Institut Matériaux Microélectronique Nanosciences Provence

Bases de la diffusion (dans les solides)

Dominique Mangelinck

ATELIER : Diffusion dans les oxydes amorphes, solides et liquides

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Acknowledgment

Patrick Gas, Alain Portavoce


Benoît Appolaire
ONERA: LEM


Hartmut Bracht
U. Munster


Chun Chun Fu
CEA: SRMP


Sergiy Divinski
U. Munster


Fréderic Soisson
CEA: SRMP

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Philippe Knauth
AMU/CNRS: Madirel

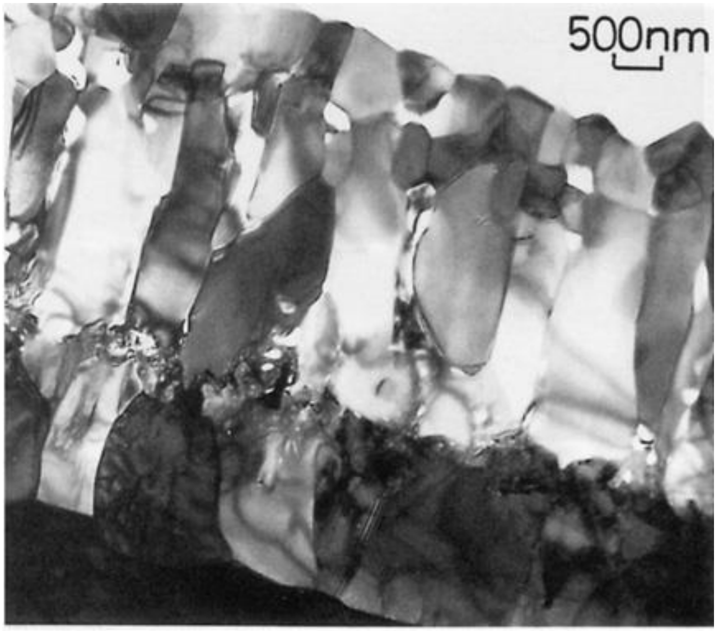

Alain Portavoce
CNRS/AMU: IM2NP


Jean Philibert
U. Paris 11

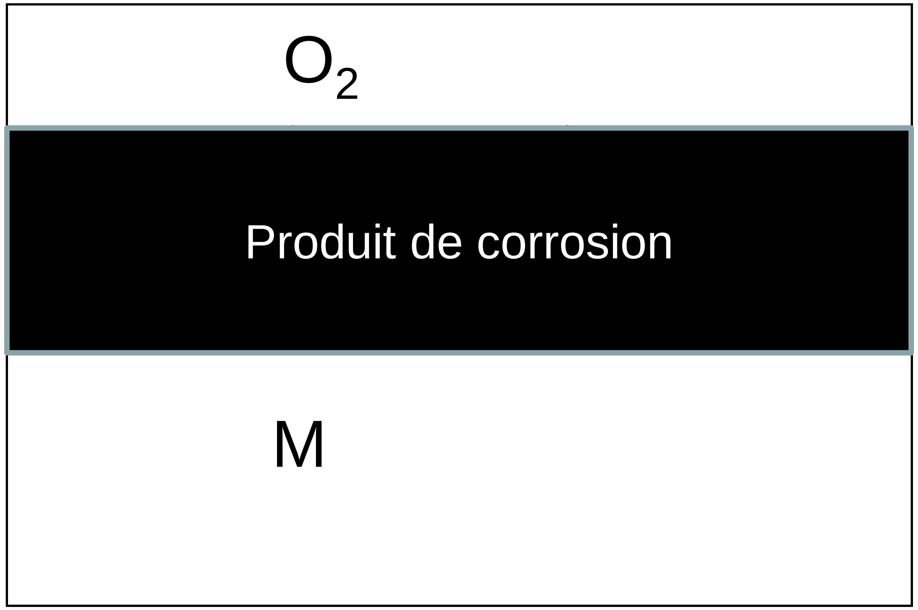

Maylise Nastar
CEA: SRMP


Dominique Mangelinck
CNRS/AMU: IM2NP

Diffusion and corrosion



TEM view of Al_2O_3 on Fe-20Cr-6Al-0.08La after 400 h at 1,150C [Stott, Hiramatsu, Mater. High Temp. 2000].



Corrosion haute température (oxydation)

→ **Rôle prépondérant de la diffusion**

→ **Quelle diffusion?**

Definition of various diffusion coefficients

1. Composition is constant

Self-diffusion coefficient: D_A

Tracer diffusion coefficient: D_A^*

$$D_A^* = f \cdot D_A$$

Correlation coefficient: f (Z: coordination number)

$$f \approx 1 - \frac{2}{Z}$$

Defect diffusion coefficient: D_d ([d]: molar fraction of defects)

$$D_A = \sum_d D_d [d]$$

2. Composition changes (chemical diffusion)

Intrinsic diffusion coefficient: $D_{A,AB}$

$$D_{A,AB} = D_A . \Phi$$

Chemical diffusion (interdiffusion) coefficient: $\check{D}$

Darken equation:

$$\check{D} = x_A . D_{B,AB} + x_B . D_{A,AB}$$

Integrated diffusion coefficient (Wagner, Van Loo)

$$\tilde{D}_{\mathrm{int}}^{\beta} = \int_{N_B^{\beta 1}}^{N_B^{\beta 2}} \tilde{D}\, dN_B$$

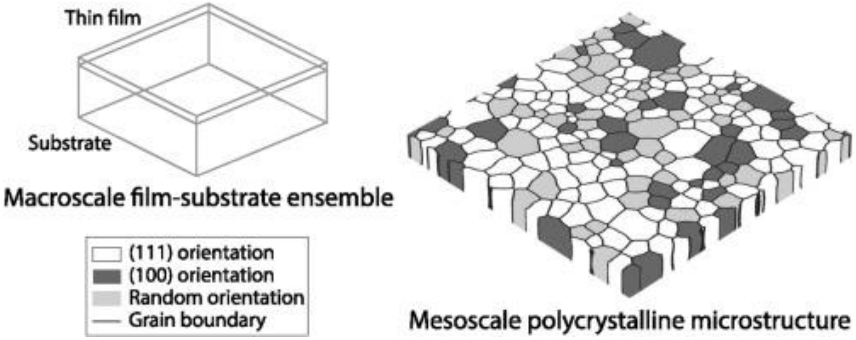
3. Ionic systems (ceramics)

Ambipolar diffusion: transport limited by the slower component (electroneutrality)

In oxides with predominant electronic conduction (transference number: $t_{el} >>> t_A$):

$$\check{D} = t_{el} . D_A . \Phi$$

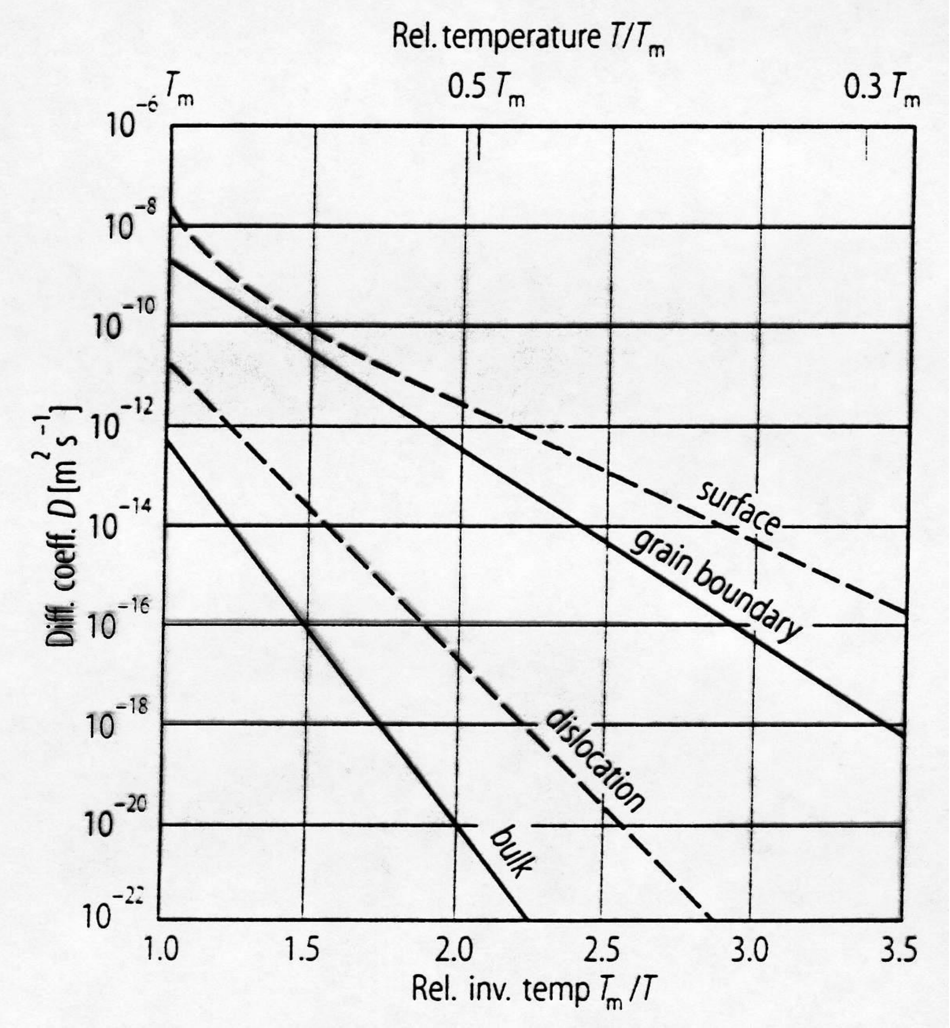
Diffusion paths



Macroscale film-substrate ensemble

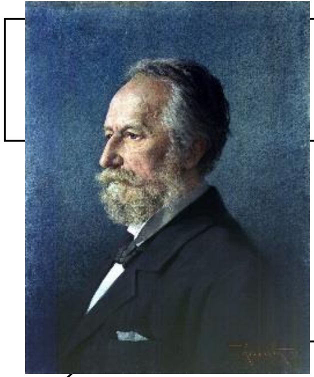
Mesoscale polycrystalline microstructure

- → Volume diffusion
- → Grain boundary diffusion (different GB)
- → ~~Diffusion in dislocations~~
- → ~~Surface~~, interface diffusion
- → ~~Voids, cavities…~~



Outline

- **Diffusion in solid**
  - Some history
  - Fick's laws
  - Point defects
  - Diffusion mechanisms
  - Atomistic model
  - Diffusion in various materials
- **Lattice diffusion in oxide**
  - Stoichiometric oxides
  - Non stoichiometric oxides
  - Interdiffusion in oxides
  - Glass
- **Grain boundary diffusion**
  - Harrison's regimes
  - Fisher's model
  - GB diffusion in oxides
- **Surface / Interface / diffusion**
  - Effect of surface on diffusion
  - Interphase diffusion



Diffusion: a little bit of history

1 - **“ The law ”** - A. Fick - 1855

Salt in water (Phil. Mag. 10 (1855) 30)

“ It was quite natural to suppose that this law for the diffusion of salt in its solvent must be identical with that according to which the diffusion of heat in a conducting body takes place; upon this law Fourier founded his celebrated theory of heat, and it is the same which Ohm applied with such extraordinary success to the diffusion of electricity in a conductor ”

2 - **“ Solids diffuse in solids ”**

W. C. Roberts-Austen - 1889

Fe can be carburized by diamond in vacuum at low temp. (Nature 41 (1899) 14)

“ and I can measure it “

Au in Pb Phil. Trans. Roy. Soc. A187 (1896) 383

“ The following experiment constitutes so far as I am aware the first attempt to actually measure the diffusivity of one solid metal in another ”

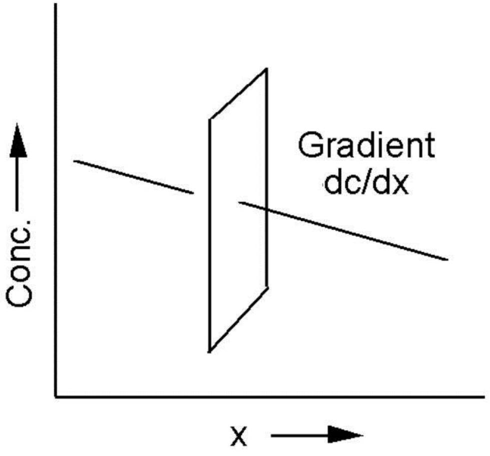
3 - **“Radioactive tracers ”** G. Hevesy - 1921

^{210}Pb in Pb J. Groh and G. v Hevesy Ann. Phys. 65 (1921) 216

Fick’s first law of diffusion

- Fick proposed a relationship of diffusion of matter similar to Fourier’s equation for heat. He proposed that the flux of particles is proportional to the gradient in concentration of particles. In one dimension this is written:

$$j = -D\frac{dc}{dx}$$



- The flux density *j* of particles has units e.g. #/(cm^{2}s) or mol/(cm^{2}s)

- The concentration is given in e.g. #/cm^3 or mol/cm^3

- The diffusion coefficient (or diffusion constant) then has units cm^2/s

- The minus sign states that the flux goes *down* the concentration gradient. The negative of the concentration gradient may be taken as the driving force.

Fick’s first law of diffusion - comments

$$j = -D\frac{dc}{dx}$$

- Fick’s first law is a phenomenological – or empirical – expression; It describes a flux in terms of a concentration gradient and a proportionality coefficient – the diffusion constant, or diffusivity.
- However, Fick’s first law applies strictly only to neutral non-interacting particles. Examples comprise dilute solutions of interstitial atoms, e.g. atomic H in metals.
- For other situations, the coefficient in Fick’s first law is not a constant.
- *D* in Fick’s first law has not been given any physical meaning up to now. In the next, we will give it more content.
- Fick’s law is useful because, in experiments, it is easier to determine the composition

Measurement methods

Macroscopic methods: Based on long range mass transport

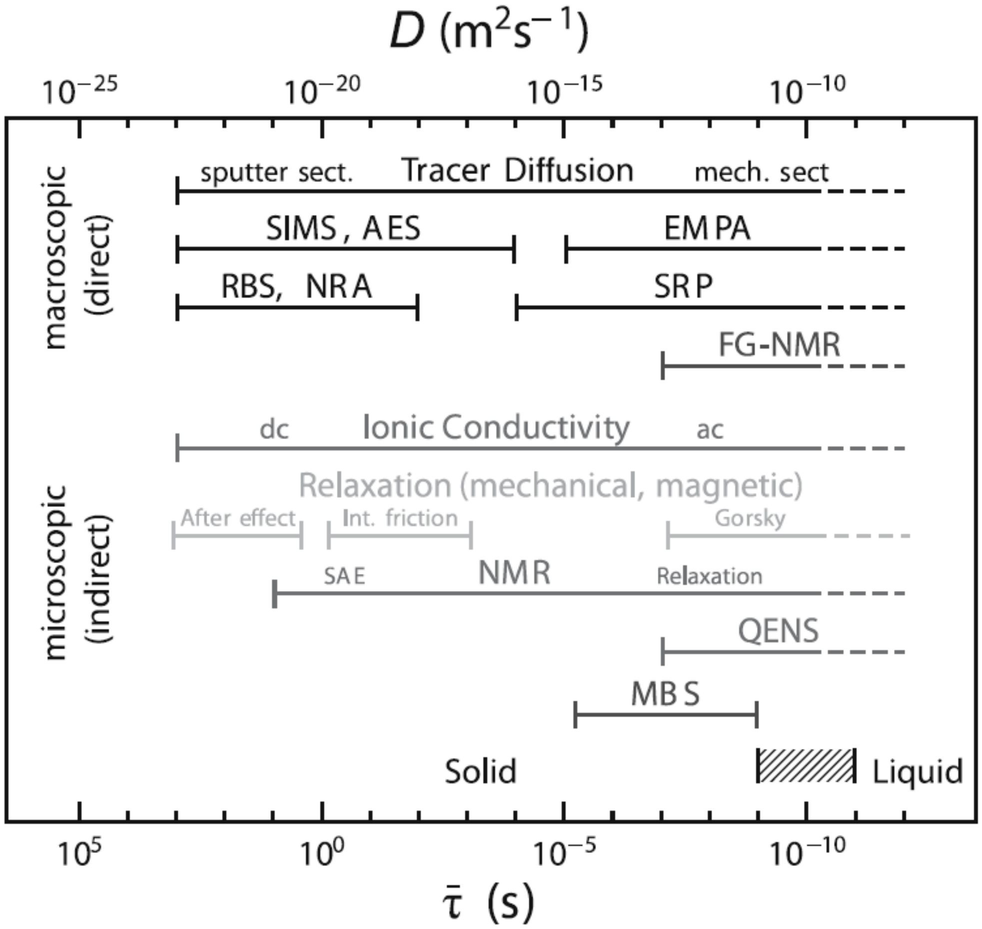
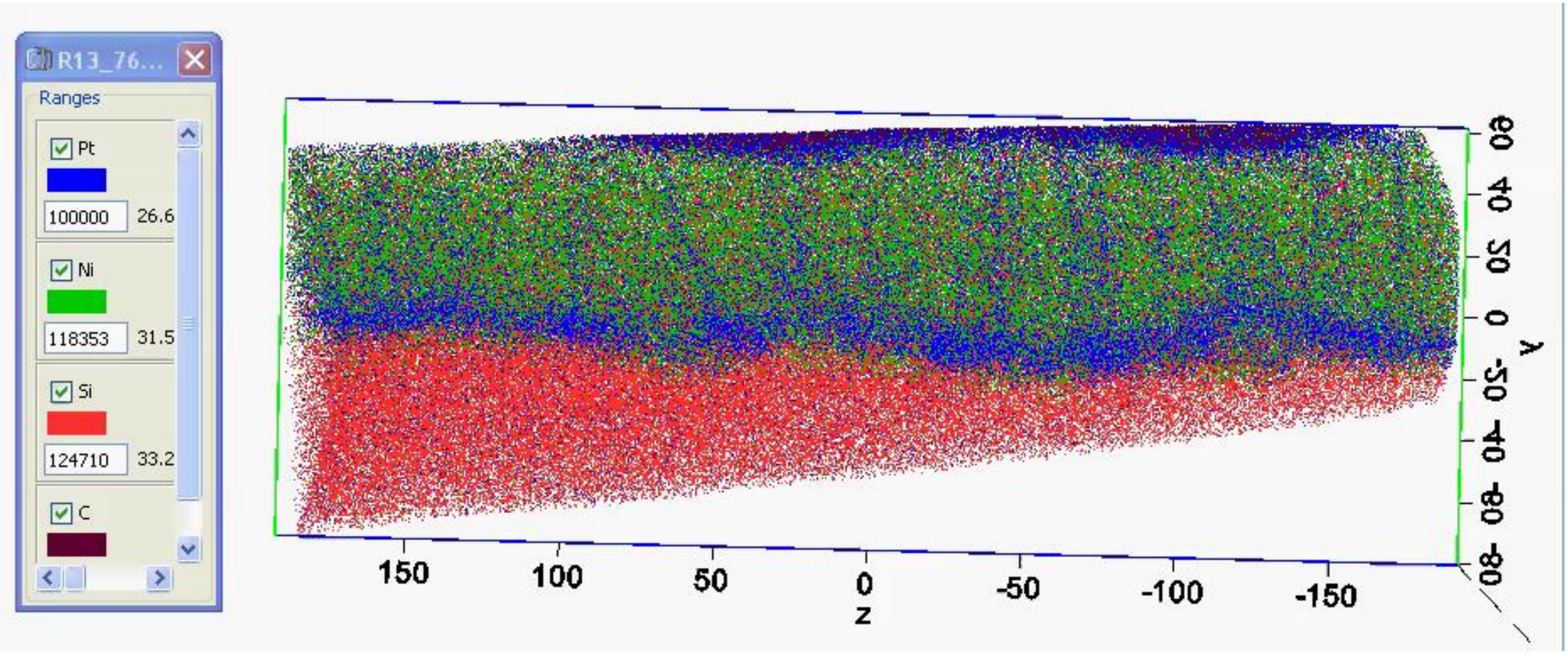


Fig. 13.1. Typical ranges of the diffusivity D and the mean residence time $\bar{\tau}$ of direct and indirect methods for diffusion studies

Microscopic methods: Based on jump frequencies

Atom probe tomography: diffusion of Pt in Ni silicide:



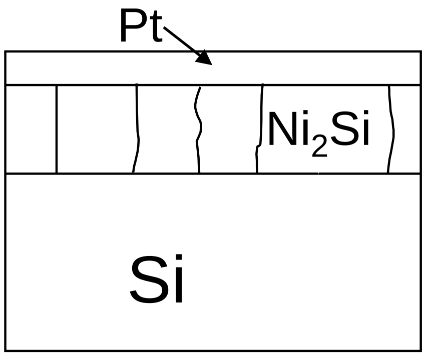
R13_76...

Ranges

☑ Pt	🟦	100000 26.6
☑ Ni	🟩	118353 31.5
☑ Si	🟥	124710 33.2
☑ C	🟥	

Atom probe tomography:

- **Atoms !!!**
- **3D**
- **Quantitative at interface → segregation**
- **Isotope → self-diffusion**



- **LEAP3000XHR**
  - **50K, 200 kHz,**
  - **0.6 nJ/pulse,**
  - **0.01 ions pulse**
  - **120x120x400 nm^3**
  - **120 10^6 atoms**

Diffusion: atomistic approach

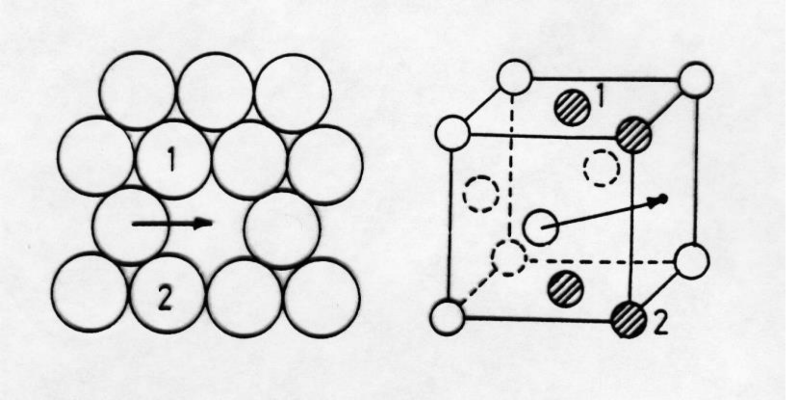
Molecular Dynamics surface diffusion of an Ag adatom on Ag(111)

- The atom vibrates on the surface
- When the temperature is increased, the vibration increase
- Some time, the atom jumps in random direction
- At high temperature, other mechanisms with higher barrier can occur

Diffusion: how atoms can move in a cristal ?

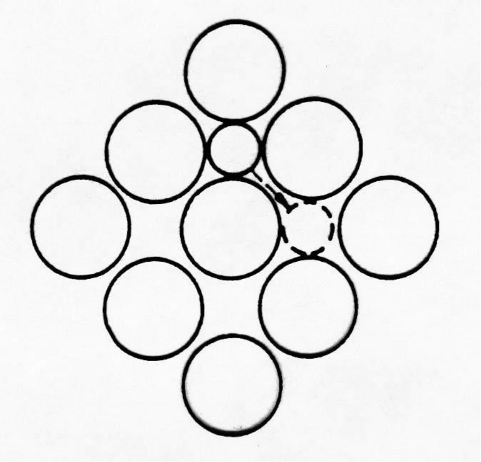
Because of point defects
(lattice perturbation with a size in the order of the atomic volume)

Atoms oscillate around a given lattice site of minimum energy (mean vibration energy ~ 3kT) but their movement is limited by their neighbors except if a vacant site exist in their vicinity



The diffusion rate depends on the jump frequency and the vacancy concentration

If the solute atoms are smaller than the atoms of the matrix, they can use interstitial sites



Diffusion rate depends only on the jump frequency

Point defects in a crystal: why?

