

# POINT DEFECTS AND CAPTURE OF IMPURITIES IN CRYSTALS

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- I. Introduction to defects
- II. Types of point defects
- III. Statistics of point defects
- IV. Diffusion in crystals
- V. Methods for creation of point defects
- VI. Point defects during crystal growth
- VII. Capture of impurities in crystals
  - Distribution coefficient of impurities
  - Equilibrium segregation coefficient
  - Effective segregation coefficient  $k_{\text{eff}}$
  - Relationship between  $k_{\text{eff}}$  and face growth rate  $R$
  - Threshold supersaturation for trapping of impurities during crystal growth

# I. Introduction to defects

Perfect or ideal crystal lattice – arrangement of points in 3D space

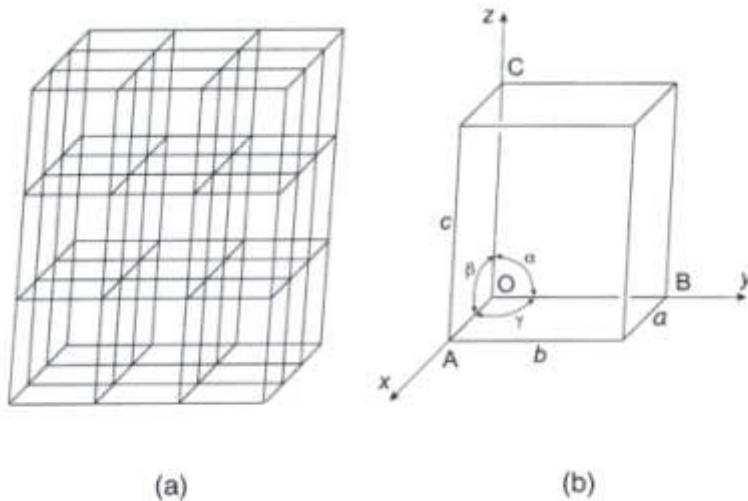


Figure 1.1 (a) A space lattice, (b) unit cell showing positions of principal axes.

- **Concept of ideal crystal useful to explain -**

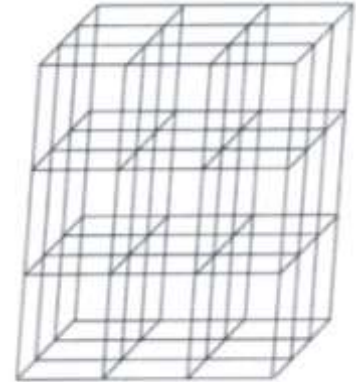
Some of the properties of crystals (for example: density, specific heat, and dielectric susceptibility, independent of details of crystal structure.

**No real crystal is ideal –**

Contains faults or flaws (known as defects or imperfections).

Many properties of crystals (e.g. mechanical strength, electric conductivity, magnetic hysteresis, etc.) are very sensitive to the extent of imperfections in them.

# Type of defects in crystals



## - Thermal vibrations of atoms

### 0 Point defects

vacancies, interstitial atoms, and impurity atoms (chemical contamination)

### 1 Line defects

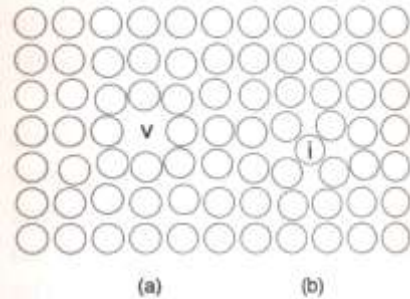
Dislocations: edge, screw, and mixed

### 2 Planar defects

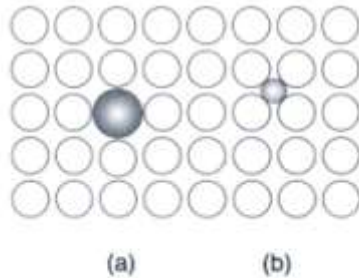
External surfaces of crystals, internal surfaces in crystals (grain boundaries, twin boundaries, and stacking faults)

