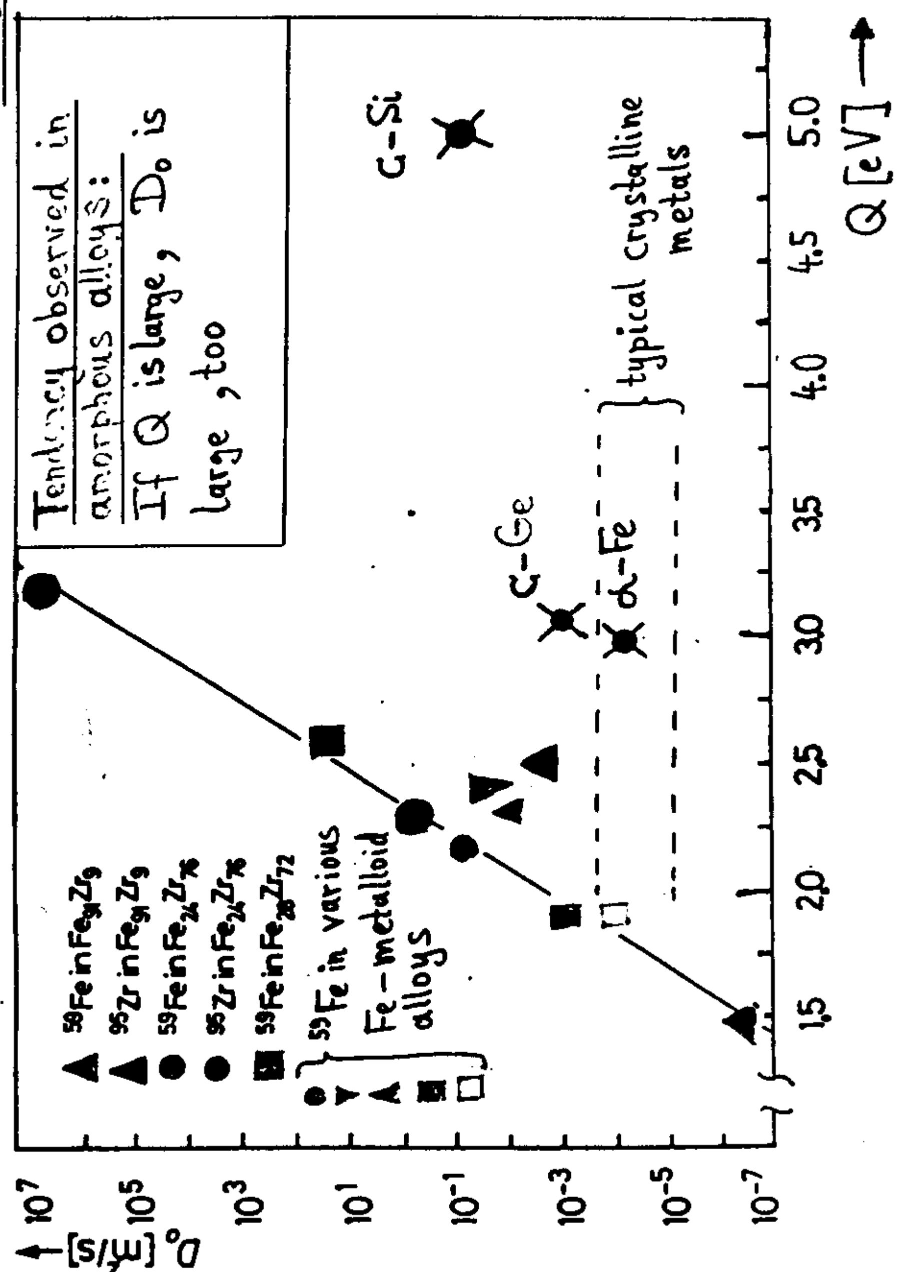




^{59}Fe diffusion in amorphous $Fe_{78}Si_9B_{13}$ obeys a quasi-Arrhenius law with $Q \simeq 2.1$ eV (In fact, $H_o = 1.76$ eV and $H_m = 0.13$ eV)

Correlation between Q and D_0 —

a key for understanding diff[illegible] state



Self-diffusion mechanisms in relaxed amorphous alloys

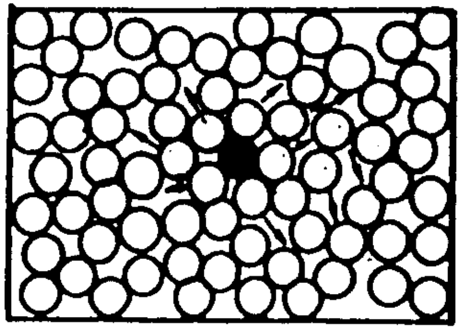
Example: Zr–Fe alloys

Limiting cases:

^{95}Zr in Zr-rich alloy (●):
Q & D_0 very large

^{59}Fe in Fe-rich alloy (▲):
Q & D_0 very small

^{95}Zr in Zr-rich matrix, e.g., $Zr_{76}Fe_{24}$



^{95}Zr large atom, Zr-rich matrix densely packed

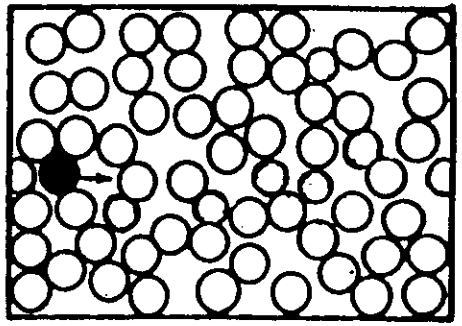
⇒ Motion of ^{95}Zr requires simultaneous motion of the neighbouring atoms:

(i) large migration enthalpy, $H_T^M \simeq 3{,}2\,eV \equiv Q$

(ii) large "diffusion efficiency", $D_0 \simeq 7 \times 10^{+6}\,\frac{m^2}{s}$; simultaneous motion of many atoms;
large migration entropy, $S_T^M \simeq 29\,k \equiv S$
(delocalization of residual free volume)

➡ collective motion of many atoms

^{59}Fe in Fe-rich matrix, e.g. $Fe_{91}Zr_{9}$



^{59}Fe small atom, Fe-rich matrix loosely packed

➡ ^{59}Fe can jump on vacant neighbouring sites formed by fluctuations:

(i) small migration enthalpy, $H_T^M \simeq 1.5\,eV \equiv Q$

(ii) small "diffusion efficiency", $D_0 \simeq 3 \times 10^{-7}\,\frac{m^2}{s}$, only 1 atom participates in jump;
negative migration entropy, $S_T^M = -1.7\,k \equiv S$
(Contraction of residual free volume on a neighbouring site of ^{59}Fe)

⇒ collective preparation of the jump of a single atom

Summary

(i) The extremely small self-diffusion coefficients in amorphous alloys became measurable by the radiotracer technique in combination with ion-beam sputtering.

(ii) In unrelaxed amorphous alloys enhanced diffusion arises from the presence of excess free volume (indirect diffusion via quasi-vacancies).

(iii) Relaxed amorphous alloys are in a meta-stable equilibrium state. In this state, self-diffusion occurs via direct collective mechanisms, which may be more or less efficient than the diffusion mechanisms in crystals.

(iv) The quasi-Arrhenius laws for D_R correspond to half-widths of the Q-spectra of less than 0.3eV.