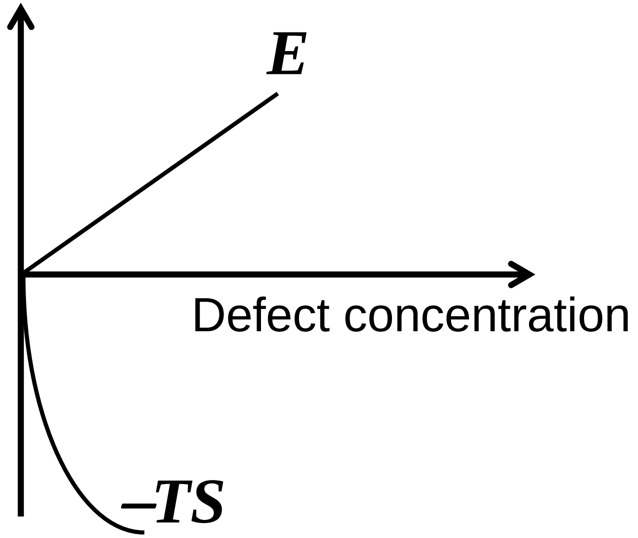
Introduction of a defect

- Increase of the internal energy of the system (formation energy of the defect)
- increase of the entropy of configuration of the system (the defect can occupy different locations of different types in the crystal)

Free energy of the system

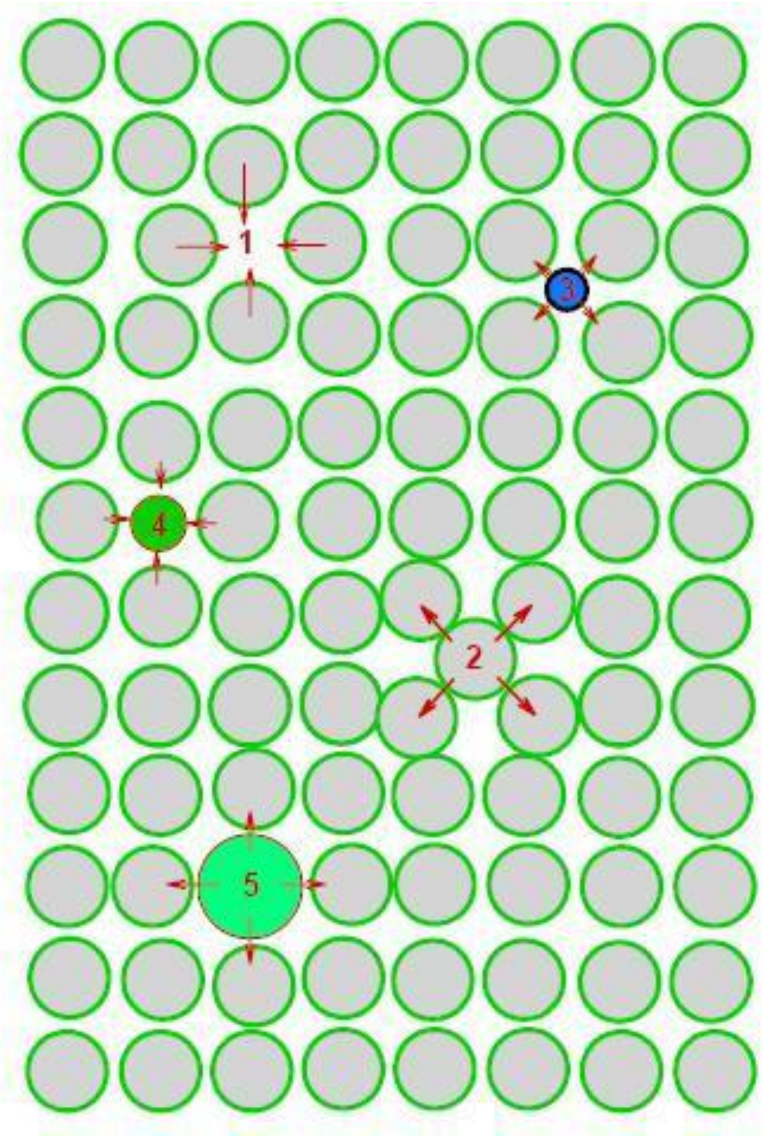
$$F = E - TS$$

$$\frac{n}{N-n} \approx \frac{n}{N} = \exp\left(\frac{-E_F}{kT}\right)$$



Under equilibrium conditions, solids always possess point defects

Point defects: examples



(1) Vacancy ⇒ V

(2) Self-interstitial ⇒ I

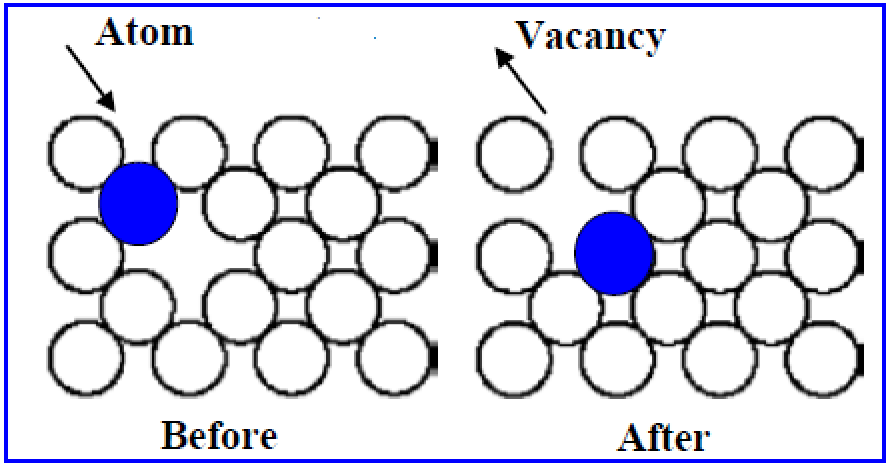
(3) Interstitial impurity ⇒ A_i

(4), (5) substitutional impurity ⇒ A_s

Arrows show the local stress introduced by the point defects

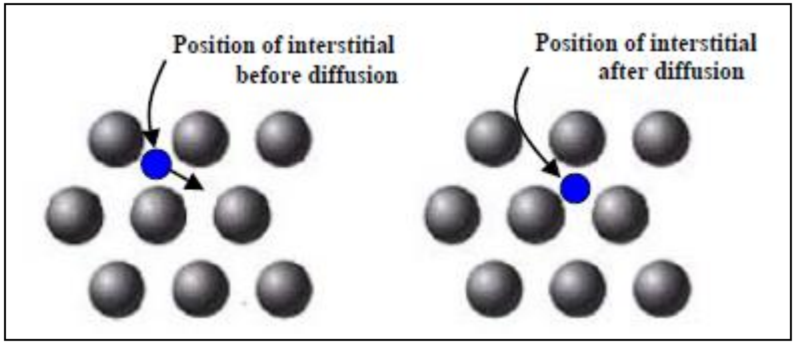
Diffusion mechanisms

Vacancy diffusion
(Ex: self- and heterodiffusion
in substitutional solid solutions)

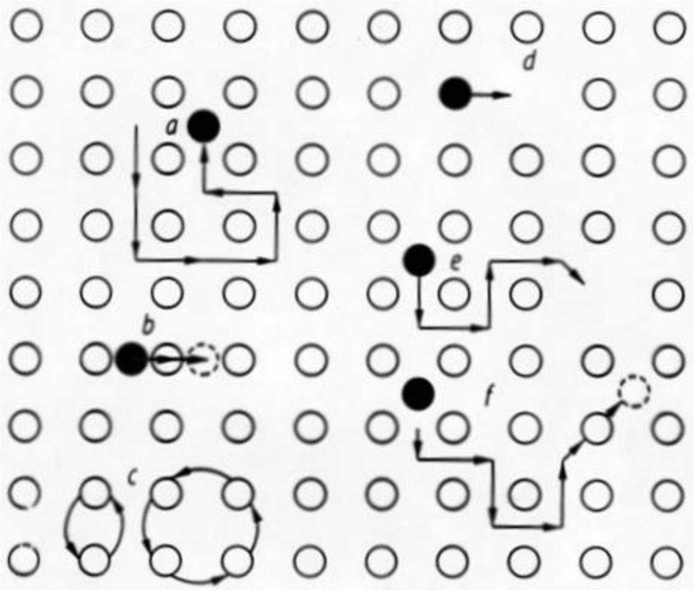


Materials flow (atoms) is opposite to the vacancy flow direction

Interstitial diffusion
(Ex: heteroatoms in interstitial
solid solutions, transitions
metals in Si)



Complex diffusion mechanisms



Diffusion in Si

d: vacancy

a: direct interstitial

b: indirect interstitial (intersticialcy)

e: dissociative $A_i + V \leftrightarrows A_s$

f: kick-out $A_i \leftrightarrows A_s + I$ (indirect interstitial)

c: ring

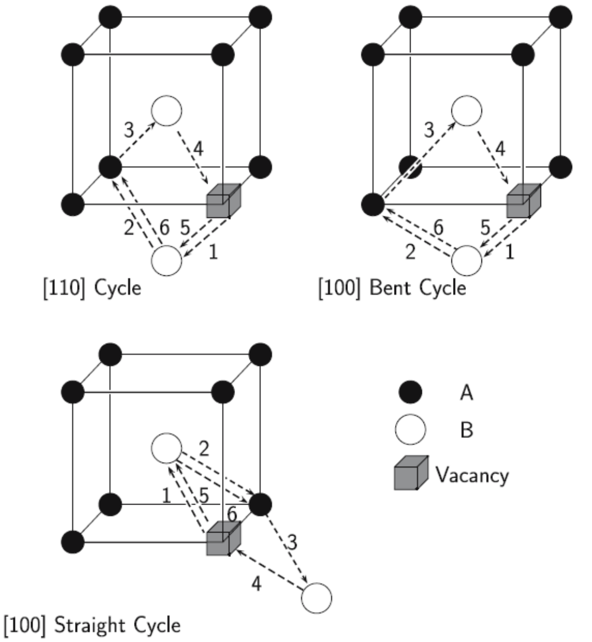
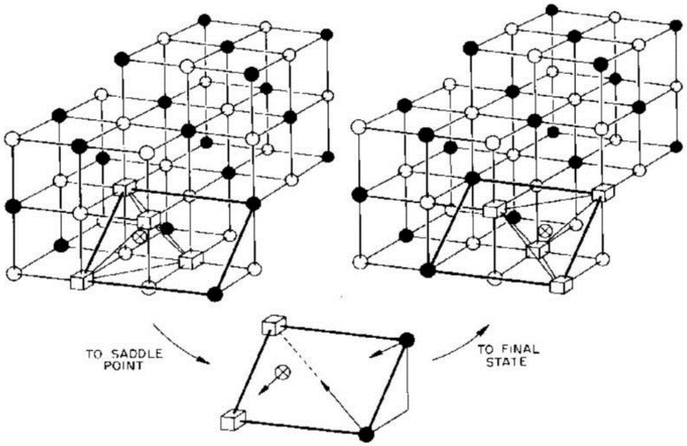
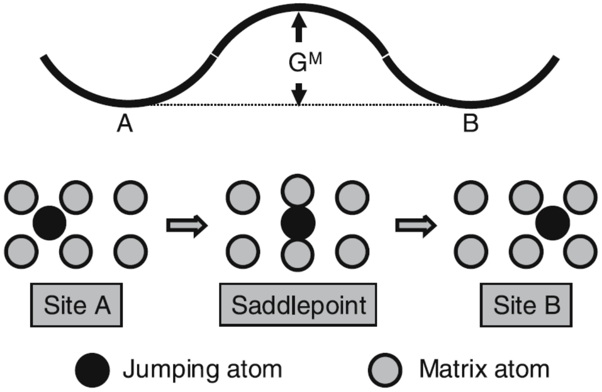


Fig. 20.5. Schematic illustration of six-jump vacancy cycles in the B2 structure. The *arrows* show vacancy jumps; the *numbers* indicate the jump sequence

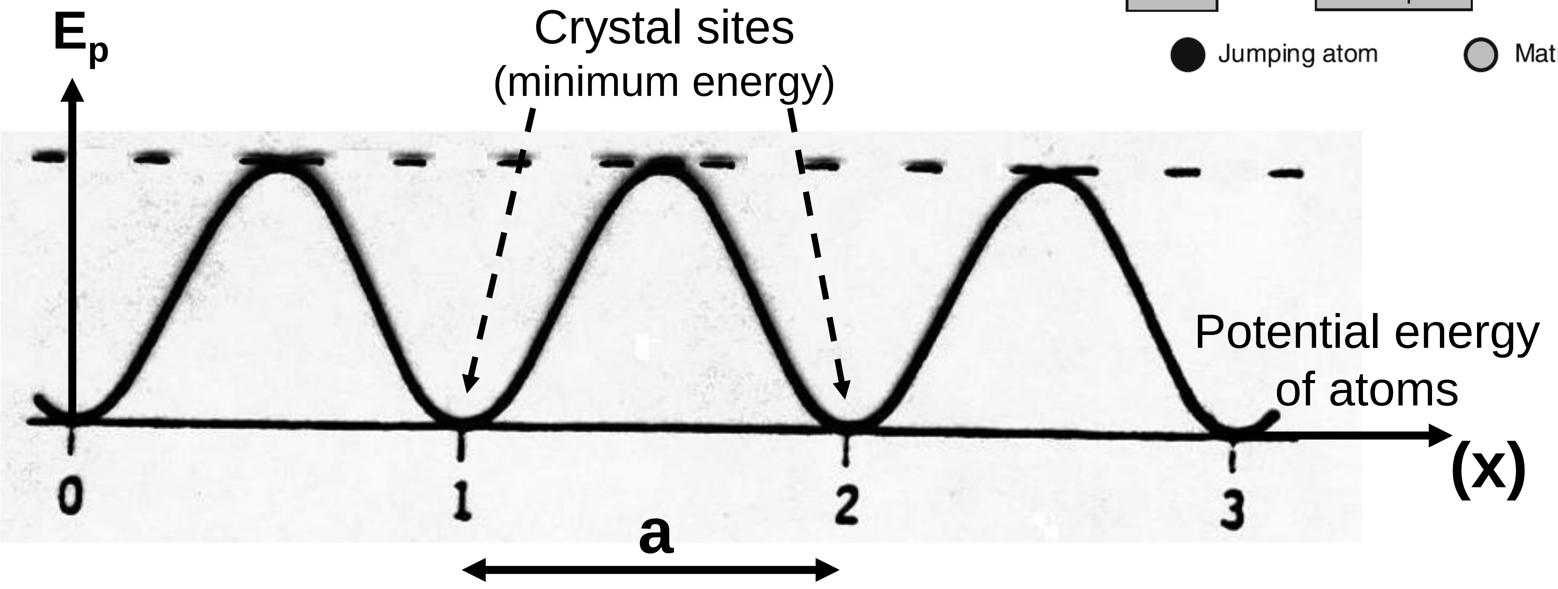


Diffusion of iron in $Fe_{1-x}O$ via a 4:1 cluster (4 vacancies and 1 interstitial): The interstitial and one atom fills two vacancies, while one atom goes into a new interstitial position between the new (moved) set of vacancies.

Diffusion: atomistic approach



A simple model of crystal



E_p

Crystal sites
(minimum energy)

Potential energy
of atoms

(x)

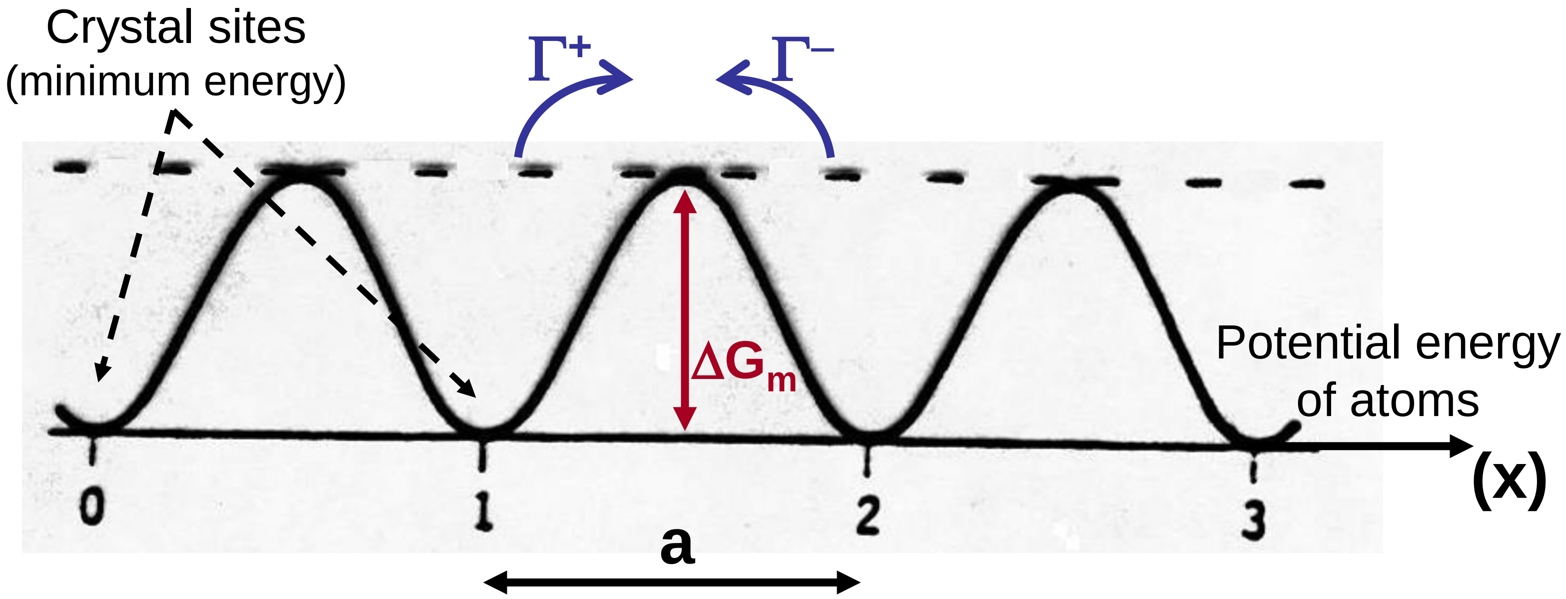
a

Lattice parameter

Boltzmann distribution $P(x) \sim \exp[-E_p / kT]$

The probability to find an atom in a given position in the crystal varies exponentially with (–) the potential energy of this atom in this position divided by the Boltzmann constant k and the temperature T

Diffusion: atomistic approach



Equilibrium

- $\Gamma^+ = \Gamma^- = \Gamma$
- same jump rate in directions (–x) and (+x)

$$\Gamma = \nu_0 \exp\left(\frac{-\Delta G_m}{kT}\right)$$

ΔG_m: energy barrier

Γ: Jump rate (jump.s^{-1})

ν_0: attempt frequency

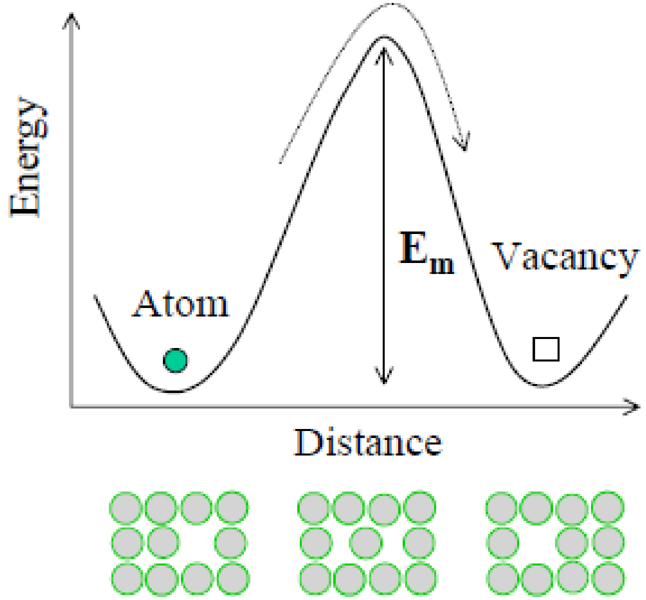
~ Debye frequency

Random motion

No flux

Diffusion – Thermally Activated Process (I)

In order for atom to jump into a vacancy site, it needs to posses enough energy (thermal energy) to to break the bonds and squeeze through its neighbors. The energy necessary for motion, E_m, is called **the activation energy** for vacancy motion.



Schematic representation of the diffusion of an atom from its original position into a vacant lattice site. At activation energy E_m has to be supplied to the atom so that it could break inter-atomic bonds and to move into the new position.

$$D_d = \beta \, \Gamma a^2 = \beta a^2 \nu_0 \exp\left[-\frac{\Delta G_m}{kT}\right]$$

$$D_d = \beta a^2 \nu_0 \exp\left(\frac{\Delta S_m}{k}\right) \exp\left[-\frac{E_m}{kT}\right]$$

$$D_d = D_0 \exp\left[-\frac{E_m}{kT}\right]$$

β: geometrical factor
a: jump distance
ν_0: attempt frequency (~10^{13} s^{-1})
ΔG_m: free enthalpy of migration
E_m: migration energy

D_0 ~ 10^{-2} cm^2 s^{-1}

Diffusion assisted by defect

$$D = p_d D_d \qquad p_d\text{=probability of defect}$$

$$p_d = \frac{n_d}{N} = C_d = \exp\left[-\frac{E_f}{kT}\right]$$

$$D = D_0 \exp\left[-\frac{E_f + E_m}{kT}\right]$$

Variation with temperature

$$\boxed{D = n_d \Gamma a^2}$$

$$n_d = p_d = c_d = c_0 \exp\left(-\frac{\Delta H_f}{kT}\right)$$

$$\Gamma = \nu_0 \exp\left(-\frac{\Delta H_m}{kT}\right)$$

$$D = D_0 \exp\left(-\frac{\Delta H}{kT}\right)$$

$\Delta H = \Delta H_f + \Delta H_m$ (= Q activation energy)

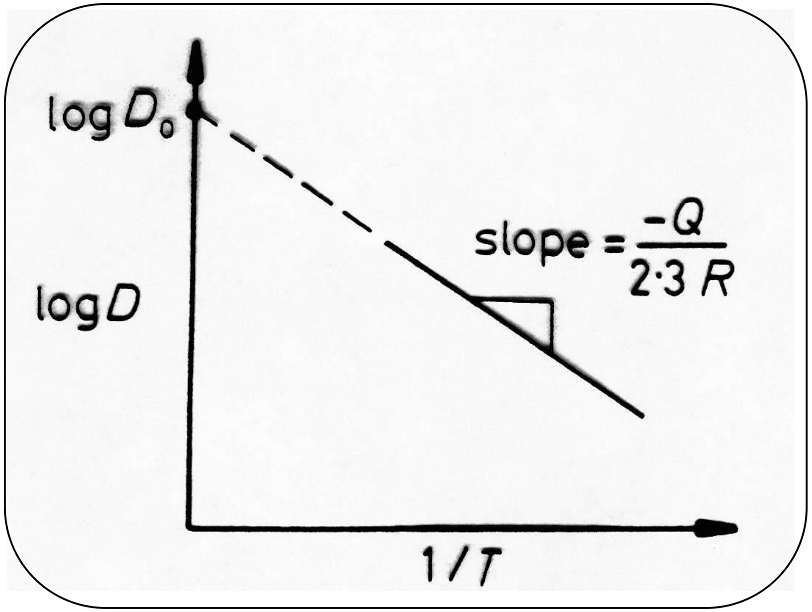
ΔH_f = enthalpy of formation of the defect

ΔH_m = enthalpy of migration of the defect

pure Interstitial: $\Delta H = \Delta H_m$

Vacancy: $\Delta H = \Delta H_m + \Delta H_f$

$\Delta G = \Delta H - T\Delta S$



Arrhenius plot

$D = C_d D_d = C_d D_{d\,0} \exp(-H_m/kT)$

D_d Diffusion coefficient of the defect

Correlation

Auto diffusion: $D = C_d D_d$

Tracer diffusion: $D^* = f\,D = f\,C_d\,D_d$

f = correlation factor

- f=1 for interstitial mechanism
- f<1 if diffusion vehicle: vacancy, divacancy, self-interstitiel
- f: complex function of T and C for alloys

→ *Nastar et al , Phil. Mag. 2000*

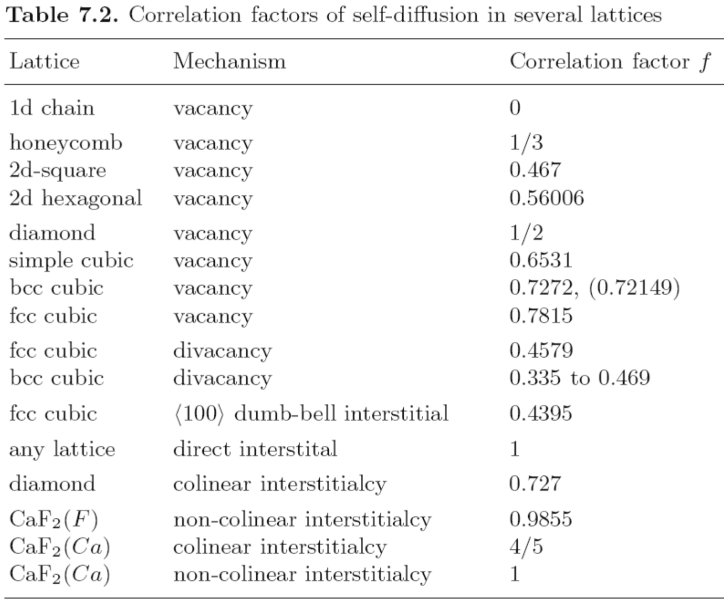


Table 7.2. Correlation factors of self-diffusion in several lattices

Lattice	Mechanism	Correlation factor f
1d chain	vacancy	0
honeycomb	vacancy	1/3
2d-square	vacancy	0.467
2d hexagonal	vacancy	0.56006
diamond	vacancy	1/2
simple cubic	vacancy	0.6531
bcc cubic	vacancy	0.7272, (0.72149)
fcc cubic	vacancy	0.7815
fcc cubic	divacancy	0.4579
bcc cubic	divacancy	0.335 to 0.469
fcc cubic	⟨100⟩ dumb-bell interstitial	0.4395
any lattice	direct interstital	1
diamond	colinear interstitialcy	0.727
$CaF_2(F)$	non-colinear interstitialcy	0.9855
$CaF_2(Ca)$	colinear interstitialcy	4/5
$CaF_2(Ca)$	non-colinear interstitialcy	1

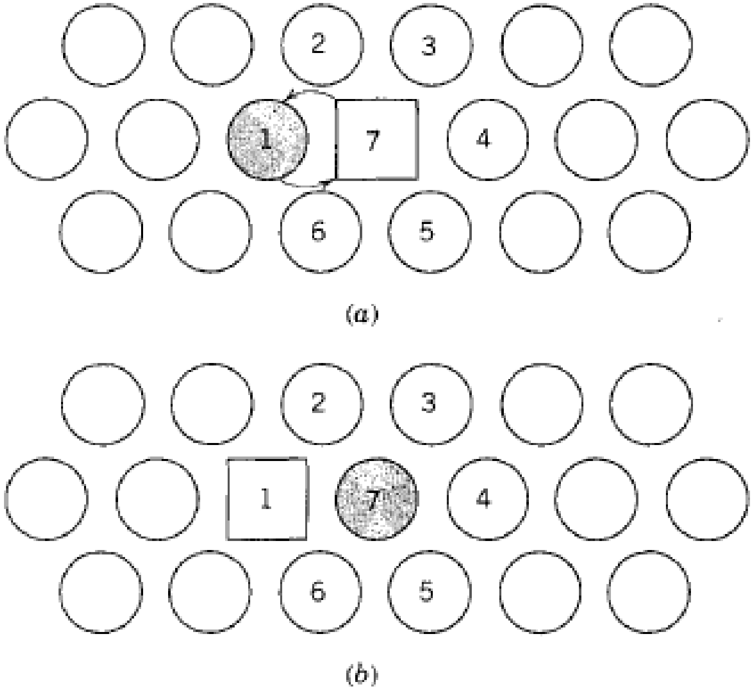
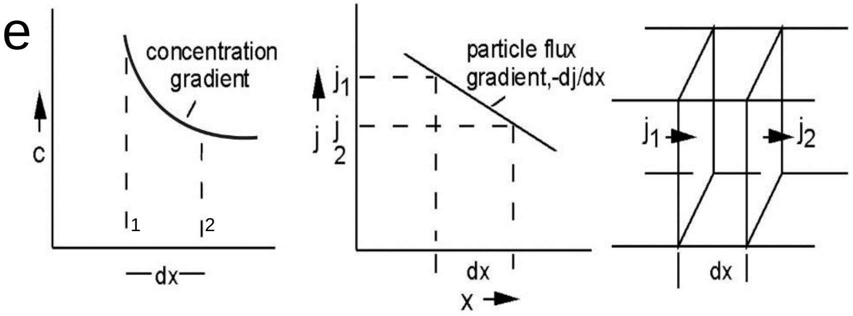


Fig. 3.7 Schematic depicting correlation effect for diffusion in a 2-D hexagonal lattice. After the atom at 1 exchanges with the vacancy at 7, there is a finite probability that the next jump will return the atom to its original position. If the atom is chemically indistinguishable from the host lattice atoms, as for a tracer atom, this probability is 1/6 in this lattice.