### 3 Volume defects

## II. Types of point defects: examples

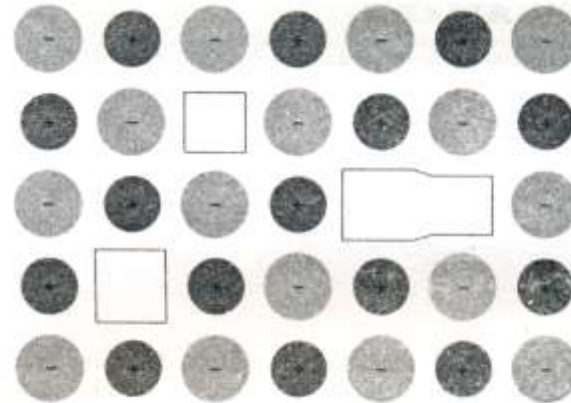


**Figure 1.10** (a) Vacancy, (b) self-interstitial atom in an (001) plane of a simple cubic lattice.



**Figure 1.11** (a) Substitutional impurity atom, (b) interstitial impurity atom.

Metals



**Figure 1** A plane of a pure alkali halide crystal, showing a vacant positive ion site, a vacant negative ion site, and a coupled pair of vacant sites of opposite sign.

1:1-type ionic crystal

Missing points **and/or** displacement of missing points to interstitial sites

# Schottky and Frenkel defects

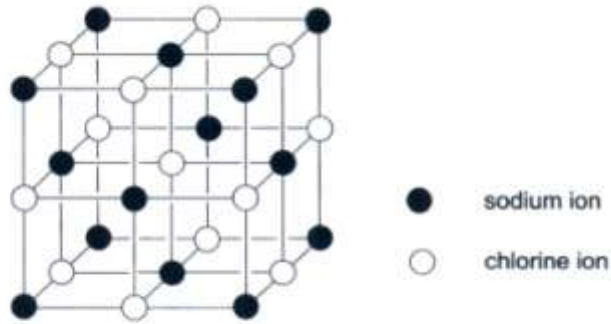


Figure 1.12 Sodium chloride structure which consists of two interpenetrating face-centred cubic lattices of the two types of atom, with the corner of one located at the point  $\frac{1}{2}, 0, 0$  of the other.

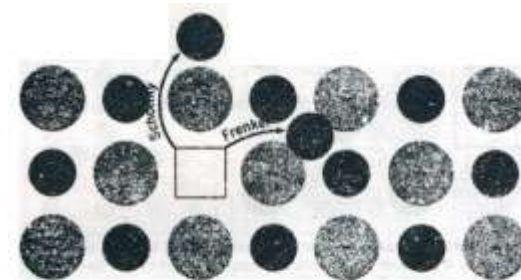


Figure 2 Schottky and Frenkel defects in an ionic crystal. The arrows indicate the displacement of the ions. In a Schottky defect the ion ends up on the surface of the crystal; in a Frenkel defect it is removed to an interstitial position.

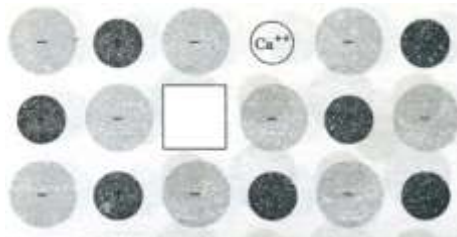
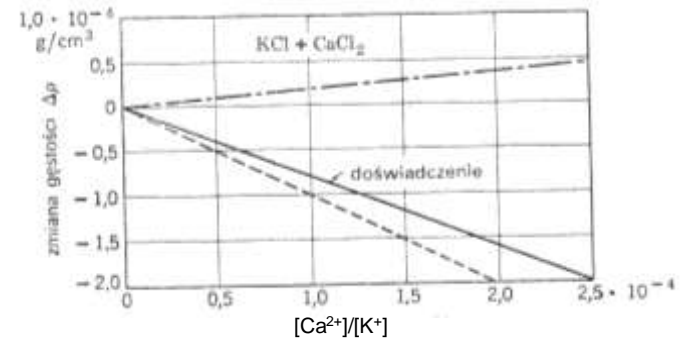


Figure 3 Production of lattice vacancy by the solution of  $\text{CaCl}_2$  in  $\text{KCl}$  to ensure electrical neutrality a positive ion vacancy is introduced into the lattice with each divalent cation  $\text{Ca}^{2+}$ . The two  $\text{Cl}^-$  ions of  $\text{CaCl}_2$  enter normal negative ion sites.