2^{nd} Fick’s law

Fick’s second law of diffusion - mathematics



- From the matter conservation, the change in concentration is given by the gradient in flux density:

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x}$$

- Fick’s first law applies in each point along *x*, and we may thus insert for the flux density *J* so as to get:

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right)$$

- If D is independent of c, we may simplify:

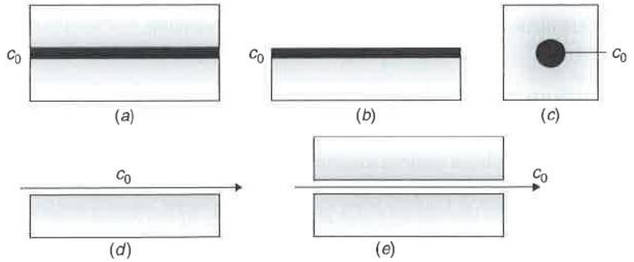
$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} = D\frac{\partial^2 c}{\partial x^2}$$

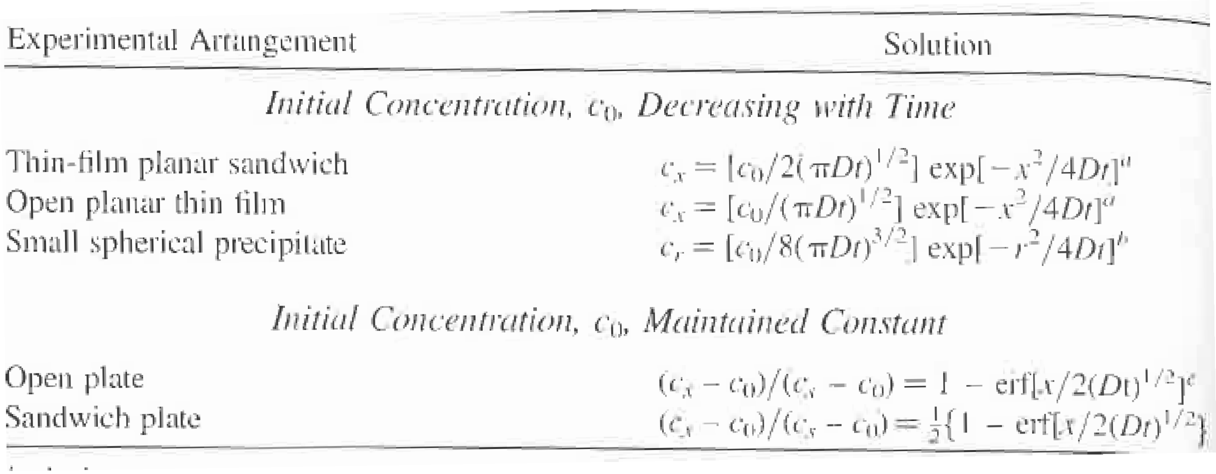
- Especially the last equation may be solved for many practically achievable geometries and boundary conditions.

These are different versions of Fick’s second law of diffusion

The “bible” of solutions to Fick’s second law is J. Crank (1956); “Mathematics of diffusion”

Fick’s second law
Non-steady state diffusion: Particular solutions





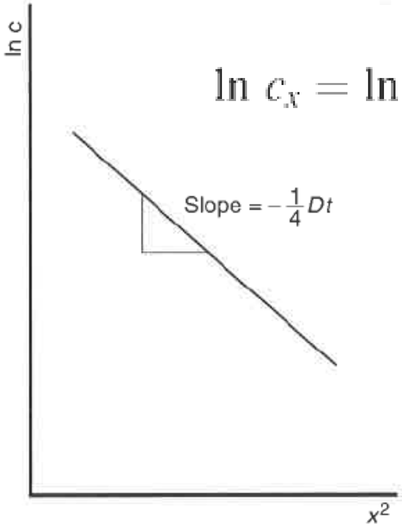
Experimental Arrangement	Solution
Initial Concentration, c_0, Decreasing with Time	
Thin-film planar sandwich	$c_x = [c_0/2(\pi Dt)^{1/2}] \exp[-x^2/4Dt]^a$
Open planar thin film	$c_x = [c_0/(\pi Dt)^{1/2}] \exp[-x^2/4Dt]^a$
Small spherical precipitate	$c_r = [c_0/8(\pi Dt)^{3/2}] \exp[-r^2/4Dt]^b$
Initial Concentration, c_0, Maintained Constant	
Open plate	$(c_x - c_0)/(c_s - c_0) = 1 - \mathrm{erf}[x/2(Dt)^{1/2}]^c$
Sandwich plate	$(c_x - c_0)/(c_s - c_0) = \frac{1}{2}\{1 - \mathrm{erf}[x/2(Dt)^{1/2}\}$

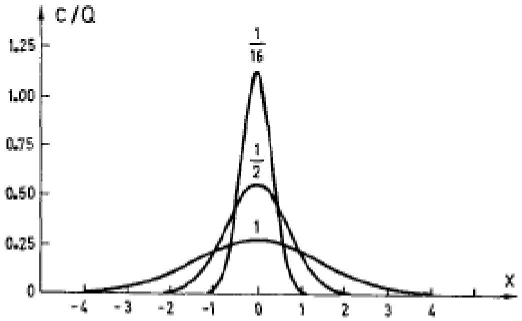
1: « Instantaneous source »

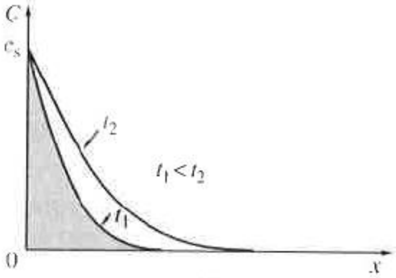
2, 3: « Constant source »

$$\ln c_x = \ln\left[\frac{c_0}{2(\pi Dt)^{1/2}}\right] - \left(\frac{x^2}{4Dt}\right)$$

$$c(x,t) = c_0 \,\mathrm{erfc}(x/2\sqrt{Dt})$$







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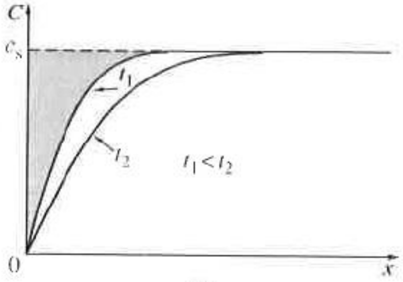

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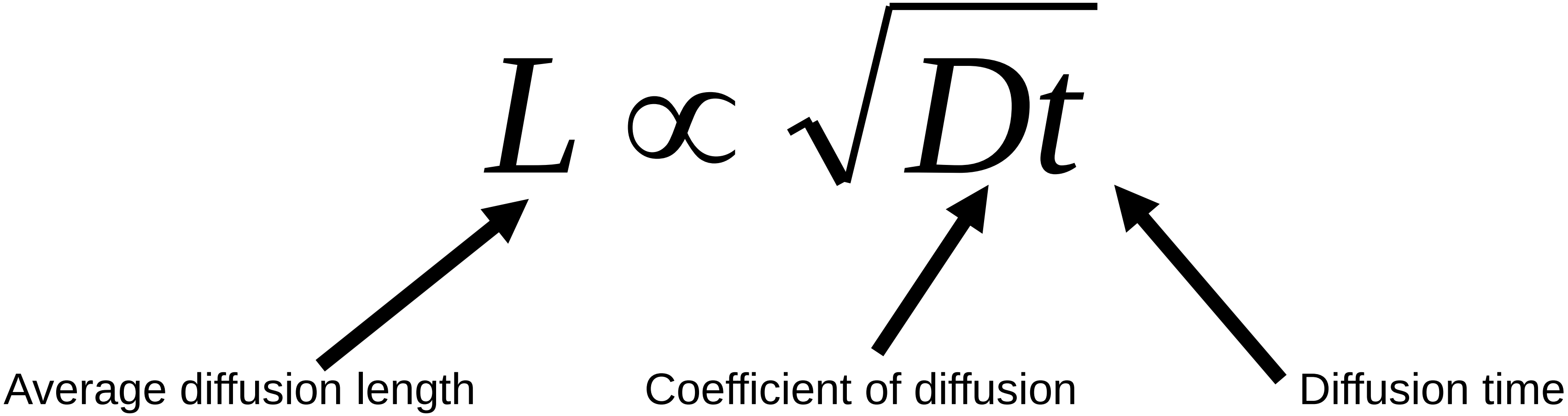
Diffusion: solution of the Fick's law

Important laws to remember

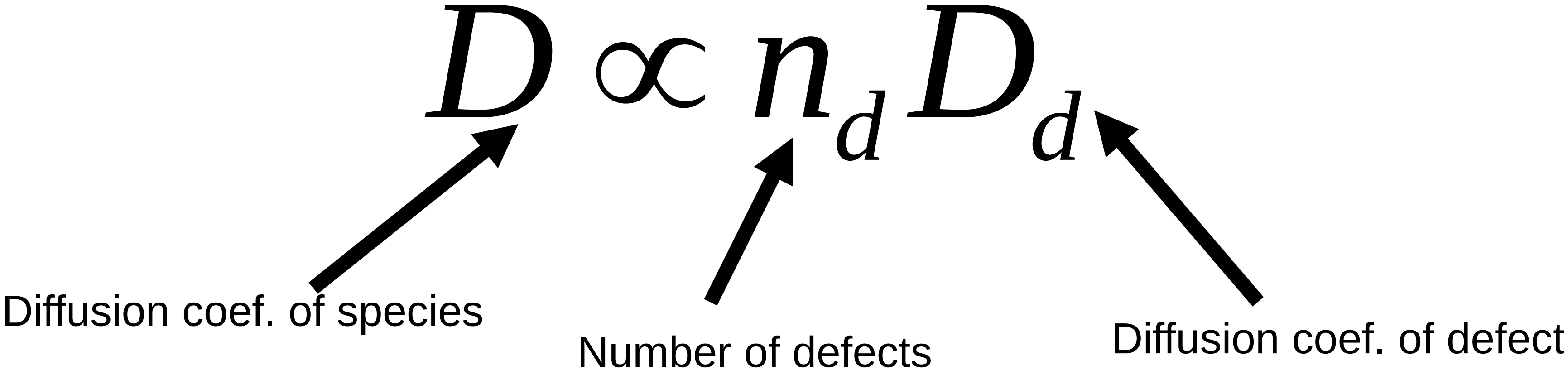


$$L \propto \sqrt{Dt}$$

Average diffusion length

Coefficient of diffusion

Diffusion time



$$D \propto n_d D_d$$

Diffusion coef. of species

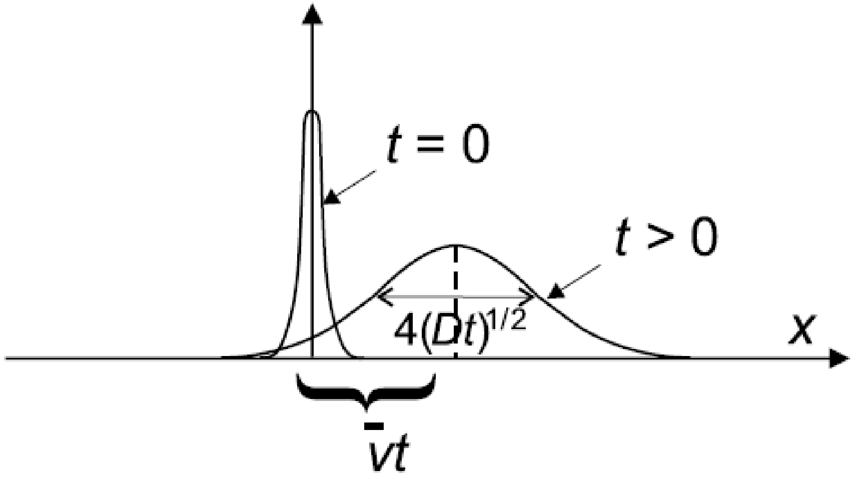
Number of defects

Diffusion coef. of defect

Something else ?

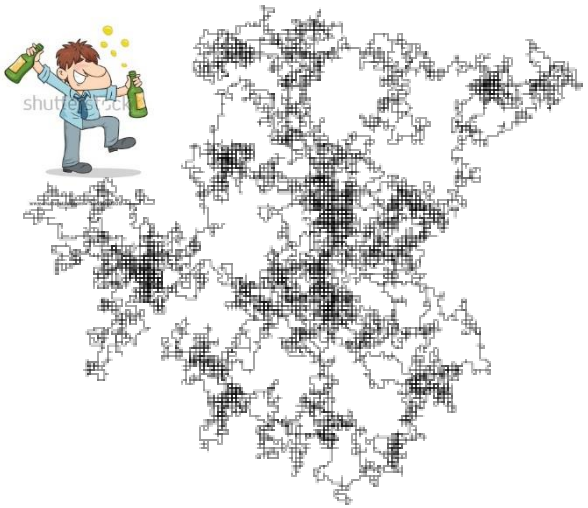
Diffusion and driving force

Diffusion and driving force



$v = M \times F$

Fig. 11.1. Schematic illustration of diffusion and drift

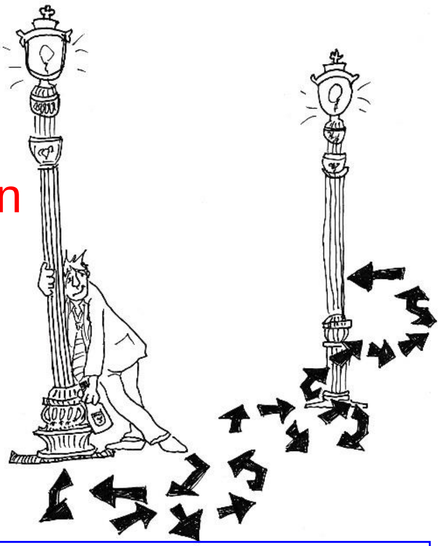


Einstein

$$\overline{R_n} = \sqrt{6 D_r t}$$

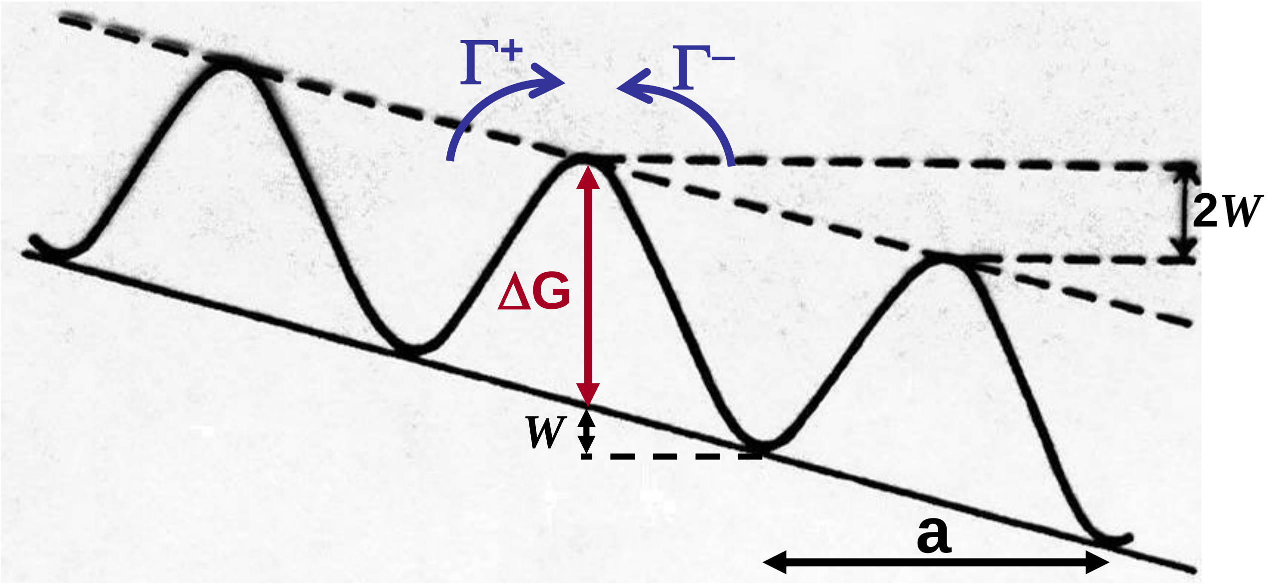
Nernst-Einstein

$$J = C\mathrm{v} = \frac{CD}{kT} F$$



Why (and when) the drunk man will reach the “reverbere”?

Diffusion: quasi-atomistic approach



F: driving force

$$W = \int_0^{a/2} \vec{F}\, d\vec{x}$$

$$F = cont \Rightarrow W = \frac{aF}{2}$$

$$\Gamma^+ = \nu_0 \exp\left(-\frac{\Delta G}{kT}\right)\exp\left(+\frac{aF}{2kT}\right) = \Gamma \exp\left(+\frac{aF}{2kT}\right)$$

$$\Gamma^- = \Gamma \exp\left(-\frac{aF}{2kT}\right)$$

$\Rightarrow$ Flux J

Diffusion: atomistic approach

$$\Gamma_{(+x)} = \Gamma^{+} - \Gamma^{-} = 2\Gamma \sinh\left[\frac{aF}{2kT}\right]$$

If $\frac{aF}{2kT} << 1 \quad \Rightarrow \Gamma_{(+x)} = \Gamma \frac{aF}{kT}$

$\Gamma_{(+x)}$: transport rate (at.s^{-1})

v: transport velocity (at.cm.s^{-1})

J: diffusion flux (at.cm^{-2}.s^{-1})

C: atom concentration (at.cm^{-3})

If the jump frequency varies linearly with F, $v = a\Gamma_{(+x)}$

$$J = Cv = \frac{C\Gamma a^2}{kT} F = \frac{CD}{kT} F$$

Nernst Einstein relation

Diffusion: atomistic approach

$$D = p_d \Gamma a^2$$

a: jump distance

p: probability to find a defect

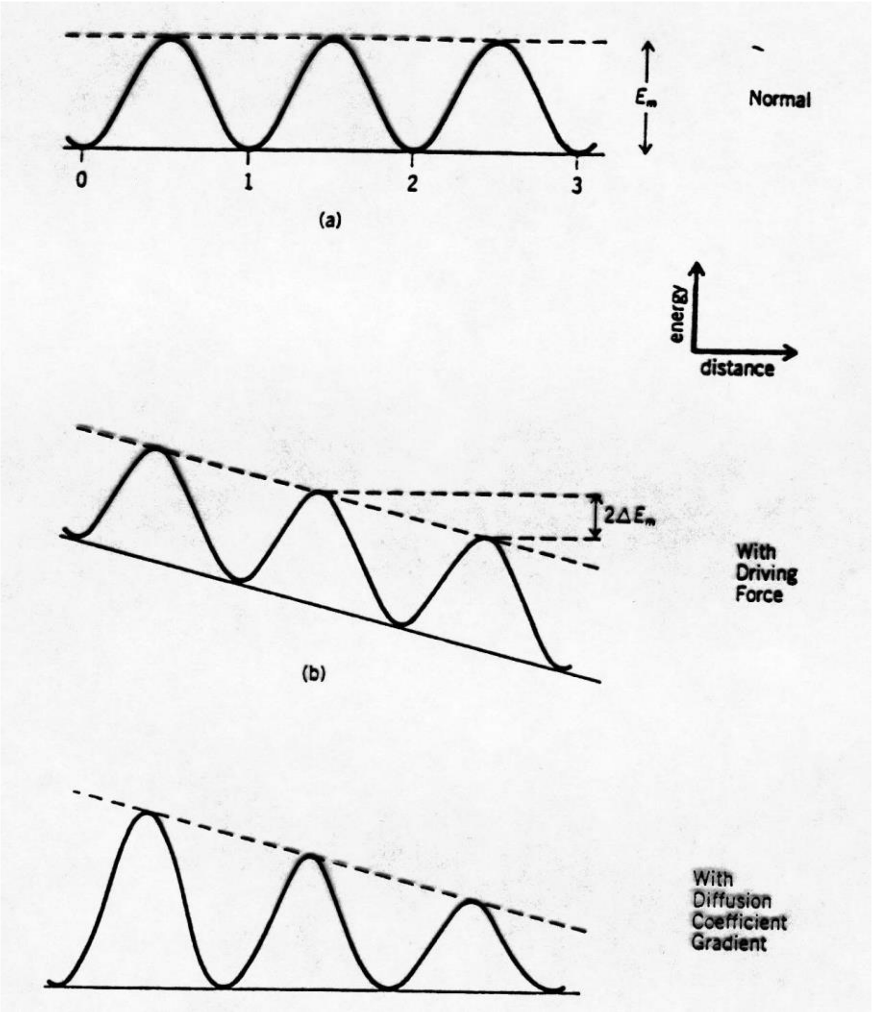
Γ: jump rate

Everything which affects Γ and p will affect D

The mass transport is characterized by the flux

Quantity of atoms which pass a surface unit in unit of time

$$J = \frac{CD}{kT} F$$



Diffusion flux, mobility, Onsager

J (at s^{-1}): particle flux = number of particles that are going through a surface unit (section) per time unit

$$J = CMF = LF$$

J proportional to the number of particles (C) and to their mobility (M) or J proportional to L (Onsager coefficient)

$$J = \frac{CD}{kT} F$$

C: particle concentration in the matrix, *F*: driving force

$$D = Mk_B T$$

M: mobility of uncharged particles in a given matrix ,
1/*M*: friction coefficient, v=*M*×*F* = particles' velocity (m s^{-1})

$$D = \frac{L\, k_B T}{C}$$

D ($m^2\ s^{-1}$): diffusion coefficient

If several mechanisms and/or diffusion paths with different mobility:

$$J_i = \sum_k C_k M_k F_k$$

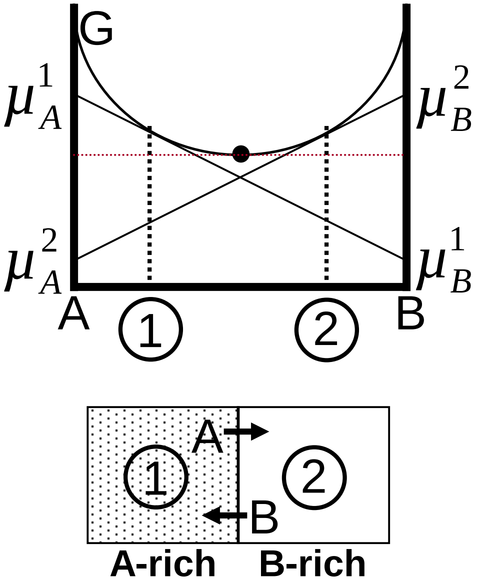
k: mechanisms, paths

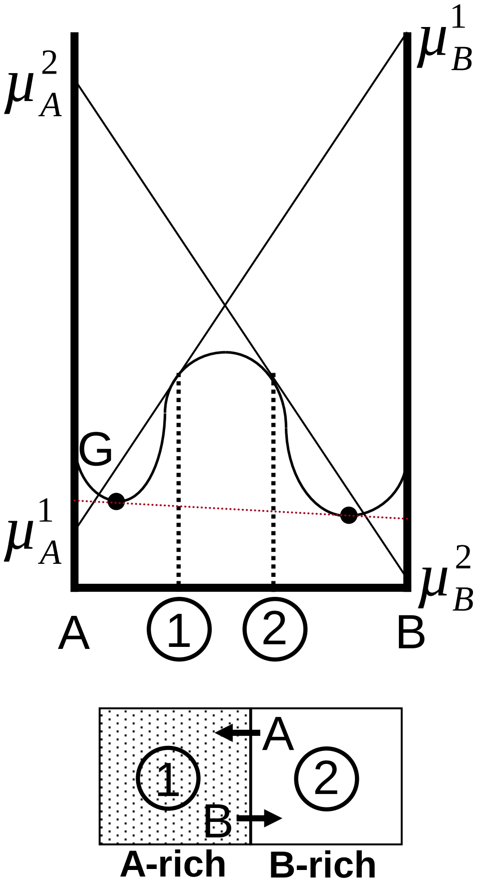
If several components (elements, vacancy…), Onsager equations:

$$J_i = \sum_j L_{ij} F_j$$

j: components

Driving force: an example





Driving force =
difference of chemical potential

$$F = -\frac{\partial \mu}{\partial x}$$

Nernst Einstein equation

$$J = -\frac{CD}{kT}\frac{\partial \mu}{\partial x}$$

Diffusion flux and diffusion equation

Driving force = minimum chemical potential ⇒ $F = -\frac{d\mu}{dx}$

"–" ⇒ atoms diffuse in the direction of decreasing chemical potential

$$J = -\frac{CD}{k_B T}\frac{d\mu}{dx}$$ Nernst-Einstein equation

$$J = -\frac{CD}{kT}\frac{\partial}{\partial x}\left(kT\ln(\gamma C)\right) = -D\left(\frac{\partial C}{\partial x}\left(1+\frac{\partial \ln\gamma}{\partial \ln C}\right)\right) = -\underset{\text{Kinetics}}{D}\overset{\text{Thermodynamics}}{\Phi}\frac{\partial C}{\partial x}$$

Φ is called the thermodynamic factor solution

$D_i = \Phi D$ is the intrinsic diffusion coefficient

Assuming D = constant and an ideal solution (or non-ideal diluted solution)
⇒ $\gamma = 1$, $\mu = k_B T \ln(C)$

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2}$$

Fick's equation = random motion
diffusion depends only on concentration

If the composition is constant ⇒ $\gamma = 1$, $\mu = k_B T \ln(C)$

Nernst-Einstein equation for charged particules

General transport equation:
linear relation between flux *J* and driving force, gradient of electrochemical potential *η*,
both **chemical (μ) and electrical (ϕ) potentials can act as driving forces** (L: Onsager coefficient):

$$\boxed{J = -L\nabla\eta = -L\nabla\mu - LF_a\nabla\phi}$$

Uncharged species: only chemical potential term relevant, process reduced to pure diffusion:

$$J = -L\nabla\mu = -\frac{RTL}{c}\nabla c$$

Comparison with Fick's first law permits to identify:

$$\boxed{L = \frac{Dc}{RT}}$$

Conversely, if no noticeable chemical potential variation: electrical field remains only driving force.
Fulfilled for solids with high charge carrier concentrations:
metals, fast ion conductors, highly doped systems!

$$J = -LF_a\nabla\phi$$

Converting the particle flux into a current density:

$$i = FJ = -LF_a{}^2\nabla\phi$$

Ohm's law: LF_a^2 corresponds to electrical conductivity

$$\boxed{\sigma = LF_a{}^2 = F_a{}^2\frac{Dc}{RT}}$$

Electrical conductivity σ: F_a Faraday constant (96500 C/mol), *u* mobility, *c* concentration

$$\boxed{\sigma = F_a uc}$$

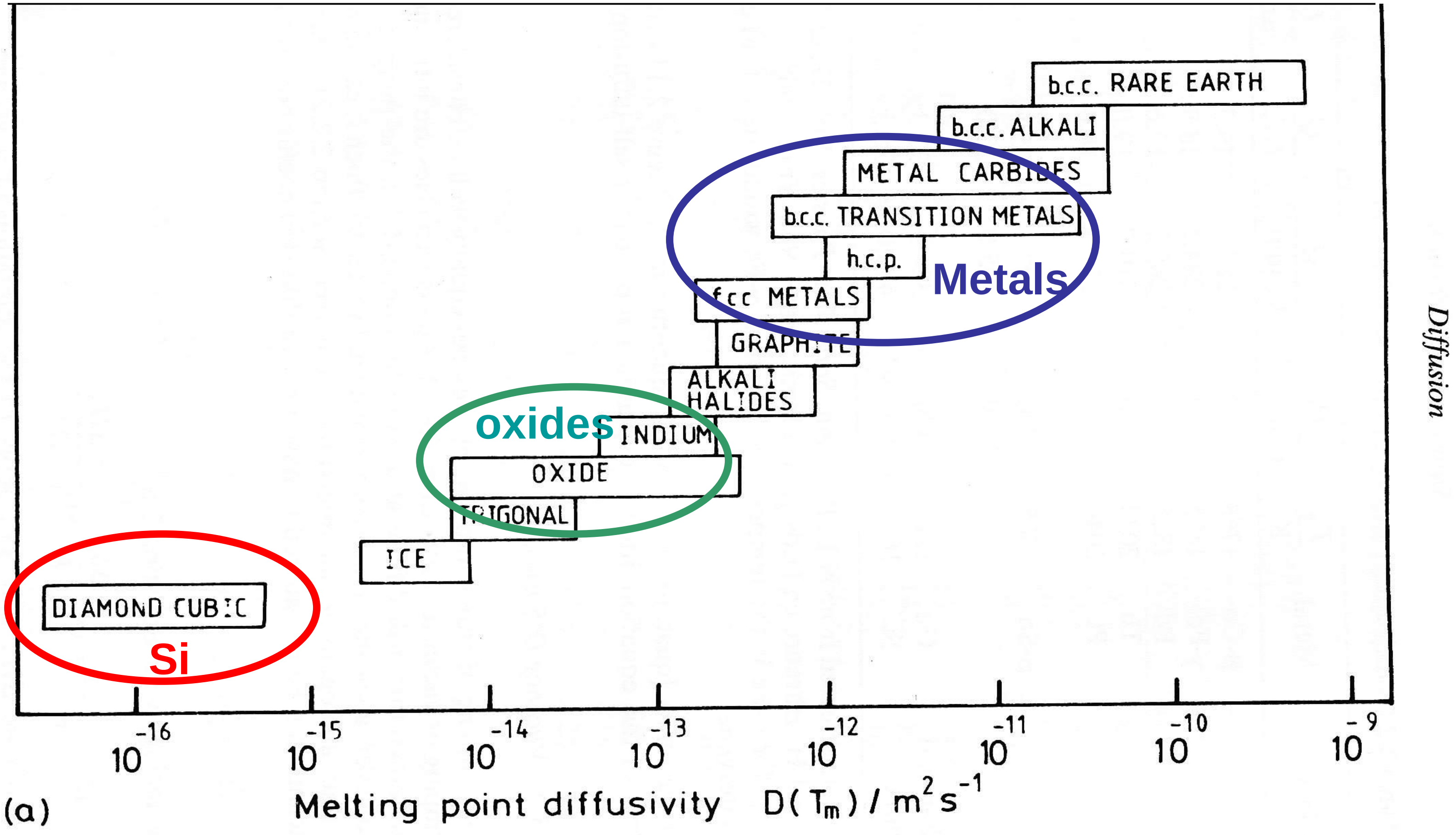
Nernst-Einstein equation between diffusion coefficient and mobility (in $cm^2.s^{-1}V^{-1}$):

$$\boxed{u = \frac{F_a D}{RT}}$$

Lattice (volume, bulk) diffusion in oxides

Diffusion behavior of various materials

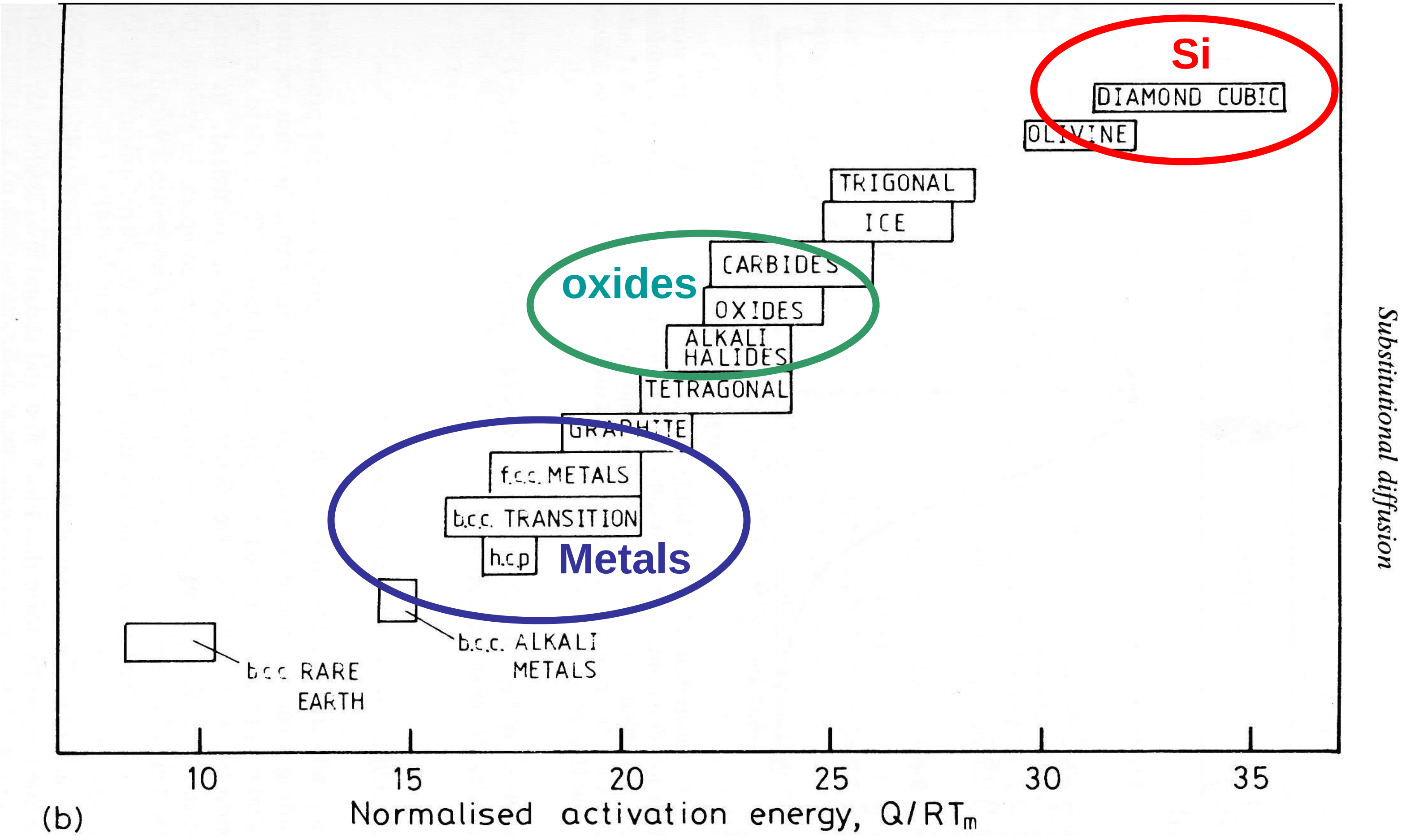
Melting diffusivity for various materials



T_m = melting temperature # bounding energy

Diffusion behavior of various materials

Activation energy for various materials



Diffusion: rules of thumb

Empirical rules

For a given crystal structure and a given bond type
(for a given class of materials)

$D(T_m) \sim$ constant, $Q/RT_m \sim$ constant and $D_0 \sim$ constant

The diffusion coefficient of all materials with a given crystal structure and bond type will be approximately the same at the same fraction of their melting temperature

$$D\left(\frac{T}{T_m}\right) \sim \text{constant}$$

If melting temperature (T_m) ↗

- Bond strength ↗ (ΔH_m ↗)
- Formation energy of defect ↗ (ΔH_f ↗) = concentration of defects ↘
- Coefficient of diffusion ↘

Rules of thumb: examples

Bulk self diffusion in pure close-packed (fcc and hcp) **metals**

Diffusion mechanism: vacancy

Empirical rules

1- Diffusion coefficient at the melting temperature (Tm) is roughly constant.

$$D(T_m) \approx 10^{-8}\ \text{cm}^2/\text{s}$$

2- Activation energy scales with the melting temperature

$$Q / RT_m \approx 18$$

3- Pre-exponential roughly constant

$$D_0 \approx 10^{-1}\ \text{cm}^2/\text{s}$$

Bulk self diffusion in oxides

César's thumb in Marseille

$$D(T_m) \approx 10^{-10}\ \text{cm}^2/\text{s}$$

$$Q / RT_m \approx 20\text{-}25$$

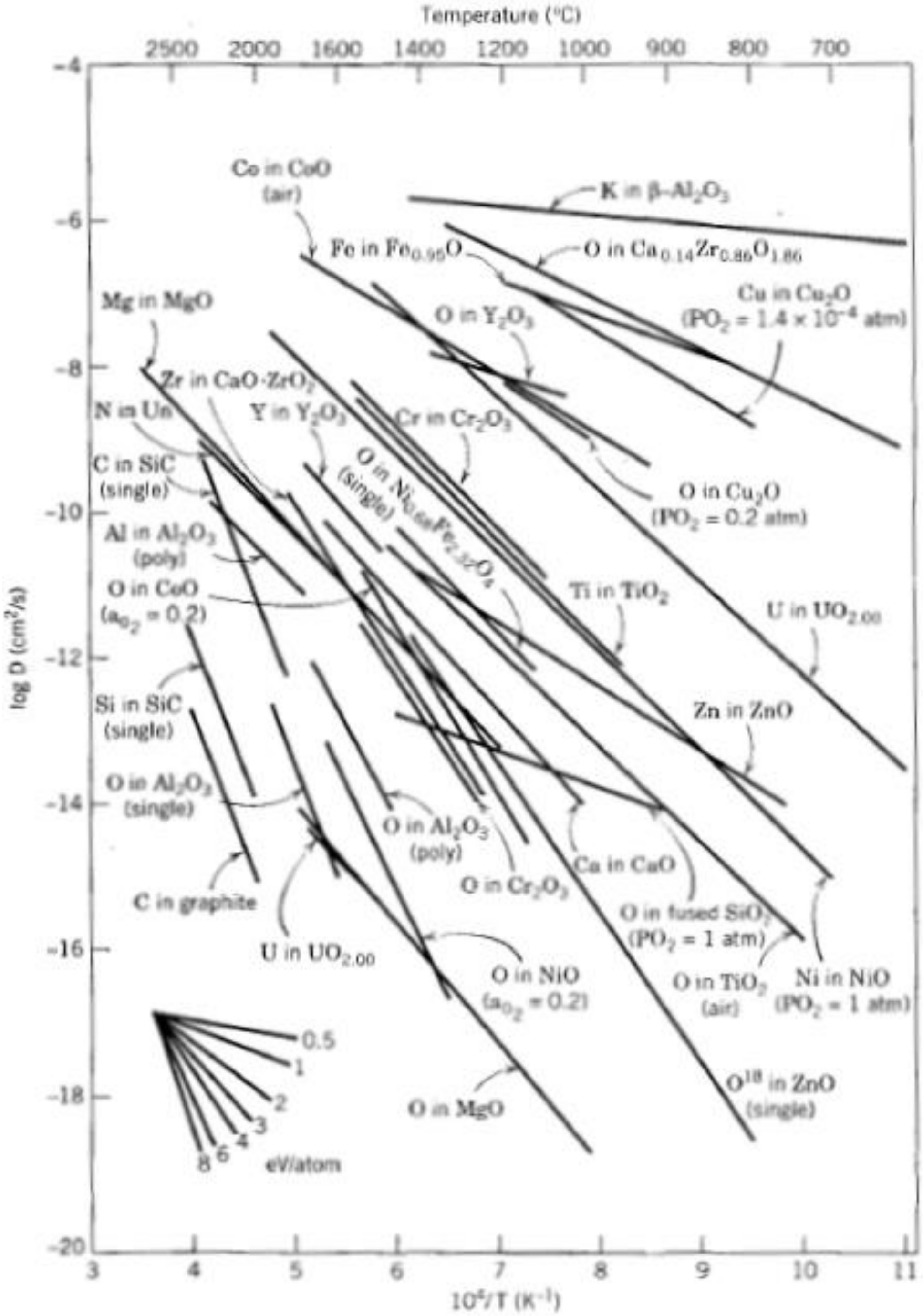
$$D_0 \approx 10^{-3}\ \text{cm}^2/\text{s}$$

Diffusion in oxyde: overview

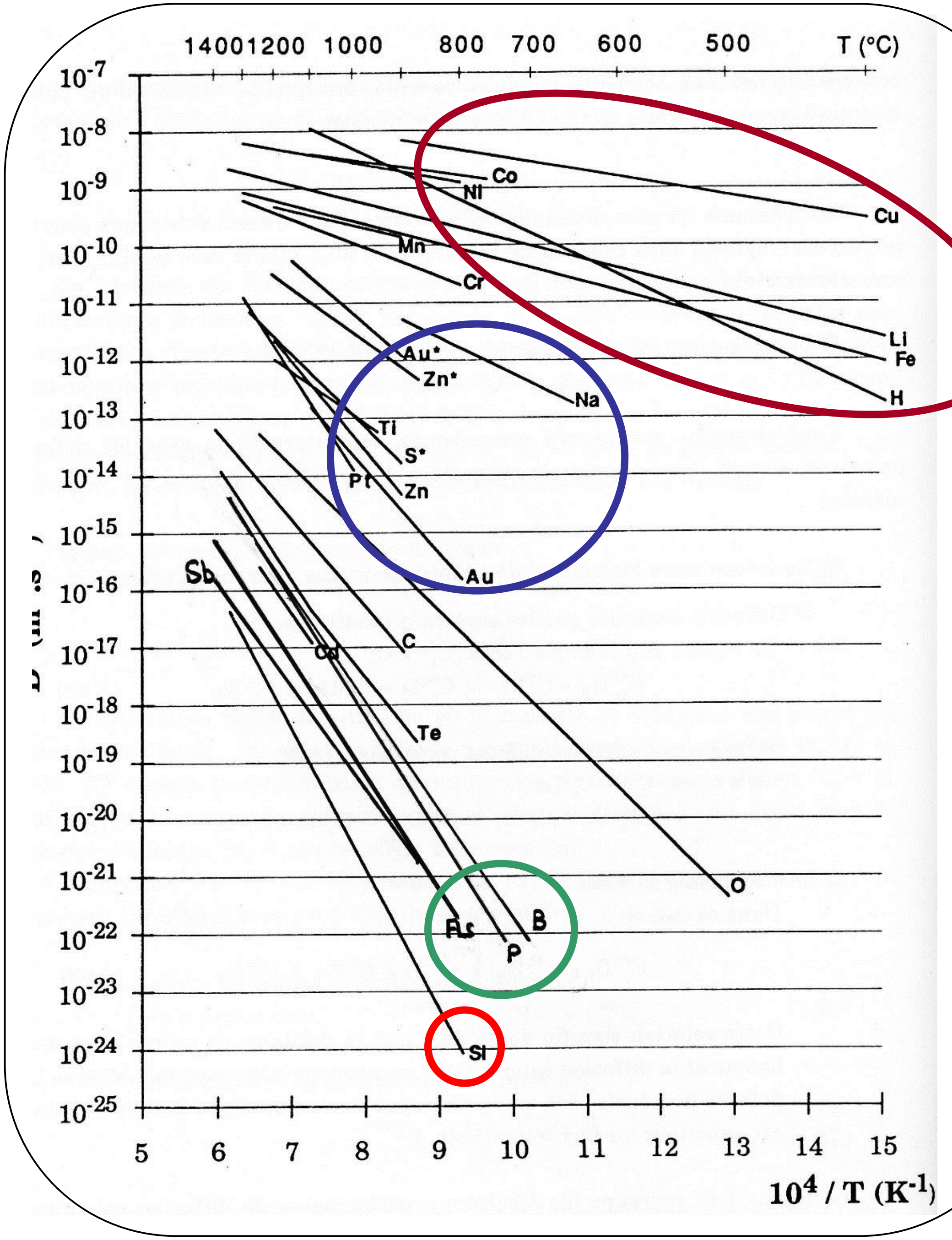
Diffusion coefficients:
13 order of magnitude

Activation energy:
0.5-8 eV

Different structures,
Different defects,
different mechanisms



Diffusion of various elements in Si



Large variations
16 orders of magnitude

Fast elements
Ni, Co, Cu, Fe, H

Intermediate elements
Au, Pt, Zn

Dopant elements
B, P, As, Sb
Close to Si

Differences between metals and ceramics

First, and most fundamentally: ceramics have charged ionic species.

Hence, electrostatic and space charge effects are basic phenomena in ceramics that do not appear in metals.

In ceramics, the transport of matter is tightly coupled to the transport of charge.

Ambipolar diffusion: chemical diffusion is limited by the slower species.

Second, formation energies of intrinsic defects are often high in ceramics.

Hence, defect concentrations are often dominated by impurities, particularly aliovalent (≠ in valence) impurities, where the requirement of overall charge neutrality induces the creation of vacancies, interstitials or electronic carriers.

In oxides, there is the additional possibility of diffusion control by the oxygen partial pressure.

Defects in oxides: Kröger-Vink notation

Schottky and Frenkel Defects:

Schottky defect : vacancies on both cation and anion sub-lattices. Because mass, site, and charge numbers remain balanced, these vacancies are always in stoichiometric ratio. Loss of ions within crystal lattice: density of the solid decreases.

Frenkel defect : vacancy on either cation or anion sub-lattice along with an interstitial site. Frenkel defect pairs maintain a balanced mass, site, and charge stoichiometric ratio. Since ions remain withinin the lattice, the density remains the same.

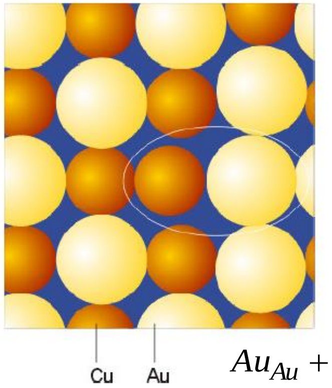
Kröger-Vink Notation: M_S^C

M corresponds to the **species**, which can be ions (Na, Ag, O, Cl…), vacancies V, electrons e and electron holes h.

S indicates the lattice **site** that the species occupies. For instance, Au might occupy a Cu site. The site may also be a lattice interstice, in this case the symbol « ***i*** » is used.

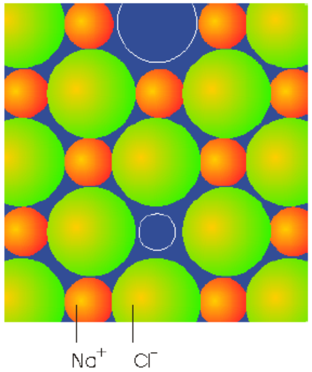
C corresponds to the **charge** of the species relative to the occupied site. To indicate zero charge, **×** is sometimes used. **•** indicates a positive charge, while **′** signifies a negative charge.

Defect reactions: imperative to keep mass, site, and charge balance in each reaction (mass conservation and electro-neutrality).



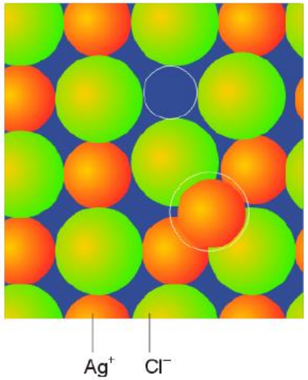
$$Au_{Au} + Cu_{Cu} = Au_{Cu} + Cu_{Au}$$

Anti-site in CuAu



$$nil = V_{Na}' + V_{Cl}^{\bullet}$$

Schottky disorder in NaCl



$$Ag_{Ag} = V_{Ag}' + Ag_i^{\bullet}$$

Frenkel disorder in AgCl

Diffusion in oxides: overview

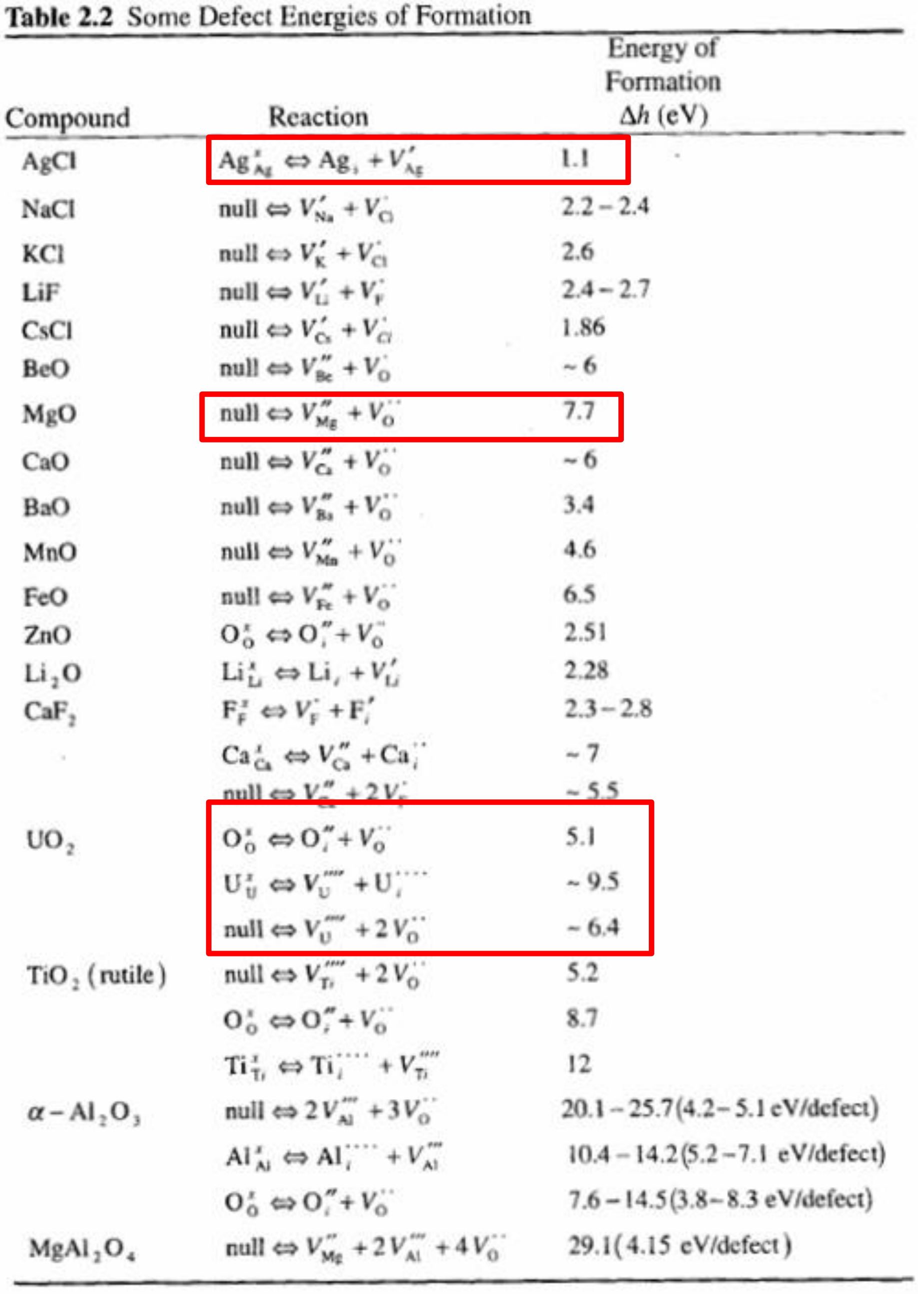
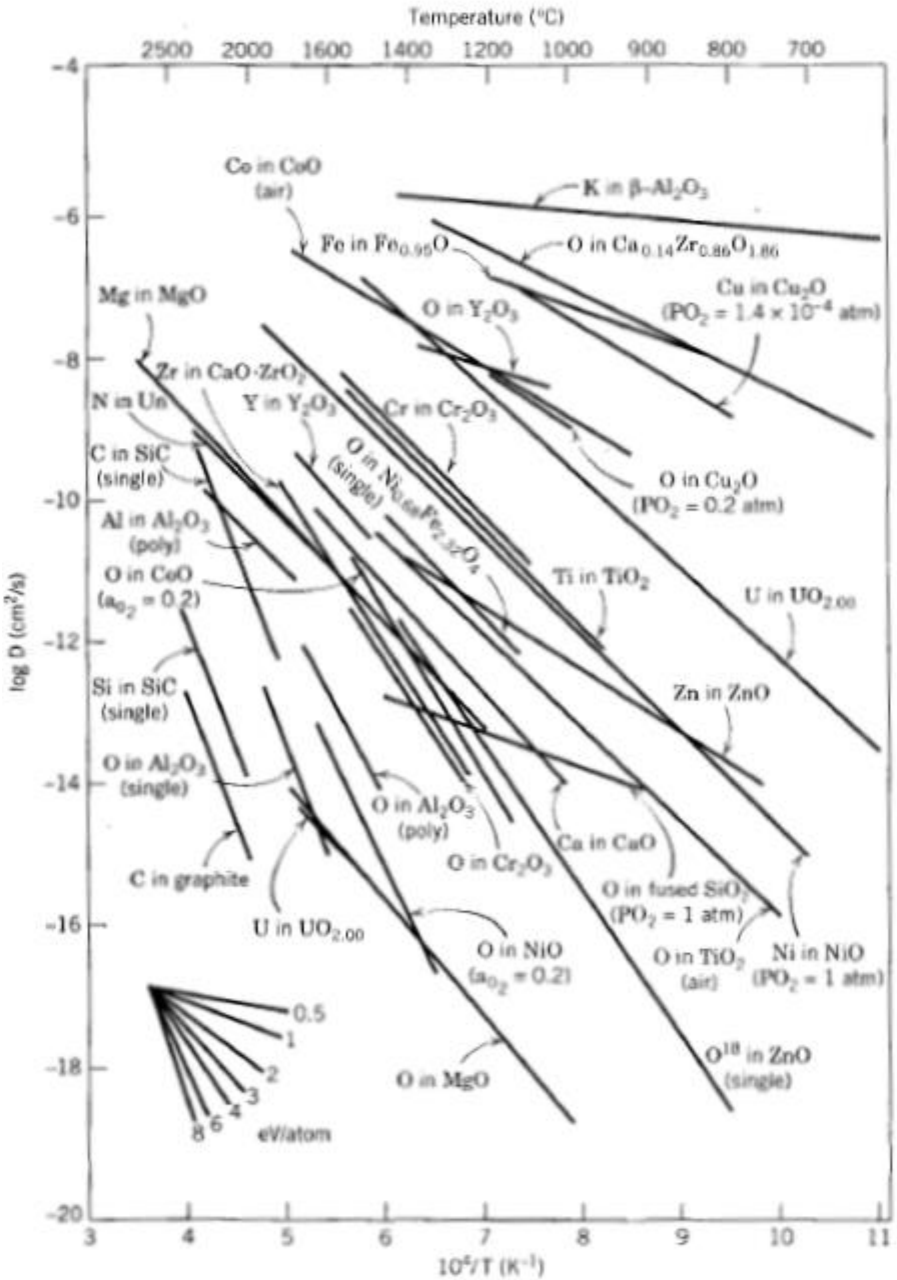