Change in the density  $\rho$  of  $\text{KCl}$  with  $\text{CaCl}_2$  concentration.

Example:  
 $\text{KCl}:\text{CaCl}_2$

From Kittel .

# III. Statistics of point defects

## Natural source of point defects

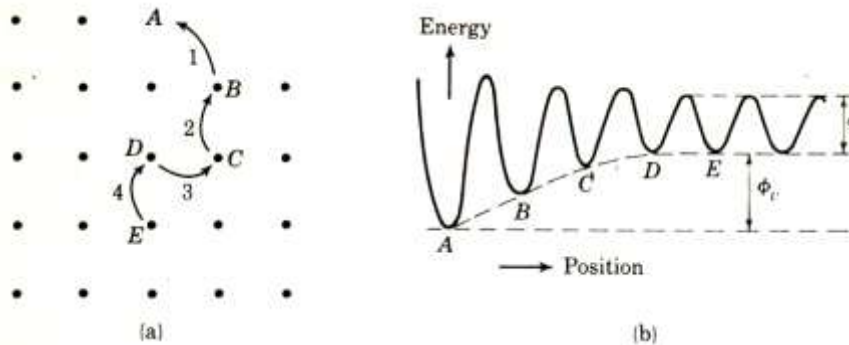


Fig. 3-5. Sequence of jumps producing a vacancy which migrates into the interior of the crystal (a). In (b) the potential energy of the vacancy is shown schematically as it diffuses in; the limiting value  $\phi_v$  is the energy of formation,  $\epsilon_j$  is the jump activation energy of the vacancy.

- Presence of phonons
- Absorption of phonons

$\epsilon_j$  – jump activation energy of vacancy  
 $\phi_v$  – energy for creation of vacancy (=  $E_v$ )

If  $E$  is the total energy to separate all  $N$  crystal atoms from each other, the sublimation energy per atom is:

$$\epsilon_s = E/N.$$

For an atom of potential energy  $\epsilon_i$  in the interior of the crystal, the dissociation energy of the crystal is

$$N\epsilon_i/2.$$

Obviously,  $\epsilon_s = \epsilon_i/2$ .

Therefore, the energy  $\phi_v = E_v$  required to transfer an atom from the interior to the surface (i.e. to form a vacancy) is:

$$\phi_v = \epsilon_i - \epsilon_r - \epsilon_s = \epsilon_s - \epsilon_r,$$

**For Cu metal,  $\epsilon_s = 3.5$  ev.**

With  $\phi_v = \phi_r$ , this gives

$$\phi_v \approx 1.7 \text{ ev} = 170 \text{ kJ/mol}$$

$$\text{Observed } \phi_v \approx 1.4 \text{ ev,}$$

$$\epsilon_j \approx 0.5 \text{ ev} = 50 \text{ kJ/mol}$$

# Thermal equilibrium

A.J. Dekker, Solid State Physics, MacMillan, London (1964).

## Concentration (fraction) of vacancies

Thermodynamic parameters for a system:

Thermal free energy or Helmholtz free energy:  $F$   
 Internal energy:  $E$   
 Entropy of the system:  $S$

Equation for free energy:

$$F = E - TS.$$

Change in system free energy:

$$\Delta F = \Delta E - T\Delta S.$$

$$\Delta E = nE_v (1 - \alpha T),$$

$$\Delta S = \Delta S_{cf} + \Delta S_{th},$$

where:

$$\Delta S_{cf} = k_B \ln[(N+n)!/N!n!],$$

$$\Delta S_{th} = 3zk_B \ln(v/v')$$

where:

$N$  – normal lattice sites

$n$  - number of defects

$(3N-3nz)$  oscillators

of frequency  $\nu$

$3nz$  oscillators

of frequency  $\nu'$

$z$  – number of atoms

surrounding a vacancy

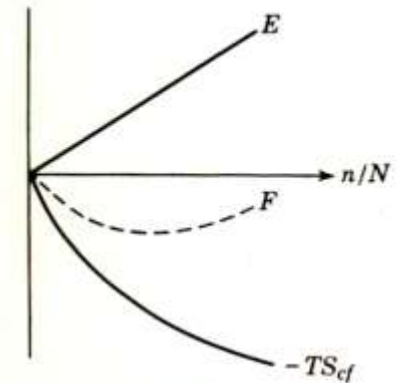


Fig. 3-4. Schematic representation of the energy and the configurational entropy term as function of the fraction of vacant lattice sites  $n/N$ . The minimum of the free energy  $F$  determines the equilibrium value of  $n/N$ .

We use Stirling's formula for  $x \gg 1$ :  $\ln x! = x \ln x$ .

For metals:

$$\frac{n}{N+n} = \exp\left(\frac{\Delta S_{th}}{k_B}\right) \exp\left(\frac{\alpha E_v}{k_B}\right) \exp\left(-\frac{E_v}{k_B T}\right).$$

Handbook equation

$$n \approx N \exp(-E_v / k_B T).$$

Two parameters:

$E_v$  and  $T$



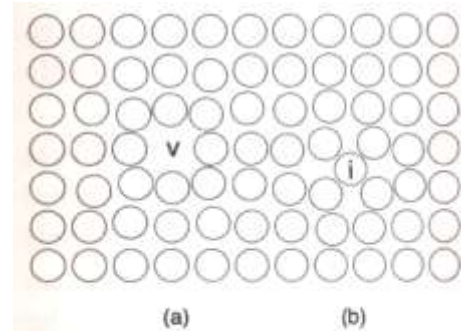
## Concentration of other defects

Concentration of Frenkel defects in metals:

$$\frac{n}{(NN')^{1/2}} = K \exp\left(-\frac{E_F}{2k_B T}\right).$$

Concentration of Schottky defects in ionic crystals:

$$\frac{n}{N} = K \exp\left(-\frac{E_p}{2k_B T}\right).$$



**Figure 1.10** (a) Vacancy, (b) self-interstitial atom in an (001) plane of a simple cubic lattice.

$n$  - number of defects  
 $N$  - normal lattice sites  
 $N'$  - interstitial sites

Origin of Factor 2 ?

# IV. Diffusion in crystals

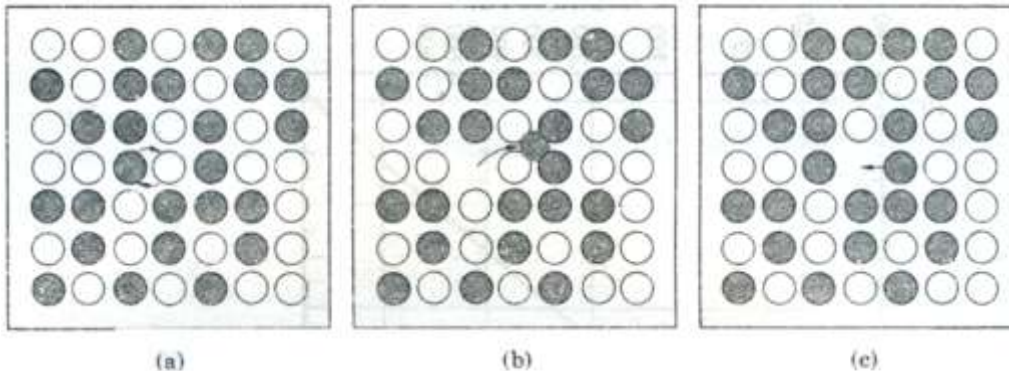


Figure 4 Three basic mechanisms of diffusion: (a) Interchange by rotation about a midpoint. More than two atoms may rotate together. (b) Migration through interstitial sites. (c) Atoms exchange position with vacant lattice sites. (From Seitz.)

$\nu$  - jump frequency

$\delta$  - jump distance

$R_G = k_B N_A$  - gas constant

$\Delta H_m$  - enthalpy of melting

$\Delta H_b$  - enthalpy of boiling

## Estimation of some energies

For evaporation: Trouton rule

$$\Delta H_b \approx 10 R_G T_b$$

For melting: empirical trend

$$\Delta H_m \approx \xi R_G T_m$$

with the factor

$\xi = 2$ , for metals;

$\xi = 3$ , for inorganic salts.