Table 2.2 Some Defect Energies of Formation

Compound	Reaction	Energy of Formation Δh (eV)
AgCl	$Ag_{Ag}^{x} \Leftrightarrow Ag_i^{\bullet} + V_{Ag}'$	1.1
NaCl	null $\Leftrightarrow V_{Na}' + V_{Cl}^{\bullet}$	2.2 – 2.4
KCl	null $\Leftrightarrow V_{K}' + V_{Cl}^{\bullet}$	2.6
LiF	null $\Leftrightarrow V_{Li}' + V_{F}^{\bullet}$	2.4 – 2.7
CsCl	null $\Leftrightarrow V_{Cs}' + V_{Cl}^{\bullet}$	1.86
BeO	null $\Leftrightarrow V_{Be}'' + V_{O}^{\bullet}$	~ 6
MgO	null $\Leftrightarrow V_{Mg}'' + V_{O}^{\bullet\bullet}$	7.7
CaO	null $\Leftrightarrow V_{Ca}'' + V_{O}^{\bullet\bullet}$	~ 6
BaO	null $\Leftrightarrow V_{Ba}'' + V_{O}^{\bullet\bullet}$	3.4
MnO	null $\Leftrightarrow V_{Mn}'' + V_{O}^{\bullet\bullet}$	4.6
FeO	null $\Leftrightarrow V_{Fe}'' + V_{O}^{\bullet\bullet}$	6.5
ZnO	$O_O^{x} \Leftrightarrow O_i'' + V_{O}^{\bullet\bullet}$	2.51
Li_2O	$Li_{Li}^{x} \Leftrightarrow Li_i^{\bullet} + V_{Li}'$	2.28
CaF_2	$F_F^{x} \Leftrightarrow V_{F}^{\bullet} + F_i'$	2.3 – 2.8
	$Ca_{Ca}^{x} \Leftrightarrow V_{Ca}'' + Ca_i^{\bullet\bullet}$	~ 7
	null $\Leftrightarrow V_{Ca}'' + 2V_{F}^{\bullet}$	~ 5.5
UO_2	$O_O^{x} \Leftrightarrow O_i'' + V_{O}^{\bullet\bullet}$	5.1
	$U_U^{x} \Leftrightarrow V_{U}'''' + U_i^{\bullet\bullet\bullet\bullet}$	~ 9.5
	null $\Leftrightarrow V_{U}'''' + 2V_{O}^{\bullet\bullet}$	~ 6.4
TiO_2 (rutile)	null $\Leftrightarrow V_{Ti}'''' + 2V_{O}^{\bullet\bullet}$	5.2
	$O_O^{x} \Leftrightarrow O_i'' + V_{O}^{\bullet\bullet}$	8.7
	$Ti_{Ti}^{x} \Leftrightarrow Ti_i^{\bullet\bullet\bullet\bullet} + V_{Ti}''''$	12
$\alpha-Al_2O_3$	null $\Leftrightarrow 2V_{Al}''' + 3V_{O}^{\bullet\bullet}$	20.1 – 25.7 (4.2 – 5.1 eV/defect)
	$Al_{Al}^{x} \Leftrightarrow Al_i^{\bullet\bullet\bullet} + V_{Al}'''$	10.4 – 14.2 (5.2 – 7.1 eV/defect)
	$O_O^{x} \Leftrightarrow O_i'' + V_{O}^{\bullet\bullet}$	7.6 – 14.5 (3.8 – 8.3 eV/defect)
$MgAl_2O_4$	null $\Leftrightarrow V_{Mg}'' + 2V_{Al}''' + 4V_{O}^{\bullet\bullet}$	29.1 (4.15 eV/defect)



How does *D* vary with *T* and *pO₂*?

- We start by analysing the influence from the concentration of defects.
- Example: Vacancies in an elemental solid:

$$N_d = \exp\left(\frac{-\Delta G_d}{RT}\right) = \exp\left(\frac{\Delta S_d}{R}\right)\exp\left(\frac{-\Delta H_d}{RT}\right)$$

- Example: Oxide ion vacancies in a non-stoichiometric oxide, e.g. $M_aO_{b-\delta}$:

Defect equation: $O_O^x = \tfrac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e'$

Electroneutrality: $\left[V_O^{\bullet\bullet}\right] = 2\left[e'\right]$

Law of mass action: $[V_O^{\bullet\bullet}][e']^2 P_{O_2}^{1/2} = K_{V_O^{\bullet\bullet}} = \exp\left(-\frac{\Delta G^0_{V_O^{\bullet\bullet}}}{kT}\right) = \exp\left(\frac{\Delta S^0_{V_O^{\bullet\bullet}}}{k}\right)\left(-\frac{\Delta H^0_{V_O^{\bullet\bullet}}}{kT}\right)$

$$N_d = [V_O^{\bullet\bullet}] = \left(\tfrac{1}{4}K'_{vO}\right)^{1/3} p_{O_2}^{-1/6} = \left(\tfrac{1}{4}K'_{0,vO}\right)^{1/3}\exp\left(\frac{-\Delta H^0_{vO}}{3RT}\right)p_{O_2}^{-1/6}$$

p_{O2} dependency

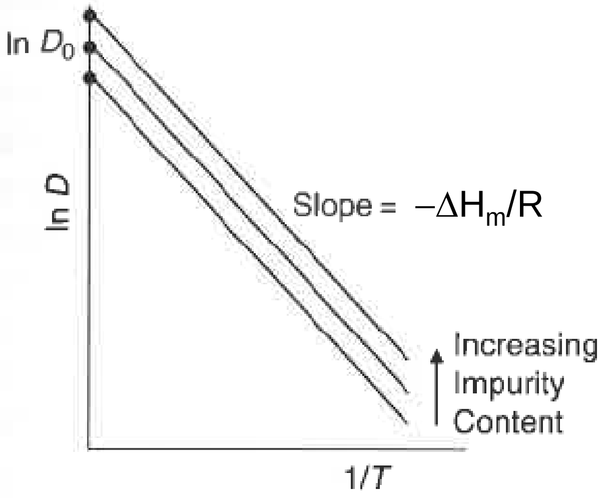
- Example: Oxide ion vacancies in an acceptor-doped oxide, e.g. Ca-doped $ZrO_{2-\delta}$:

$$CaO \xrightarrow{ZrO_2} Ca''_{Zr} + O_O^x + V_O^{\bullet\bullet}$$

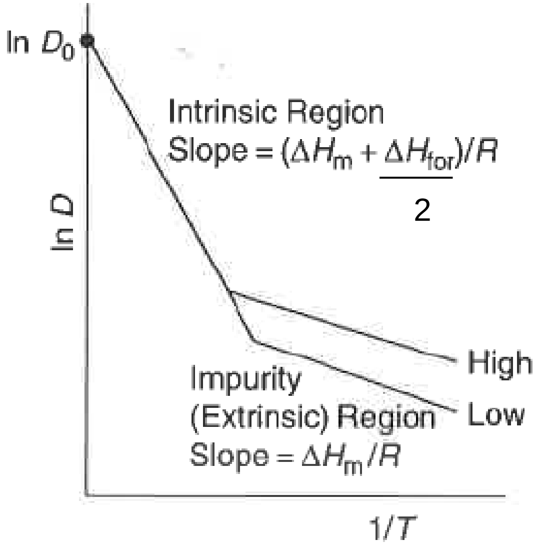
$$\boxed{[V_O^{\bullet\bullet}] = [A''_M]}$$

No p_{O2} dependency

Arrhenius plots in crystalline solids



(*a*)



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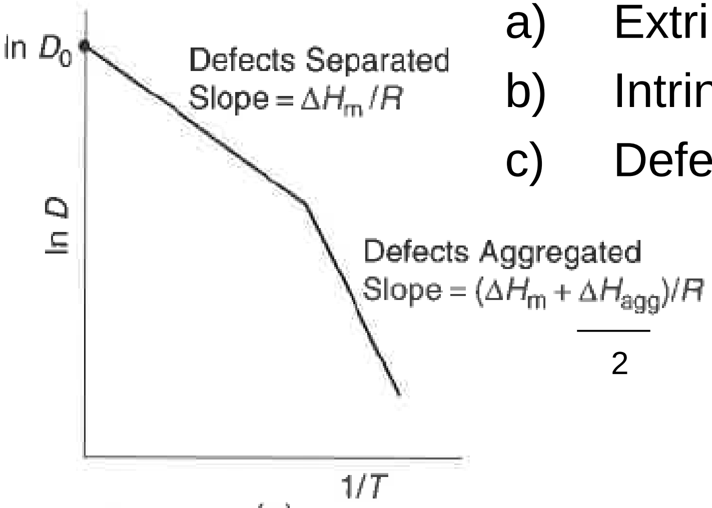


(*c*)

a) Extrinsic (dopants/impurities)
b) Intrinsic (« high » temperature)
c) Defect association (« low » temperature)

Brouwer (Kröger-Vink) diagrams: electronic disorder

Kofstad and Norby: Defects and transport in cristalline solids

$$K'_{vO} = [v_O^{\bullet\bullet}]n^2 p_{O_2}^{1/2}$$

$$K'_{Oi} = [O_i'']p^2 p_{O_2}^{-1/2}$$

$$K'_i = np$$

$$K_{AF} = [O_i''][v_O^{\bullet\bullet}]$$

The full electroneutrality condition is given by

$$2[v_O^{\bullet\bullet}] + p = 2[O_i''] + n$$

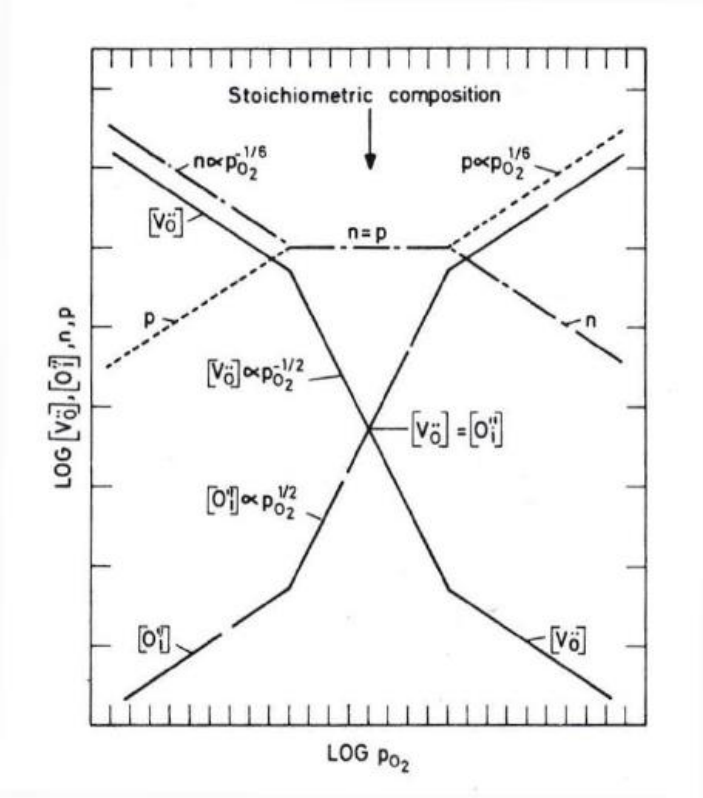


Figure 3-4. Schematic presentation of oxygen point defects and electronic defects as a function of oxygen pressure in an oxide which depending on the partial pressure of oxygen may have an excess or deficit of oxygen. Intrinsic electronic equilibrium is assumed to predominate at stoichiometric composition.

At large oxygen deficit

$$n = 2[v_O^{\bullet\bullet}] >> 2[O_i''], p$$

$$n = 2[v_O^{\bullet\bullet}] = (2K'_{vO})^{1/3} p_{O_2}^{-1/6}$$

$$[O_i^{\bullet\bullet}] = 2^{2/3} K_{AF} (K'_{vO})^{-1/3} p_{O_2}^{1/6}$$

$$p = K'_i (2K'_{vO})^{-1/3} p_{O_2}^{1/6}$$

For relatively large excess oxygen

$$p = 2[O_i''] >> 2[v_O^{\bullet\bullet}], n$$

$$p = 2[O_i''] = (2K'_{Oi})^{1/3} p_{O_2}^{1/6}$$

$$[v_O^{\bullet\bullet}] = 2^{2/3} K_{AF} (K'_{Oi})^{-1/3} p_{O_2}^{-1/6}$$

$$n = K'_i (2K'_{Oi})^{-1/3} p_{O_2}^{-1/6}$$

Diffusion in oxides

$$D_A^* = \sum_d f_d [d] D_d$$

$$\tilde{D} = D_A t_{el} \Phi$$

Non-stoichiometric oxides

Transition metal oxides with NaCl structure, such as NiO, CoO, MnO, FeO are generally metal-deficient: $M_{1-\delta}O$.

The concentration of cation vacancies can be high: $\delta \sim l0^{-4}$ in NiO, 10^{-1} in FeO: normally intrinsic behavior (metal vacancy concentration >> impurity concentration). Deviation from stoichiometry depends on temperature and oxygen partial pressure.

→ $D_M/D_O \approx 10^4 - 10^5$

In oxides with fluorite structure (CeO_2,ZrO_2, ThO_2, UO_2), majority defects are oxide ion vacancies for oxygen deficiency (MO_{2-x}) and oxide ion interstitials for oxygen excess (MO_{2+x}) .

→ $D_M < D_O$

“Stoichiometric“ oxides

Stoichiometric oxides (MgO, Al_2O_3, ...) show generally extrinsic behavior.

Given the high enthalpy of formation of Schottky defects (theory: ~ 8 eV for MgO), the intrinsic defect concentration is very low: some ppm of impurities are sufficient to impose the extrinsic regime, so that $[V_M''] >> [V_O^{\bullet\bullet}]$ and $D_M^* >> D_O^*$

Lattice diffusion in stoichiometric oxides

Diffusion in stoichiometric oxides

Effect of impurities or dopants

High defect formation energy → extrinsic regime → impurity controlled diffusion

MgO

$$D_{Mg} = [V''_{Mg}]\,D_{V''_{Mg}}$$

$$F_2O_3 \rightarrow 2F^{\bullet}_{M} + 3O^{x}_{O} + V_{M}''$$

$$D_{V''_{Mg}} = (0.38 \pm 0.15)\exp\left[\frac{-2.29 \pm 0.21\,eV}{kT}\right] \quad (cm^2/sec)$$

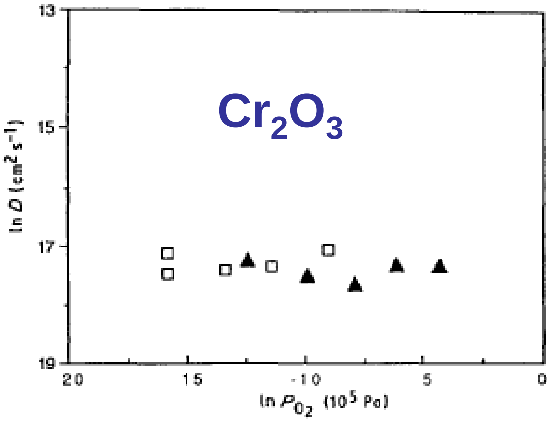


Fig. 5. — Dépendance en pO_2 des coefficients de diffusion en volume de Cr à 1300 °C (▲) et de O (☐) à 1100 °C dans des monocristaux de Cr_2O_3 [15, 16].
[pO_2 dependence of the lattice diffusion coefficients of Cr at 1300 °C (▲) and O (☐) at 1100 °C in single crystals of Cr_2O_3 [15, 16].]

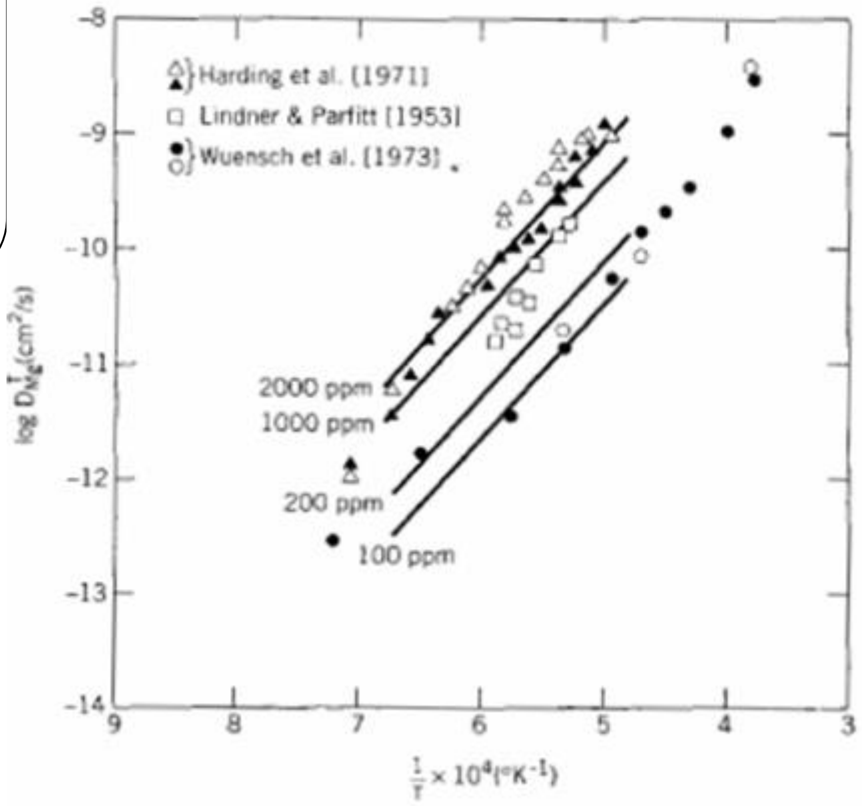
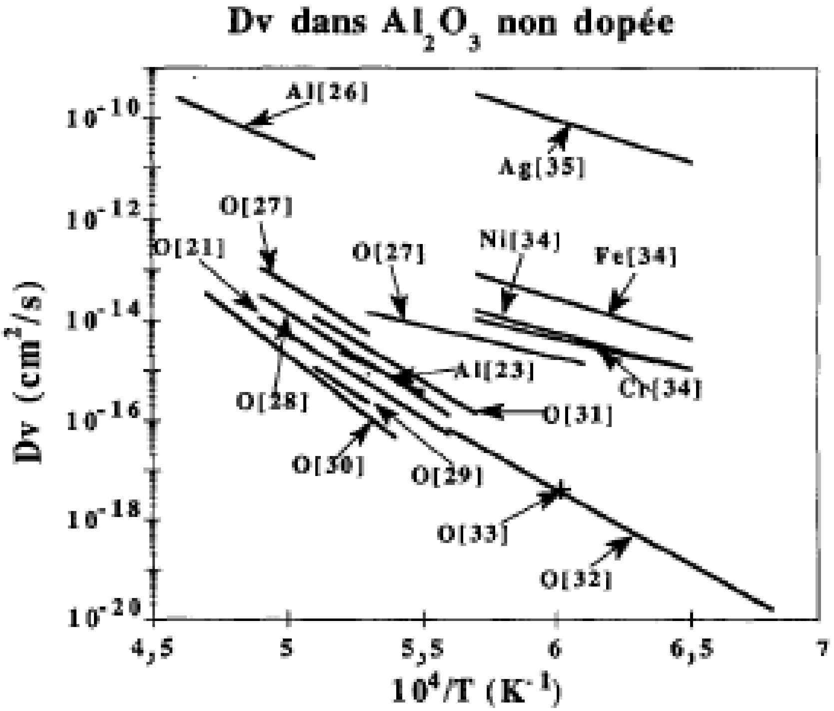


Fig. 3.10 Comparison of measured magnesium tracer diffusion coefficient in MgO (data points) with that calculated from the magnesium vacancy diffusion coefficient (solid curves).

Diffusion in stoichiometric oxides

AM Huntz, J. Phys. III, 1995



Volume diffusion in Al_2O_3

Impurity controlled diffusion = scattering of experimental results

Lattice diffusion in non-stoichiometric oxides

Self diffusion in non-stoichiometric oxides: cation versus oxygen diffusion

$M_{1-\delta}O$ (NiO, CoO, MnO, FeO): **$D_M > D_O$**

$MO_{2-\delta}$ (CeO_2, ZrO_2, ThO_2, UO_2): **$D_M < D_O$**

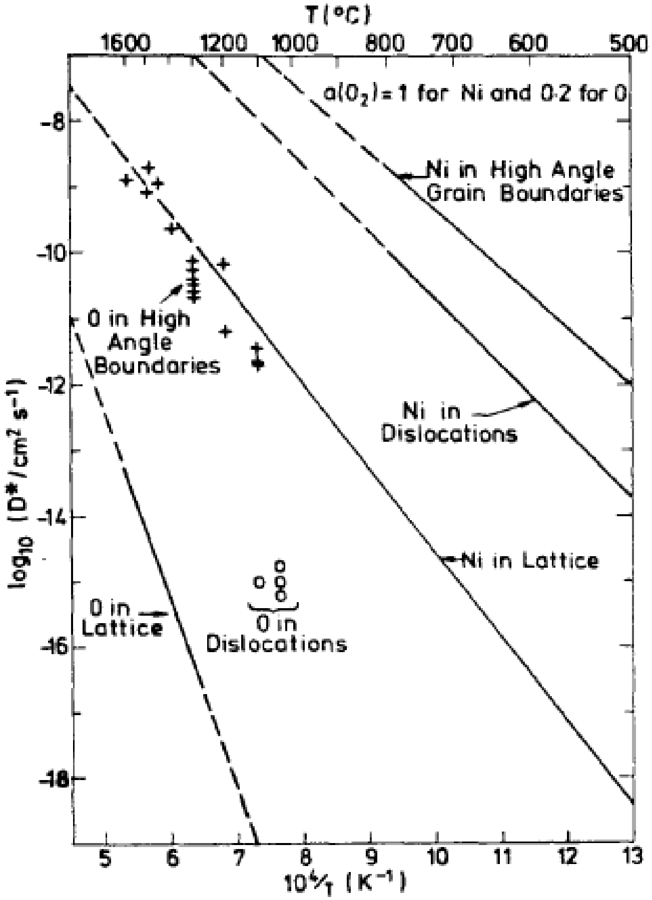
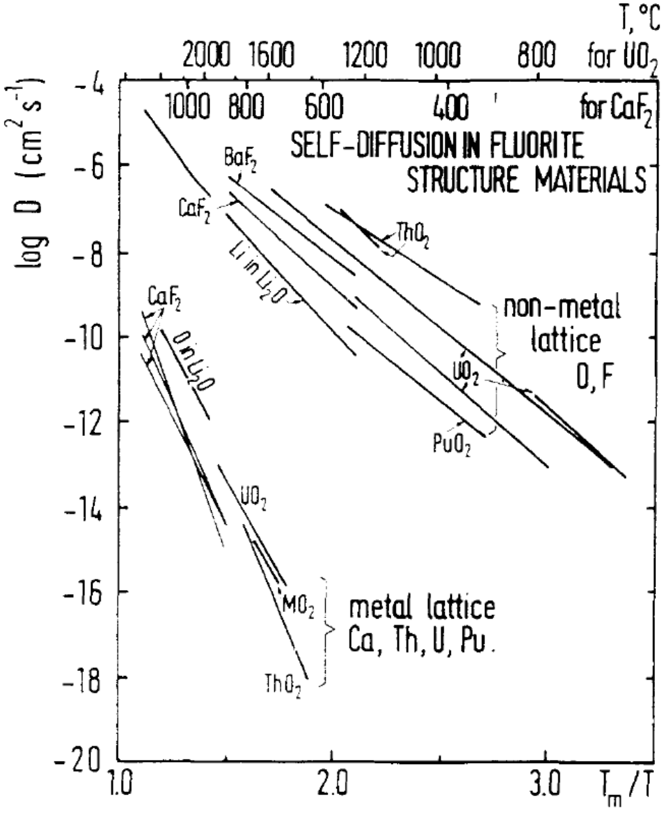
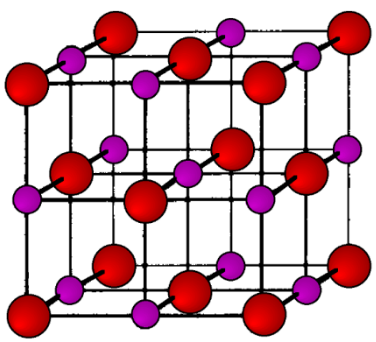


Fig. 7. Ni and O tracer self diffusion in the lattice, dislocations and grain boundaries in NiO (2)(10)(49)(52).