Diffusion coefficient  $D$  in vacancy diffusion

$$D = \nu \delta^2 \exp\left(-\frac{E_v + \Delta H_m}{R_G T}\right)$$

Diffusion coefficient  $D$  in interstitial diffusion

$$D = \nu \delta^2 \exp\left(-\frac{\Delta H_m}{R_G T}\right)$$

For Cu,

$T_b = 2835$  K,  $T_m = 1358$  K,  
one obtains

$$\Delta H_b = 235.7 \text{ kJ/mol} = 2.4 \text{ eV}$$

$$\Delta H_m = 33.9 \text{ kJ/mol} = 0.34 \text{ eV}$$

$$\varepsilon_s = \Delta H_m + \Delta H_b = 2.74 \text{ eV}$$

## V. Methods for creation of point defects

1. Quenching from high temperature
2. Strong deformation i.e. plastic treatment (forging or rolling)
3. Bombardment by ions or high-energy charged particles
4. Growth processes (doping)

Two modes:

- Energy supplied by different means: thermal, mechanical, energy transfer
- structural changes

# VI. Point defects during crystal growth

Mechanism: Structure of elementary steps

Rough steps:  
- vacancies,  
- impurities.

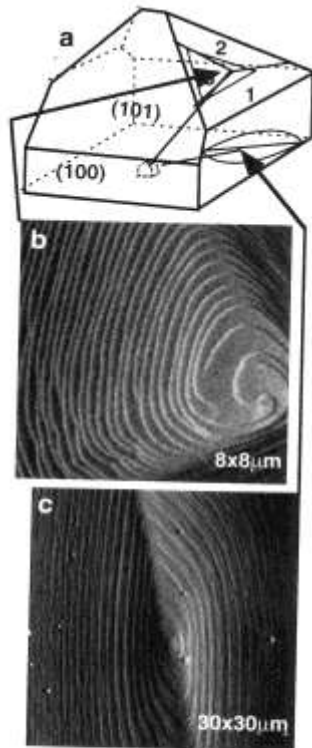


Figure 6. Example of KDP crystal surfaces preserved by pulling through hexane. (a) shows schematic of crystal structure. (b and c) Growth hillocks on the (b) {101} and (c) {100} face generated by dislocations emanating from the seed crystal interface.

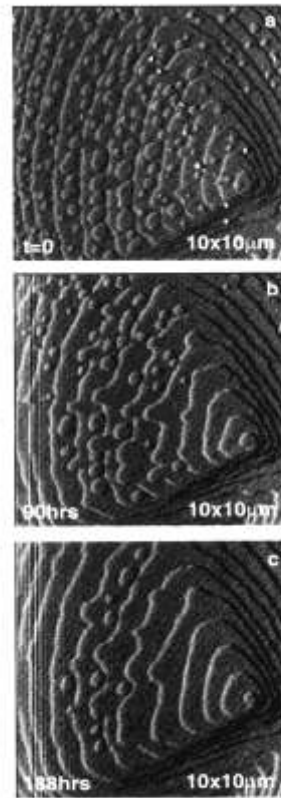


Figure 9. Coarsening of islands and steps on KDP {101}. With time, the material from the islands diffuses to the steps which in turn exhibit smoothing.

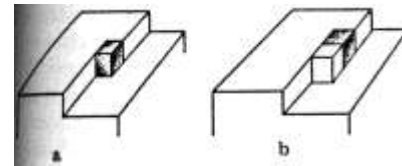


Fig.4.8a,b. Consecutive acts of entrapment of an impurity particle (shaded cube) during the building of a row with host particles (open cubes)

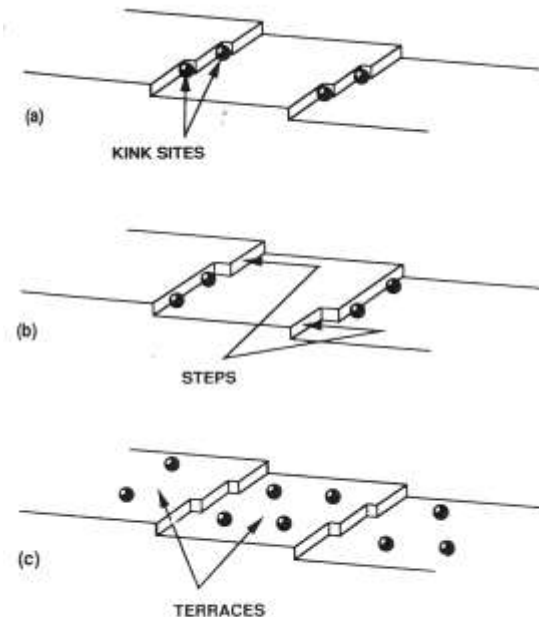


Figure 3.5 Key surface structures on an idealized crystal face: (a) kinks; (b) steps; and (c) terraces. Adsorbed impurities at each of these sites is illustrated. (Reproduced with permission from Mullin 1980.1)