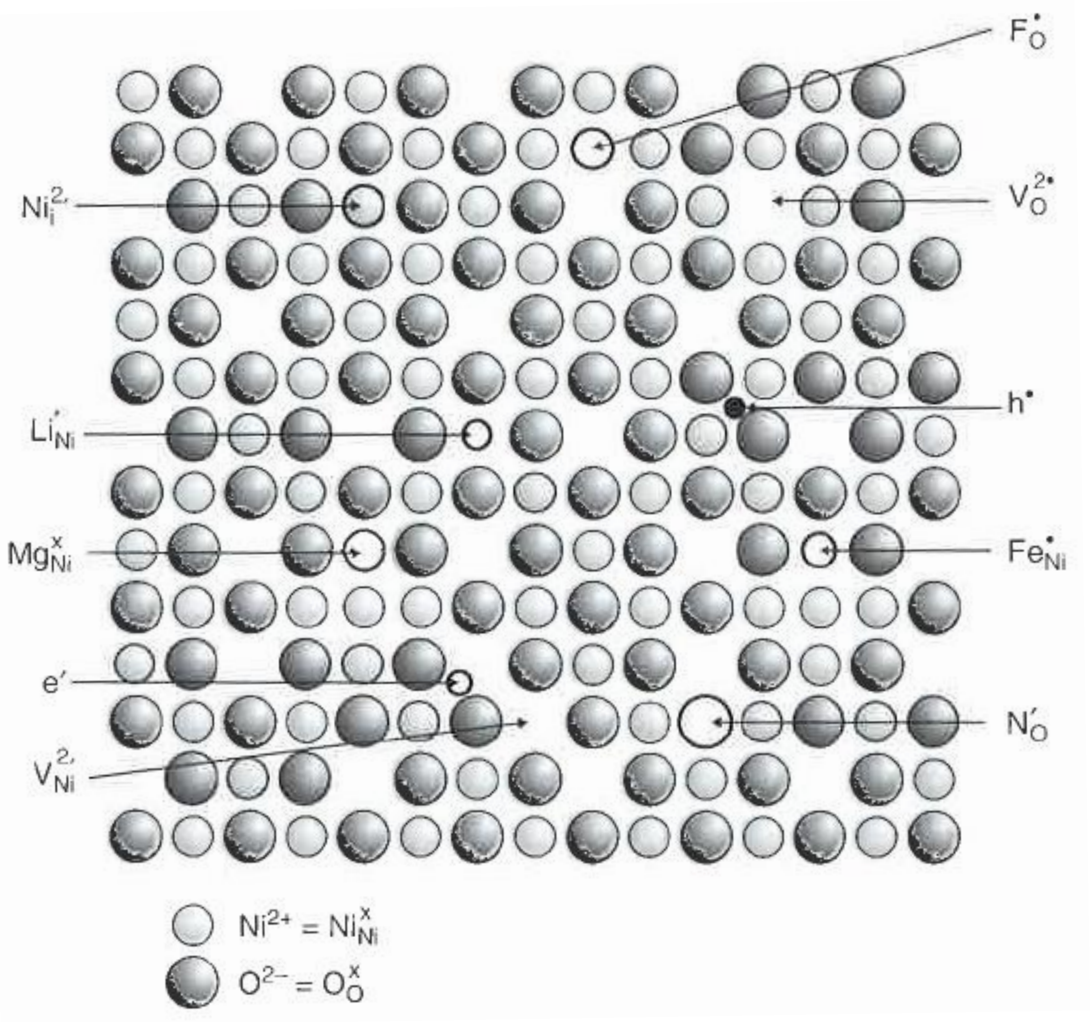


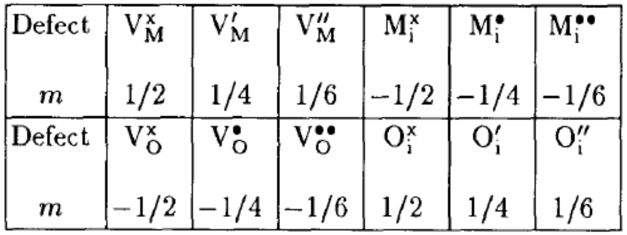
Summary of diffusion data for oxygen and metal diffusion in fluorite-type oxides in an Arrhenius diagram normalized to the melting point; included are data for fluorides (fluorine in CaF_2 and BaF_2; calcium in CaF_2). Data for material of the antifluorite structure, Li_2O, are also shown (for references see Matzke (1986a)). The upper scale shows temperatures in degrees celsius for a typical fluoride, CaF_2, and a typical oxide, UO_2.

Ionic and electronic defects in $Ni_{1-\delta}O$



Rocksalt (NaCl) structure of NiO, CoO, MnO, FeO





Defect	V_M^x	$V_M^{\prime}$	$V_M^{\prime\prime}$	M_i^x	$M_i^{\bullet}$	$M_i^{\bullet\bullet}$
m	1/2	1/4	1/6	−1/2	−1/4	−1/6
Defect	V_O^x	$V_O^{\bullet}$	$V_O^{\bullet\bullet}$	O_i^x	$O_i^{\prime}$	$O_i^{\prime\prime}$
m	−1/2	−1/4	−1/6	1/2	1/4	1/6

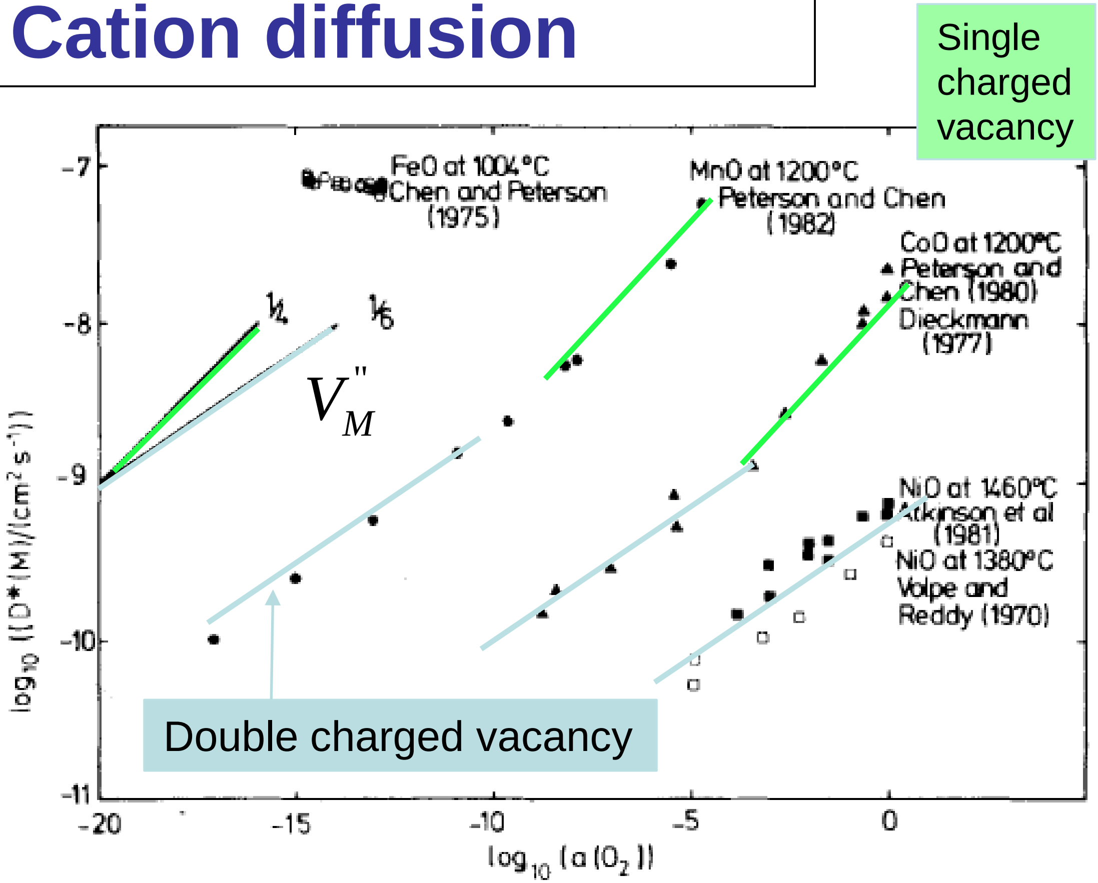
Non stoichiometry ($M_{1-\delta}O$) → major defects: V_M'', V_M'

Self-diffusion in non-stoichiometric oxides: Cation diffusion

Non stoichiometry ($M_{1-\delta}O$) = reaction with oxygen gas

$$\tfrac{1}{2}O_2 \rightarrow V_M^{''} + O_O^x + 2h^\bullet$$

$$\left[V_M^{n'}\right] \propto P(O_2)^{1/2(n+1)}$$



Single charged vacancy

Double charged vacancy

Fig. 3. The tracer self-diffusion coefficient for lattice diffusion of metal ions, in transition metal oxides having the rocksalt structure, as a function of oxygen activity. The solid lines indicate the slopes expected when either singly or doubly charged cation vacancies are the majority defects (19)-(24).

Cation diffusion in rocksalt structure by vacancy:

- Main “natural” vacancy = V_M”

  $$\left[V_M^{''}\right] \propto a(O_2)^{1/6} \propto P(O_2)^{1/6}$$

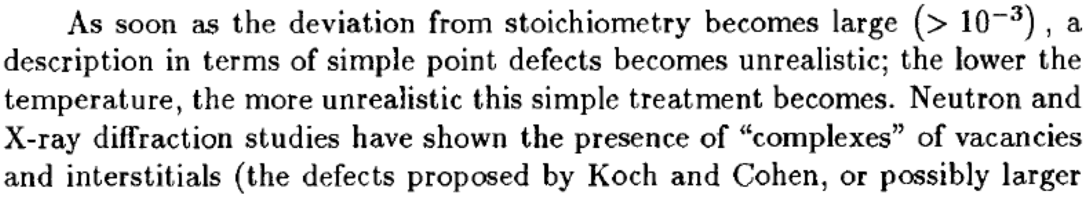
- + association of defects (NiO, CoO): V_M” + h˙ → V_M’

  $$\left[V_M'\right] \propto P(O_2)^{1/4}$$

- MnO, FeO : more complex

Cation diffusion in rocksalt structure: low pressure = V_M”, high pressure = V_M’

Large deviation of stoichiometry and diffusion



As soon as the deviation from stoichiometry becomes large $(> 10^{-3})$, a description in terms of simple point defects becomes unrealistic; the lower the temperature, the more unrealistic this simple treatment becomes. Neutron and X-ray diffraction studies have shown the presence of "complexes" of vacancies and interstitials (the defects proposed by Koch and Cohen, or possibly larger

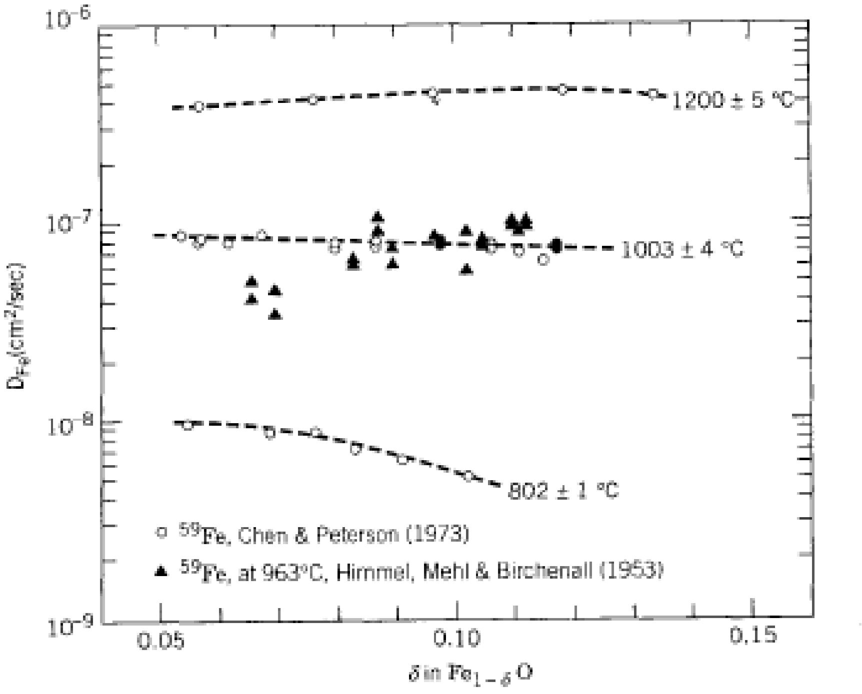


Fig. 3.12 Diffusion coefficient of ^{59}Fe tracer in $Fe_{1-x}O$ as a function of the deviation from stoichiometry. Notice the weak dependence on defect concentration. [From N.L. Peterson, *Mat. Sci. Forum*, 1, 85, (1984).]

→ Defect clusters

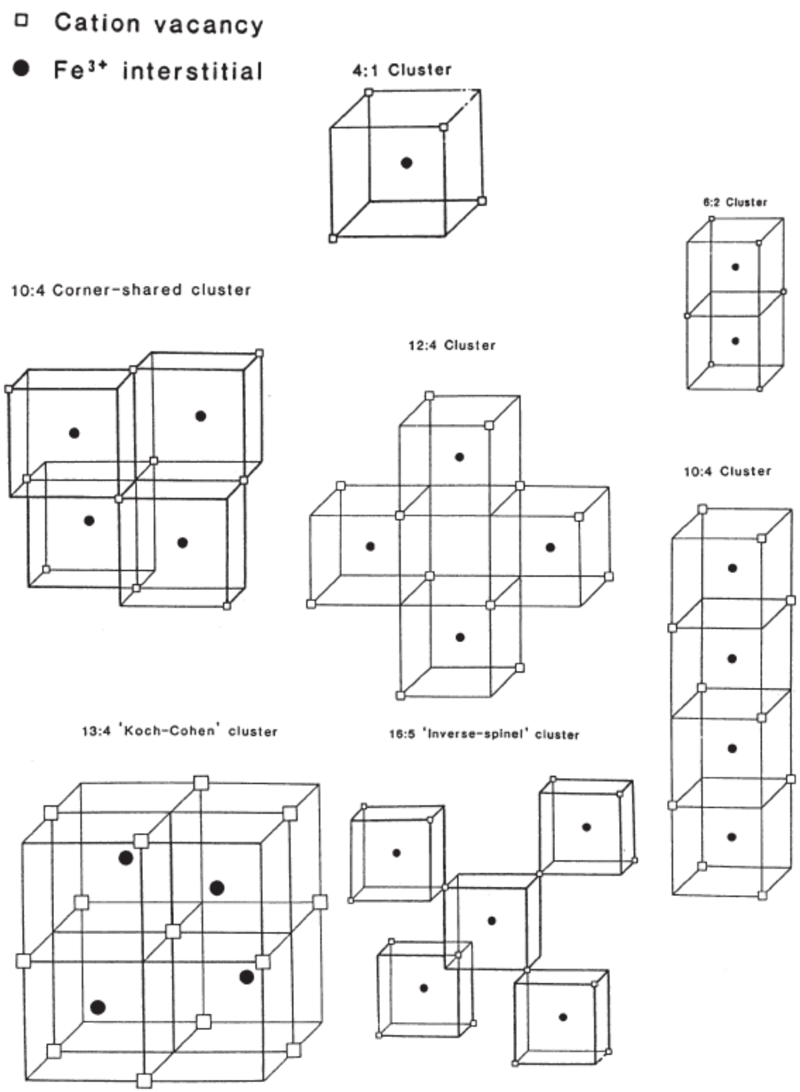


Figure 5 : Complex defects (so-called clusters) in $Fe_{1-x}O$

Self-diffusion in non-stoichiometric oxides
Oxygen diffusion in $UO_{2\pm\delta}$

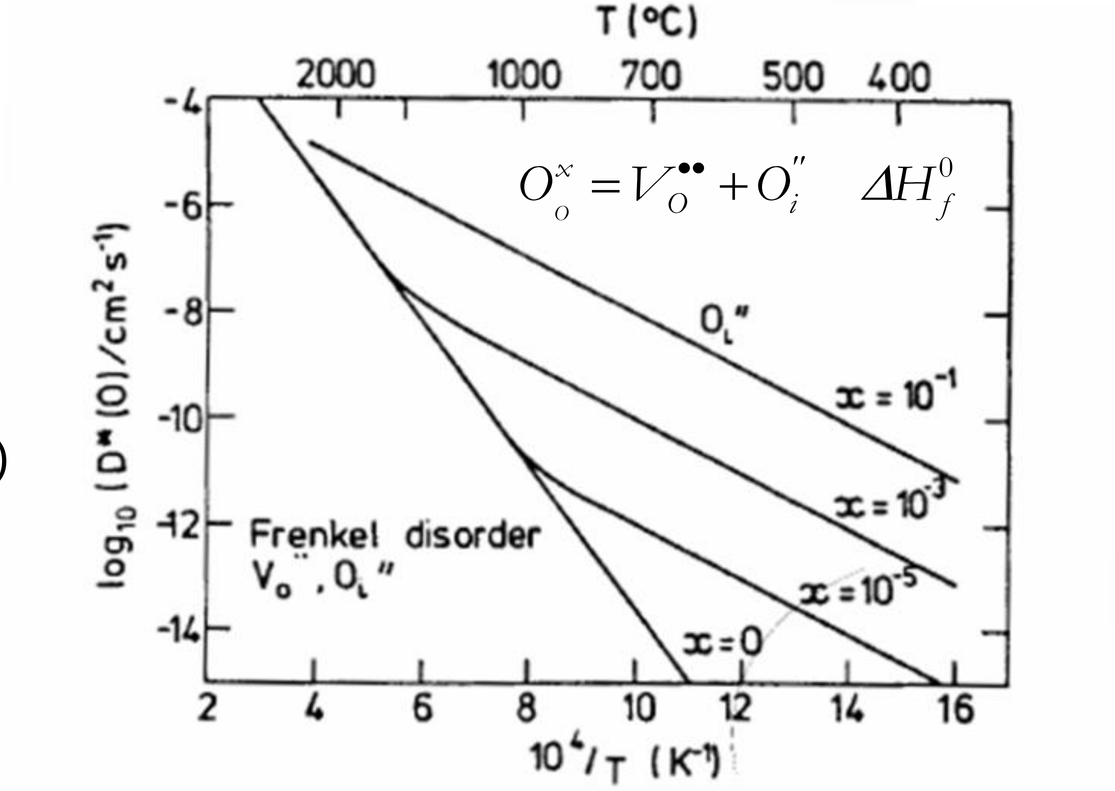
Fluorite structure
(CeO_2, ZrO_2, ThO_2, UO_2):
- $MO_{2-\delta}$: $V_O^{\circ\circ}$
- $MO_{2+\delta}$: O_i''

Cation diffusion in UO_2
→ Vacancy ($UO_{2+\delta}$ = high $P(O_2)$)
→ Interstitial ($UO_{2-\delta}$ = low $P(O_2)$)

Oxygen diffusion in UO_{2+x}

→ low T: constant number of interstitials (extrinsic) → determination of migration enthalpy ΔH_m

→ high T: determination of $\Delta H_m + \frac{1}{2}\Delta H_f$



Oxygen Ion Self-Diffusion. UO_2 is probably the most widely-studied example of an oxide in which oxygen diffusion is more rapid than cation self-diffusion. The measurements for UO_{2+x} have been summarized by Brietung (30) and are shown in Fig. 4. These data are presented as functions of T at constant x and therefore there is no contribution from the concentration of defects to the activation energy at large x and/or low T. The activation energy (0.52 eV) is ΔH_m for the interstitial defect O_i''. At the stoichiometric composition (or at high T) Frenkel disorder on the oxygen sublattice is dominant (reaction 3b) and the activation energy is greater by an amount equal to half the enthalpy change of reaction (3b).

Self-diffusion in non-stoichiometric oxides

Cation diffusion in Magnetite

Cation diffusion in Fe_3O_4 ($Fe_{3-\delta}O_4$)

→ Cation vacancy ($Fe_{3-\delta}O_4$= high $P(O_2)$)

→ Interstitialcy ($Fe_{3+\delta}O_4$ = low $P(O_2)$)

Magnetite, Fe_3O_4, is an oxide in which the point defect properties of the cation sublattice are particularly well-understood. In Fe_3O_4 cation self-diffusion takes place by a vacancy mechanism at high $a(O_2)$ and by an interstitialcy mechanism at low $a(O_2)$ (27). This is related to the ability of Fe_3O_4 to exhibit deviations on both sides of stoichiometry as indicated in Table 1. There is some evidence that Cr_2O_3 shows a similar behavior (28).

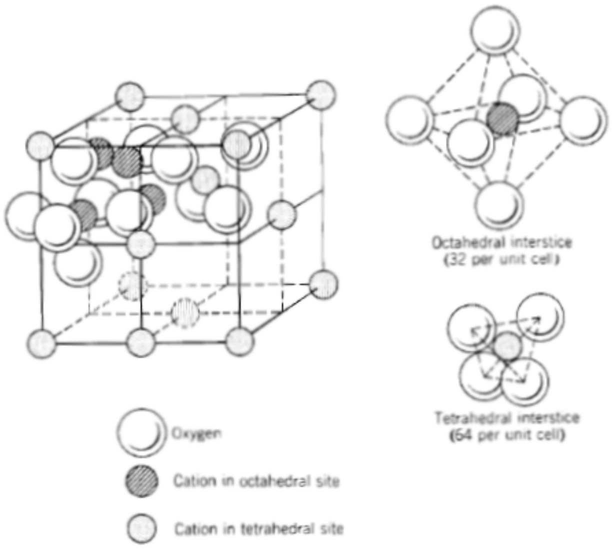
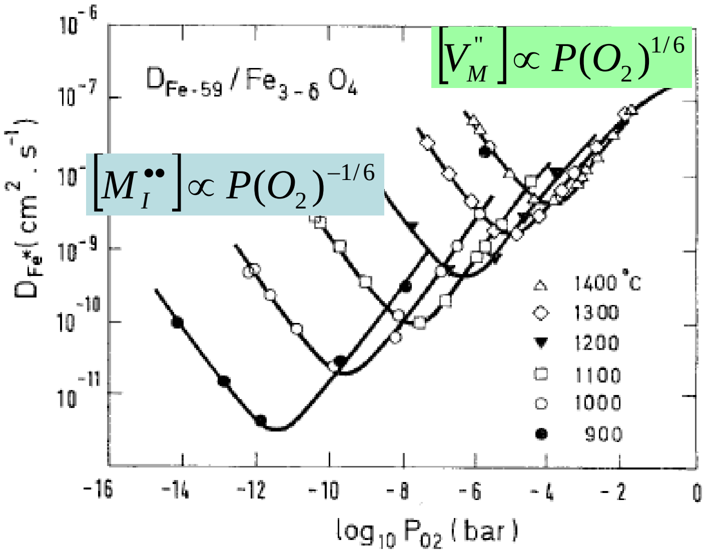


Fig. 1.30 Atomic layers parallel to the (001) plane in spinel.



$$\left[V_M''\right] \propto P(O_2)^{1/6}$$

$$\left[M_I^{\bullet\bullet}\right] \propto P(O_2)^{-1/6}$$

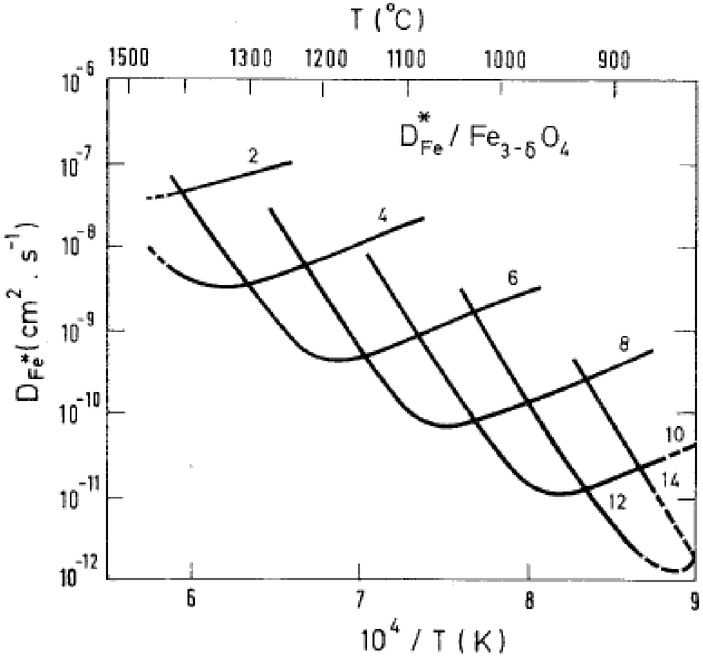


Fig. IV.19. — Autodiffusion du fer dans la magnétite $Fe_{3-\delta}O_4$. Effet de la température et de la pression d'oxygène (valeurs de $-\log_{10}P_{O_2}$ (bar) reportées auprès de chaque courbe). D'après Dieckmann et Schmalzried (1977).

Diffusion in oxides glass

Diffusion in oxides glass

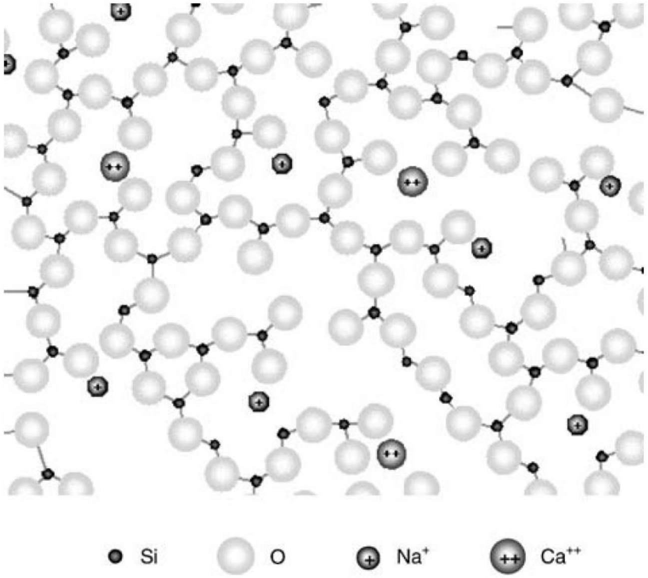


Fig. 30.7. Structure of a soda-lime silicate glass (schematic in two dimensions)

Glass (network) former: slow diffusion
Glass modifier : fast diffusion

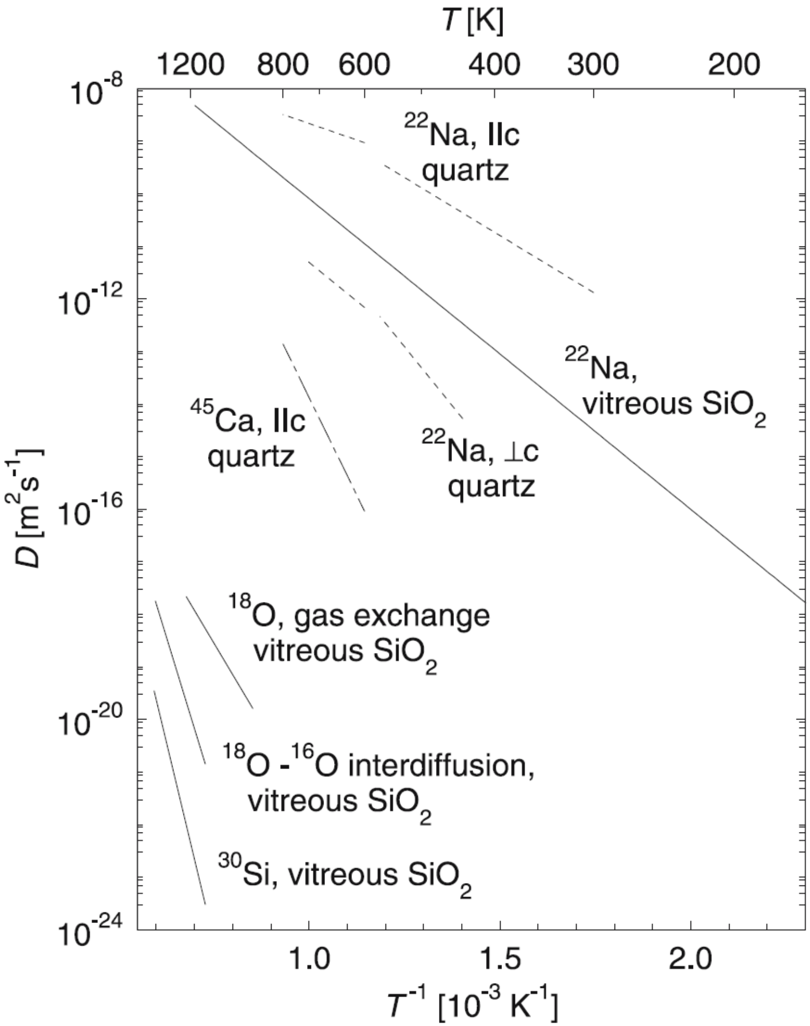
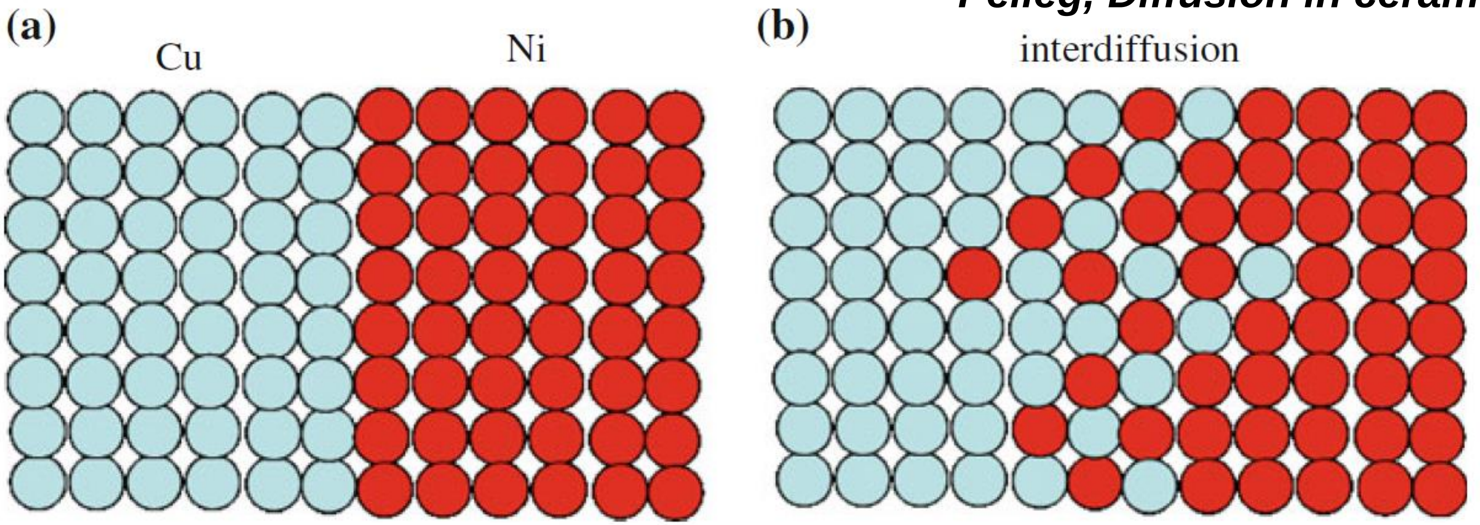


Fig. 30.6. Diffusion in vitreous silica and in quartz (for references see text)

Interdiffusion in oxides:

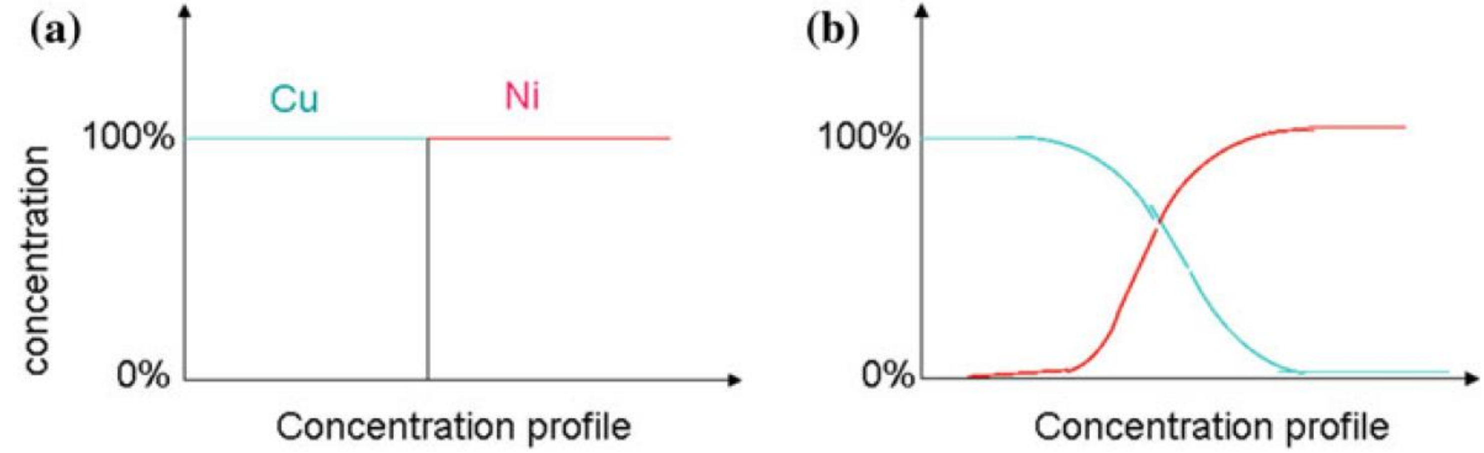
Diffusion in alloy: Interdiffusion

Pelleg, Diffusion in ceramics, 2016



$\eta \equiv$

Fig. 6.1 A schematic illustration of an intermixing Cu–Ni diffusion couple: **a** before diffusion; **b** after diffusion



a binary

$-2\eta\frac{\mathrm{d}}{\mathrm{d}}$

Fig. 6.2 Schematic illustration of a concentration profile: **a** before diffusion; **b** the intermixing of the components after diffusion

Interdiffusion in metallic alloy

Intrinsic flux (crystal lattice frame):

$$j_A = -D_A^I \frac{\partial C_A}{\partial x}, \quad j_B = -D_B^I \frac{\partial C_B}{\partial x}$$

Intrinsic flux (crystal lattice frame):

$$v_K = -(\tilde{V}_A j_A + \tilde{V}_B j_B)$$

$$v_K = \tilde{V}_B (D_B^I - D_A^I) \frac{\partial C_B}{\partial x}$$

$$J = -D_i^I \frac{\partial C_i}{\partial x} \pm v_K C_i \quad i = A, B$$

$$\tilde{D} = C_B \tilde{V}_B D_A^I + C_A \tilde{V}_A D_B^I$$

$$j_i = -B_i C_i \frac{\partial \mu_i}{\partial x} \qquad D_i^* = B_i RT$$

$$\tilde{D}_{Darken} = (N_A D_B^* + N_B D_A^*)\, \Phi$$

$$\tilde{D} = (N_A D_B^* + N_B D_A^*)\, \Phi S = \tilde{D}_{Darken} S$$

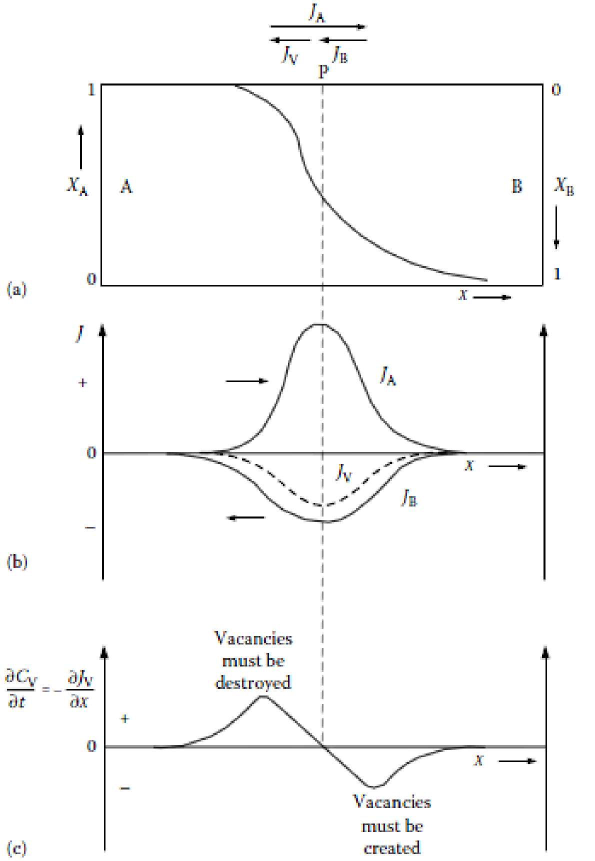


FIGURE 2.15
Interdiffusion and vacancy flow. (a) Composition profile after interdiffusion of A and B. (b) The corresponding fluxes of atoms and vacancies as a function of position x. (c) The rate at which the vacancy concentration would increase or decrease if vacancies were not created or destroyed by dislocation climb.

Porter and Easterling, Phase transformation in metals and alloys, 1992

Interdiffusion in metallic alloy

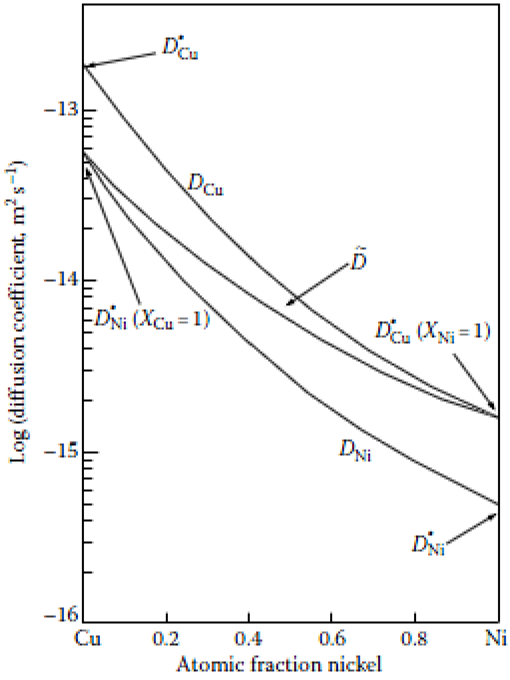


FIGURE 2.21
The relationship between the various diffusion coefficients in the Cu-Ni system at 1000°C (After A.G. Guy, *Introduction to Materials Science*, McGraw-Hill, New York, 1971.)

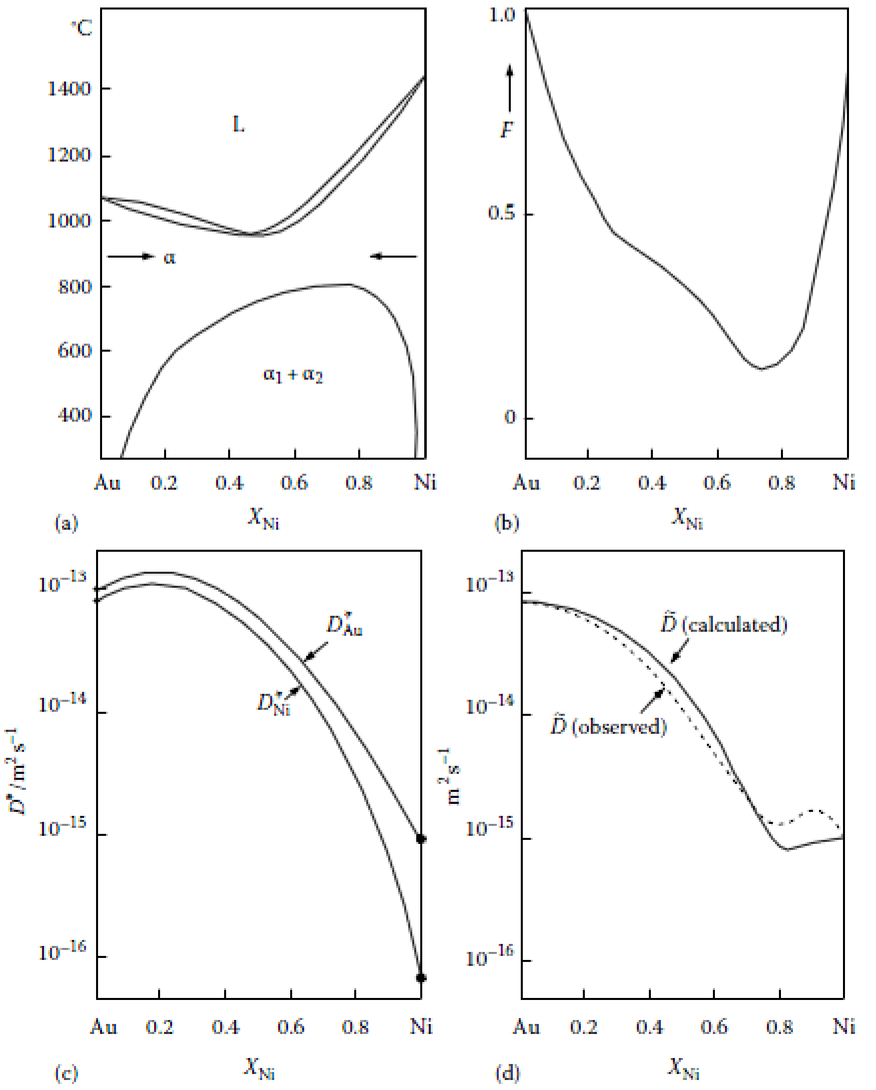


FIGURE 2.22
Interdiffusion in Au-Ni alloys at 900°C (a) Au-Ni phase diagram, (b) the thermodynamic factor, *F*, at 900°C, (c) experimentally measured tracer diffusivities at 900°C, (d) experimentally measured interdiffusion coefficients compared with values calculated from (b) and (c). (From J.E. Reynolds, B.L. Averbach and Morris Cohen, *Acta Metallurgical* **5** (1957) 29.)

Porter and Easterling, Phase transformation in metals and alloys, 1992

Ambipolar diffusion

Ambipolar diffusion = two diffusing species of different signs

$$j_A = -D_A^* \frac{\partial C_A}{\partial x} + \frac{q C_A D_A^*}{k_{\mathrm{B}} T} E$$

$$j_B = -D_B^* \frac{\partial C_B}{\partial x} + \frac{q C_B D_B^*}{k_{\mathrm{B}} T} E$$

Electrical neutrality $j_A + j_B = 0$

$$E = \frac{k_{\mathrm{B}} T}{q} \frac{D_A^* - D_B^*}{C_A D_A^* + C_B D_B^*} \frac{\partial C_A}{\partial x}$$

$$j_A = -D_A^I \frac{\partial C_A}{\partial x} \quad \text{and} \quad j_B = -D_B^I \frac{\partial C_A}{\partial x}$$

$$D_A^I = D_B^I = \frac{D_A^* D_B^*}{N_A D_A^* + N_B D_B^*}$$

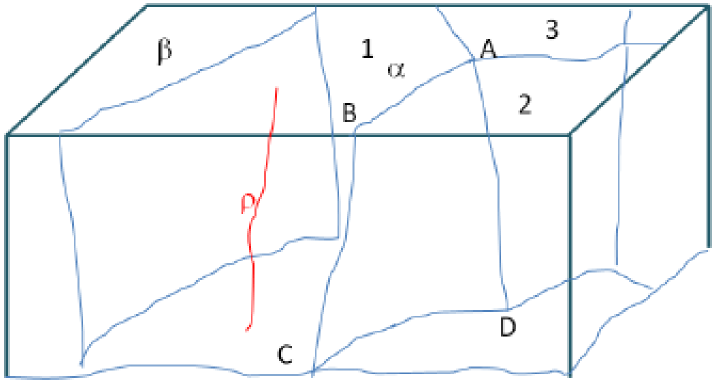
Non ideal solution

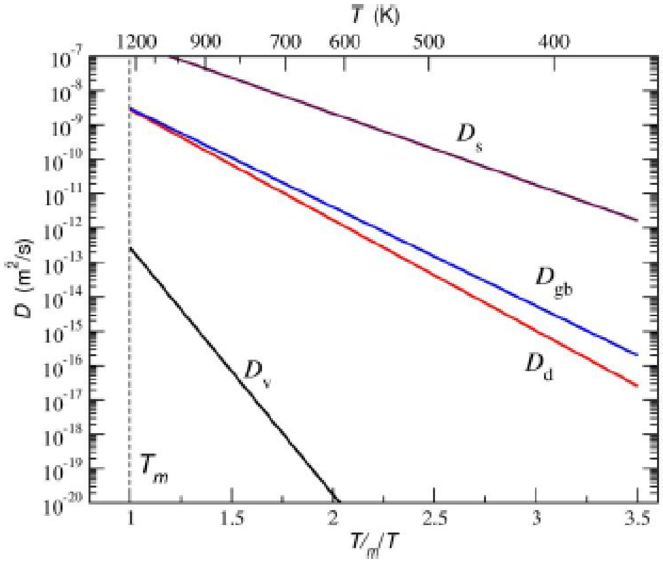
$$D_A^I = D_B^I = \frac{D_A^* D_B^*}{N_A D_A^* + N_B D_B^*} \Phi \equiv \tilde{D}_{Nernst-Planck}$$

→ Diffusion controls by the slower species

Diffusion in polycrystalline oxides

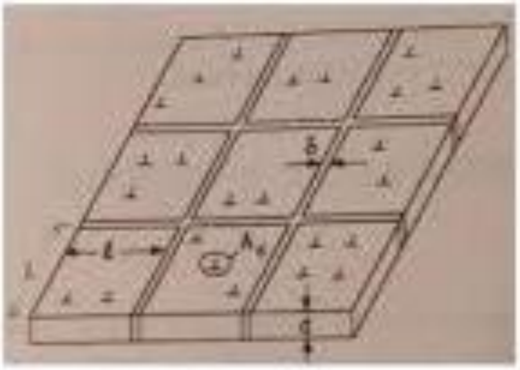
Diffusion in polycrystalline solids





- Schematic representation of defects which may act as short-circuit paths in a polycrystalline material: dislocation line ρ; grain boundaries, e.g. ABCD one; triple lines as AD one; phase boundaries as the interface between phases α and β.

- Comparison of experimental data on diffusion rates in pure Ag in bulk, D_v, along dislocations, D_d, along grain boundaries, D_{gb}, and on surface in vacuum, D_s. For generality, the temperature scale is normalized on the melting point of Ag, T_m = 1235 K.

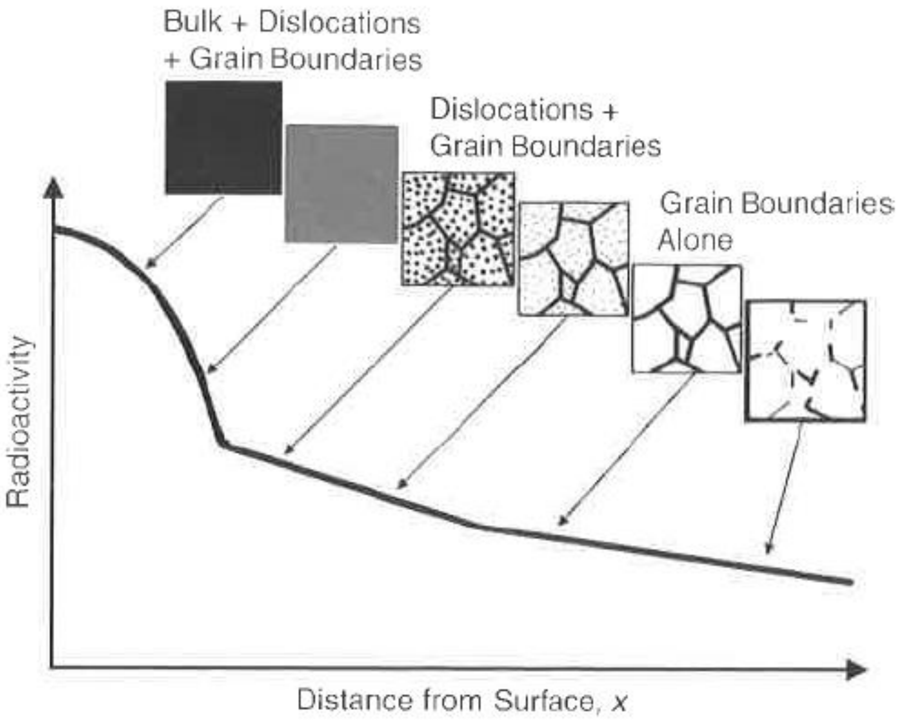


Diffusion models:

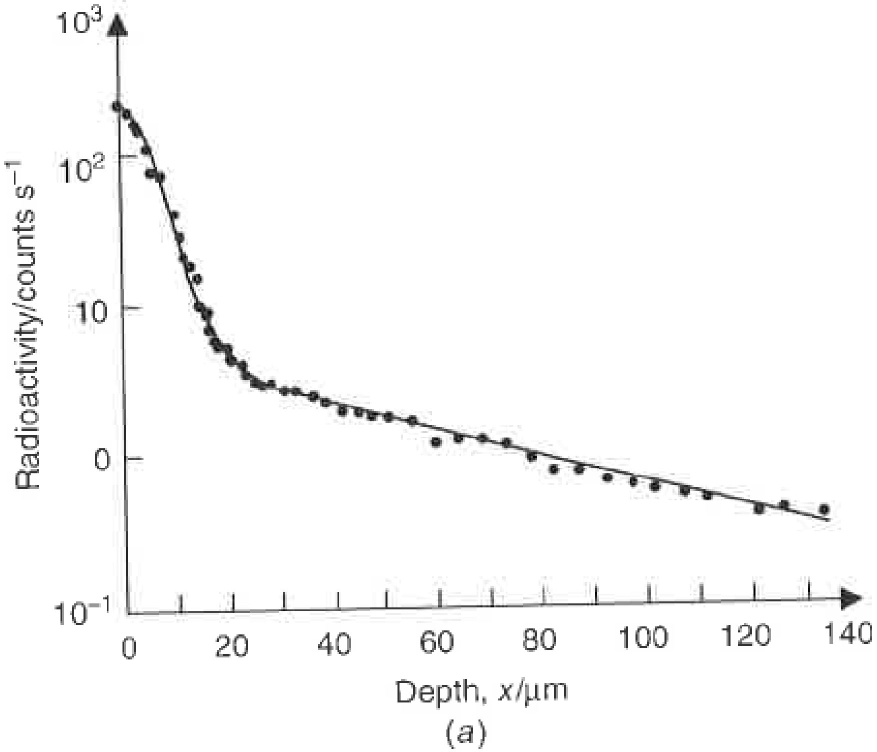
- Dislocation = cylinder with radius r
- Grain boundary = slab with a width δ
- …

Penetration curves in polycrystalline solids

Radiotracers (self-diffusion, impurities) and radiography



Theory



Experiment: ^{63}Ni in CoO at 1230 K

M. Le Gall et al. Phil. Mag. 1994

Diffusion in polycrystals
Grain boundaries

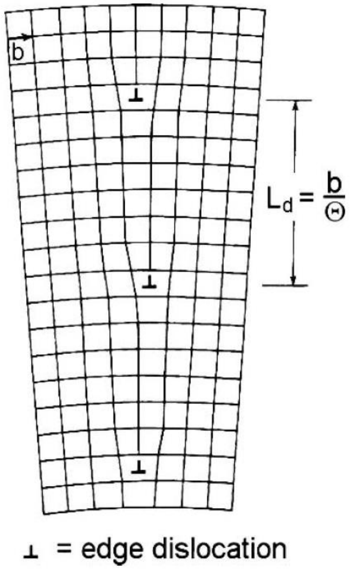


Fig. 32.2. Low-angle tilt boundary after BURGERS [19]

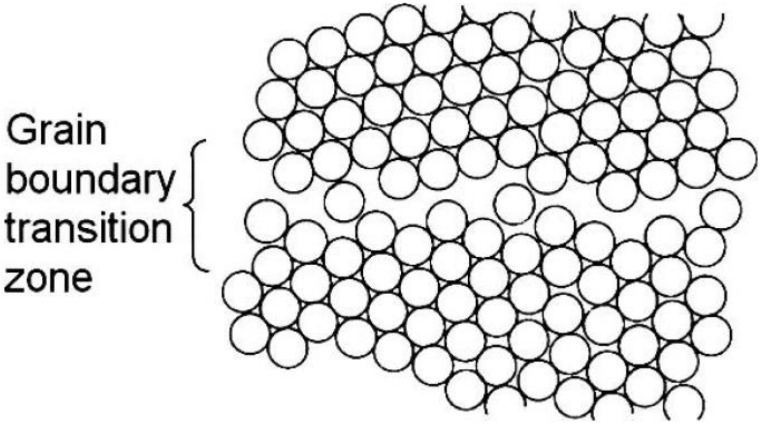


Fig. 32.3. Random high-angle grain boundary (schematic)

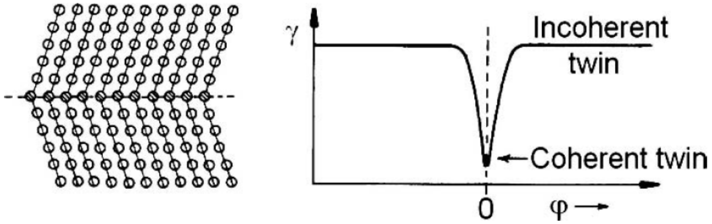
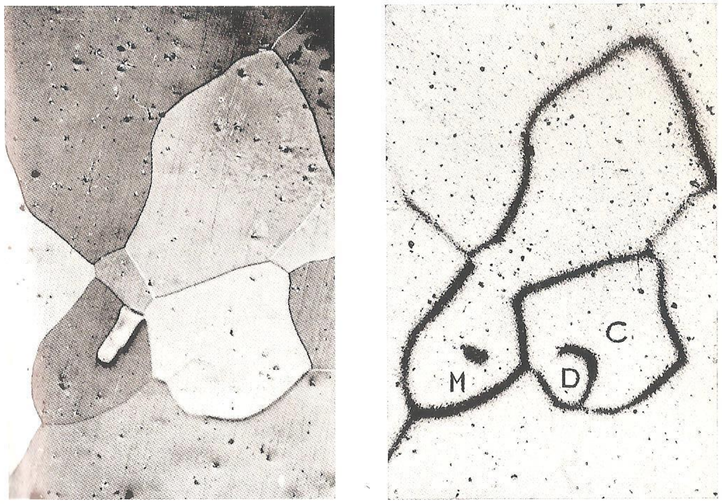


Fig. 32.4. A coherent twin boundary (*left*). Twin-boundary energy γ as a function of the orientation ϕ of the grain-boundary plane (*right*)



(*a*) (*b*)

Influence de l'orientation du joint de grains par rapport au réseau des deux cristaux contigus sur la pénétration intergranulaire du fer radioactif dans le fer inerte après recuit de 30 jours à 650 °C. Seule la partie non-cohérente M du joint séparant les cristaux A et B en position de macle {112} a subi la diffusion intergranulaire. On observe de grandes différences de pénétration aux joints suivant l'orientation du joint séparant les cristaux C et D.

a) Micrographie. *b*) Autoradiographie. × 175

D'après C. Leymonie et P. Lacombe.

Different types of grain boundaries
→ different GB diffusion coefficient

Grain boundary diffusion

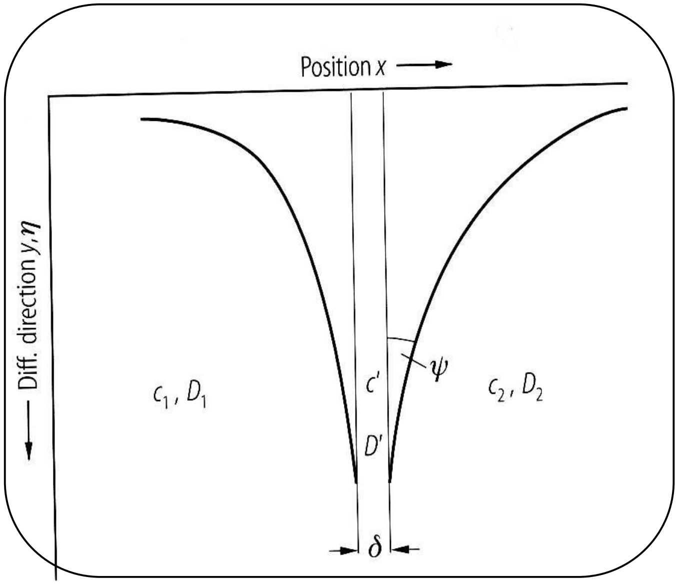
Fisher's model, Leclair, Wipple, Suzuoka

Fisher's model of grain boundary diffusion

gb slab of thickness δ with
diff. coeff. $D_{gb} >> D$

Solution of Fick's laws (Suzuoka)
$\delta < (Dt)^{1/2} < d/2$

$$D_{gb}\delta = (d\ln C/dx^{6/5})^{-5/3} \times (4D/t)^{1/2}\ \beta^{0.03} \times 0.578$$



Structures of a bicrystal of alumina and a Y-doped alumina

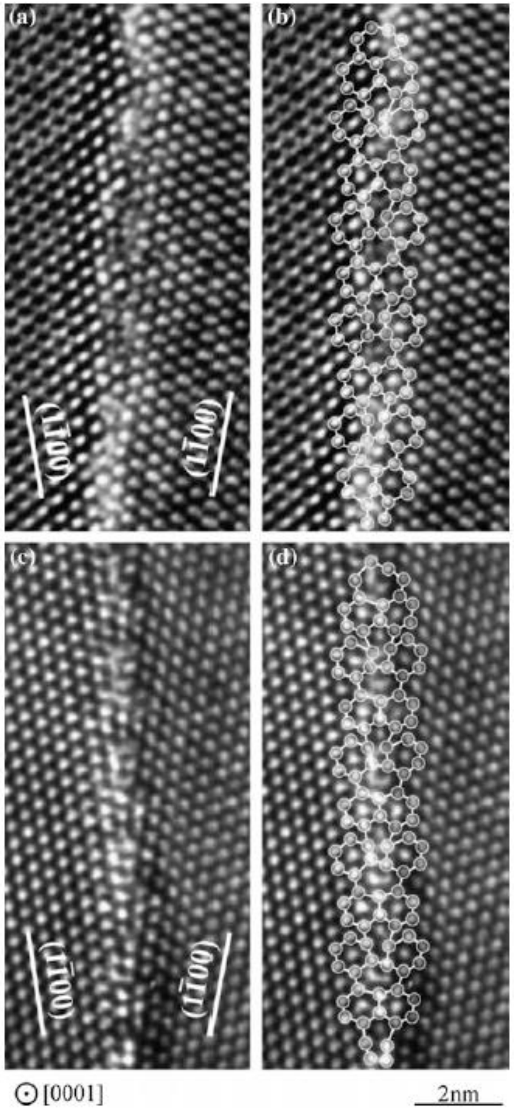
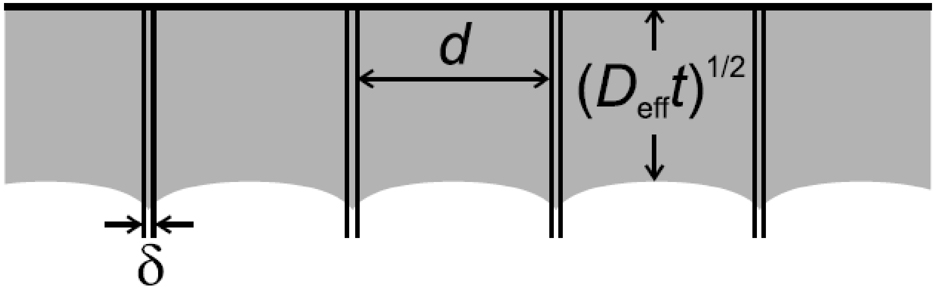


Fig. 11.36 High-resolution TEM images of (**a**) the pristine and (**c**) the yttrium-doped grain boundaries; (**b**) and (**d**) show the same images with overlays to show the anion column arrangement at each grain boundary. It can be seen that both grain boundaries have similar unit structures. Nakagawa et al. (2007). With kind permission of Elsevier

Diffusion in polycrystals

Type A



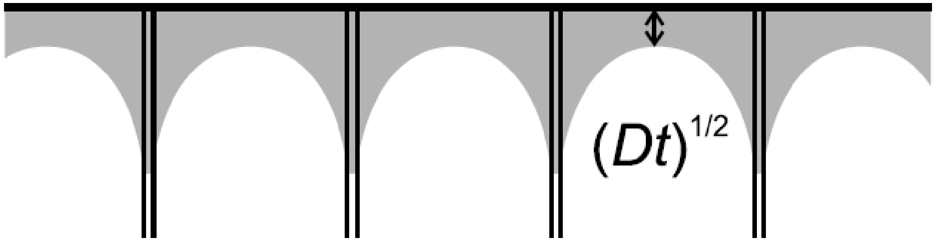
Type A

$(Dt)^{1/2} >> d$

$D_{eff} = \alpha D_{gb} + (1-\alpha) D$

Hart

Type B

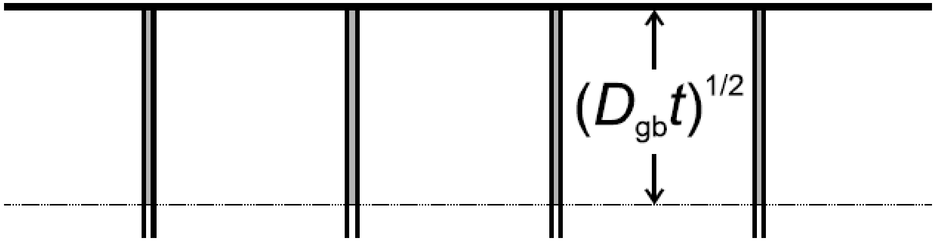


Type B

$\delta < (Dt)^{1/2} < d/2$

δD_{gb}, D

Type C



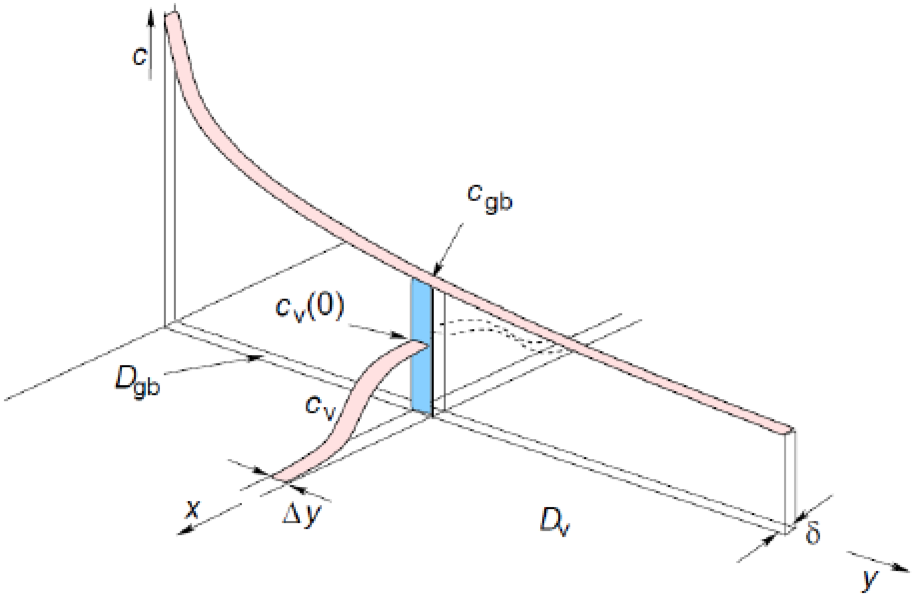
Type C

$(Dt)^{1/2} < \delta$

D_{gb}

Grain boundary diffusion

Fisher's model with segregation



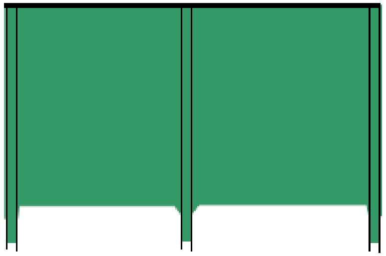
TRIPLE PRODUCT $P = s\delta D_{gb}$

$$s = \frac{C_{gb}}{C_v}$$

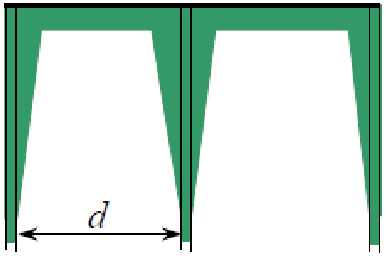
Kinetic regimes after Harrison

Harrison, 1961

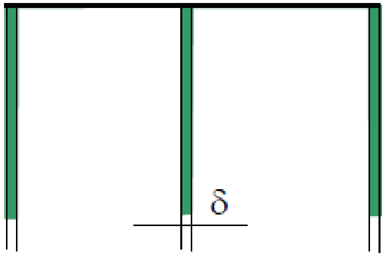
A regime



B regime



C regime

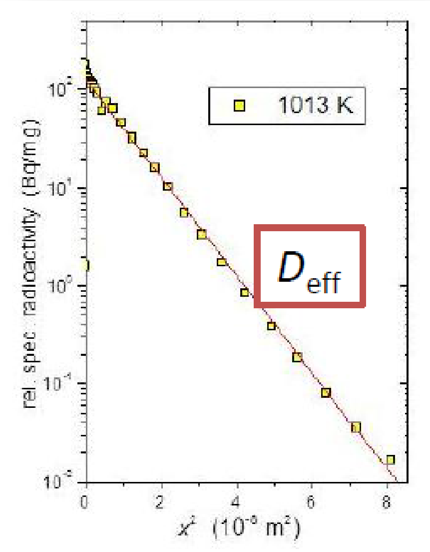


The tracer distribution after a given diffusion anneal is shown (gray regions). The grain boundaries are considered as homogeneous slabs of width *d* and diffusivity D_{gb}. The grain size *d* is indicated.

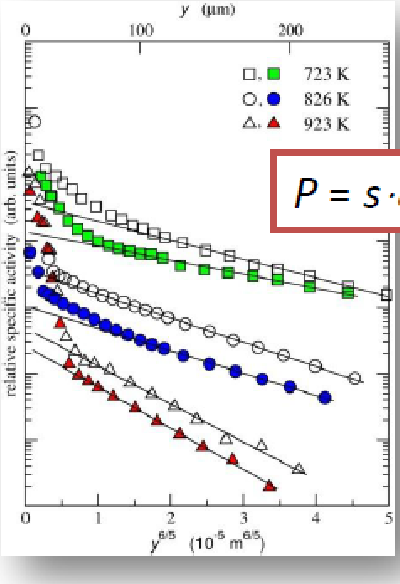
$$\alpha \equiv \frac{s\delta}{2\sqrt{D_v t}} < 0.1 \qquad \Lambda^* \equiv \frac{d}{\sqrt{D_v t}} < 0.4$$

$$\alpha \equiv \frac{s\delta}{2\sqrt{D_v t}} < 0.1 \qquad \Lambda^* \equiv \frac{d}{\sqrt{D_v t}} > 3$$

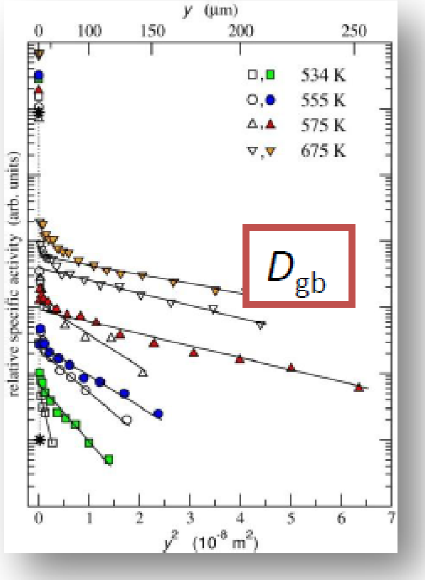
$$\alpha \equiv \frac{s\delta}{2\sqrt{D_v t}} > 1$$



D_{eff}



$P = s \cdot \delta \cdot D_{gb}$



D_{gb}

Difficulties in gb diffusion in ceramics

- Precision and reproducibility of the data are often poor, usually ascribed to impurities in the sample.

- When the **concentration of intrinsic defects** is negligible, transport properties depend on the nature and concentration of impurities, which is often unknown.

- **Interfaces** are particularly likely to be affected by these considerations, because the **segregation energies for defects** to interfaces are frequently very large

➔ concentration of defects or impurities at an interface can be very great, even if the bulk concentration is low.

- Since the segregation energies vary from defect to defect, it is likely that the grain boundary core will be charged

➔ **space-charge layers** enriched of the defects of opposite sign, which were more weakly attracted to the boundary.

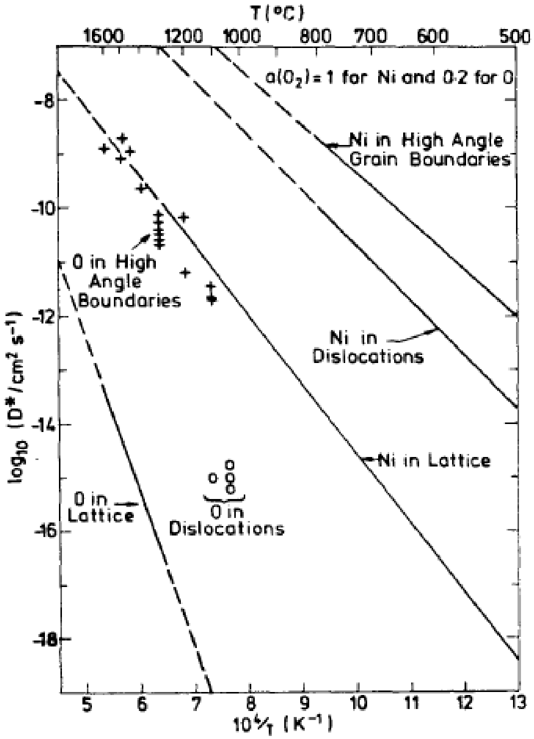
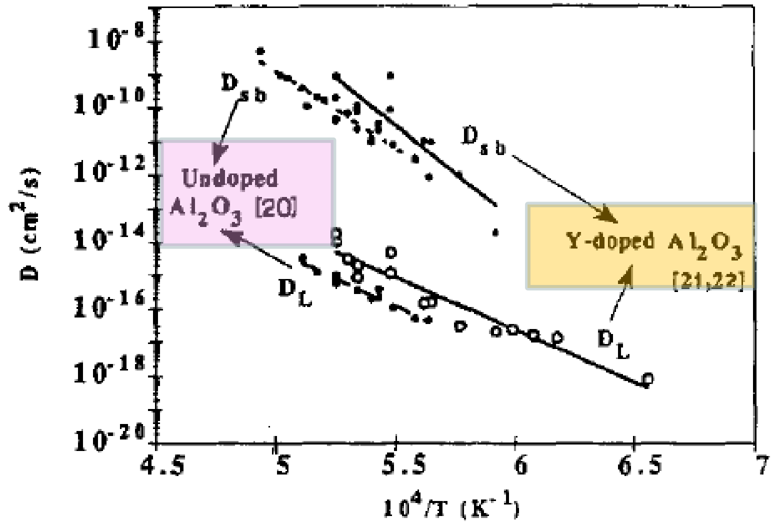


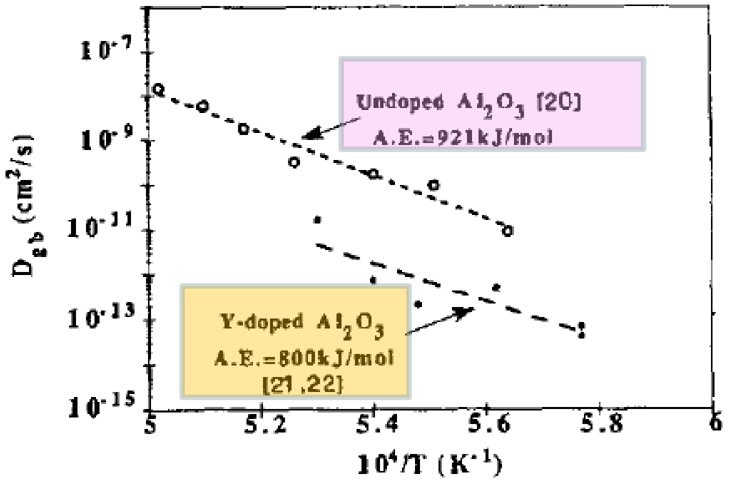
Fig. 7. Ni and O tracer self diffusion in the lattice, dislocations and grain boundaries in NiO (2)(10)(49)(52).

Diffusion in polycrystalline alumina



Oxygen diffusion in undoped and doped Al_2O_3

Fig.21- Comparaison de la diffusion de O en volume et dans les sous-joints de grains de l'alumine α non dopée ou dopée en yttrium (300ppm pds Y_2O_3).



Dgb in undoped or Y-doped polycrystalline Al_2O_3

Oxygen diffusion

Fig.22- Comparaison de la diffusion de O dans les joints de grains de l'alumine α non dopée ou dopée en yttrium (500ppm pds Y_2O_3).

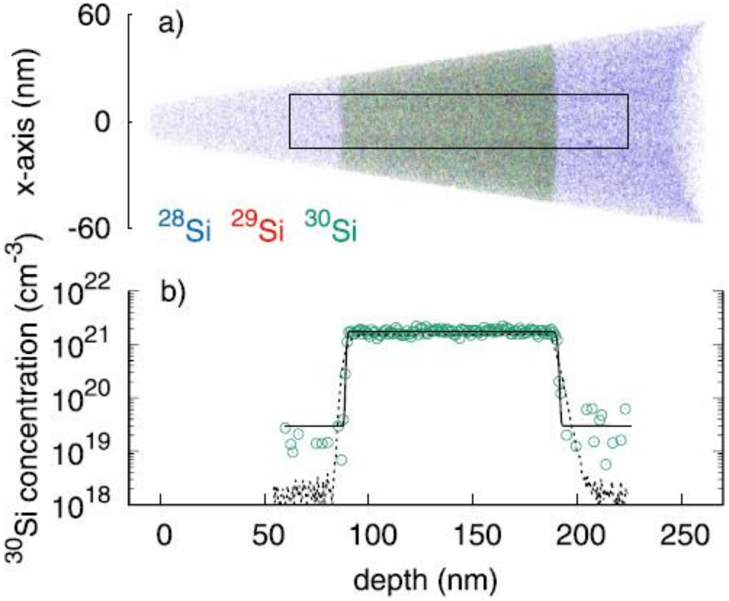
Higher activation energy for GB than for lattice diffusion !!!

Strong segregation of Y → GB diffusion lower for Y doped Al_2O_3

Strong effect of segregation on GB diffusion

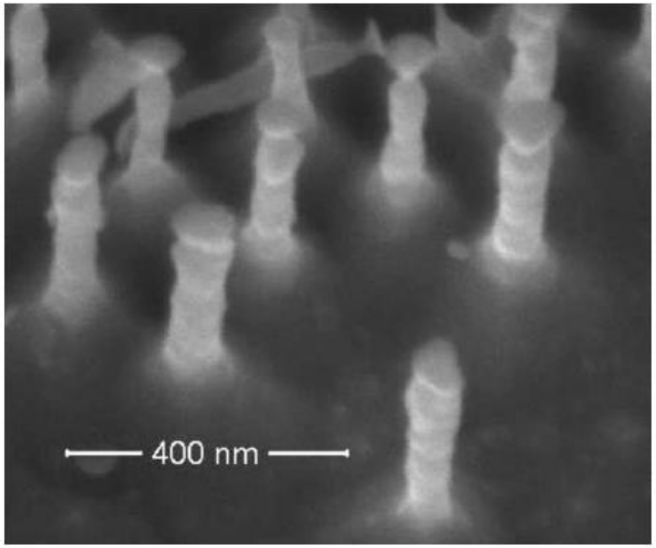
Diffusion / surface / interface

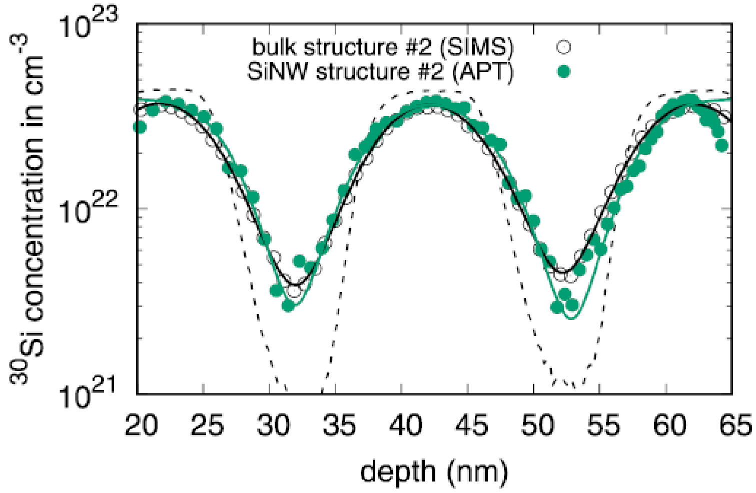
Effet de surface sur l'auto-diffusion du Si



Si isotop structure of a 400 nm diameter Si nanowire (NW) before annealing

Südkamp, JAP, 2017





^{30}Si concentration depth-profiles after annealing at 850C for 48 h for 70 nm diameter NW compared to bulk Si layers.

Effet de la surface de nanofils sur la diffusion du Si

- Surface = puit de défauts (lacunes, interstitials)
- Nanofils = rapport surface / volume depend de la taille des nanofils.
- meme diffusion dans les nanofils et le volume

→ Pas d'effet pour les nanofils de 70nm!!!

Some databases and books

1. Books

- Y. Adda and J. Philibert, La Diffusion dans les Solides (PUF, 1966)
- J. Philibert, Diffusion et transport de matiére dans les solides, (Ed. Phys., 1990) / Atom Movements, (Ed. Phys., 1992)
- H. Mehrer, Diffusion in solids, (Springer, 2007)
- Y.T. Chiang, D Birnie, WD Kingery, Physical ceramics, (Wiley)
- R.A. Swalin, Thermodynamics of Solids (Wiley & Sons, New York, 1972)
- D.A. Porter K.E. Easterling, Phase Transformations in Metals and Alloys, CRC Press (Taylor & Francis Group, 2004)
- Handbook of Solid State Diffusion, Eds A. Paul & S. Divinsky, 2017
- **Kofstad and Norby: defects and transport in cristalline solids, 2007**
- …

2. Databases

- Landolt Bornstein III-33, Diffusion in SC and non-metallic solids (Springer, 1998)
- Transport in Nonstochiometric Compounds (NATO series, 1985)
- Pelleg, Diffusion in ceramics (Springer, 2016)

3. Publication

- **AM Huntz, J. Phys. III, 1995**
- …

Diffusion in oxides: some conclusions

Oxides = ionic solids

Electrostatic and charge effects (ambipolar diffusion)

Diffusion mechanisms by vacancies and interstitials

Oxygen partial pressure dependent

Defect thermodynamics

Very sensitive to microstructure and impurities

Non stoichiometric oxides: diffusion controlled by non stoichiometry

Near stoichiometric oxides: extrinsic behaviour (impurity-dominated), scattered experimental results

→ 2nd école "Diffusion dans les solides" Marseille 2019

Diffusion in liquid, glass… → This workshop