# Examples of images of segregation of impurities

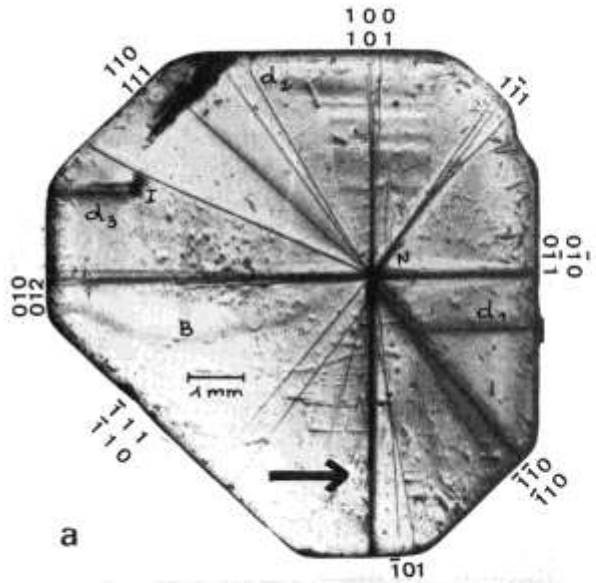


Fig. 6. Topographs of the two (010) slices cut out of an as grown KBC crystal slice, ref. 120; MoK $\alpha$ .

Sectorial nonuniformity as a result of different trapping in different growth sectors  
Zonal nonuniformity in the same sector due to nonuniform growth rate  
Growth bands or Impurity striations

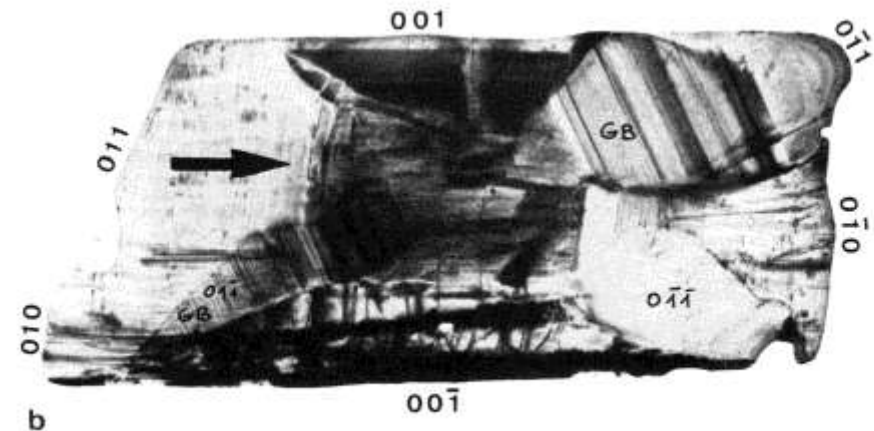
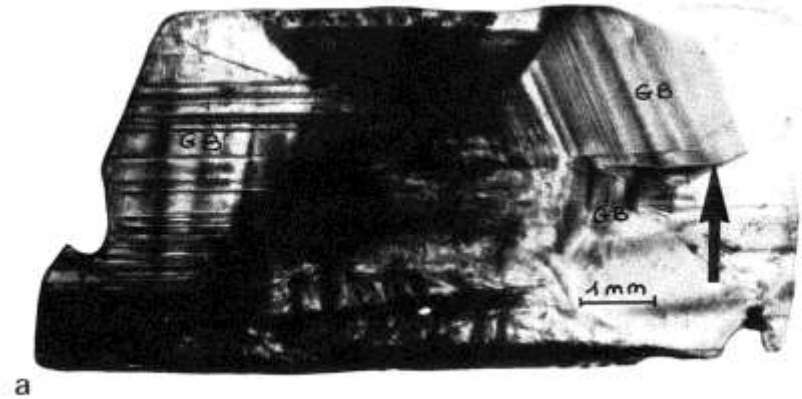


Fig. 8. Topographs of an as grown KBC crystal obtained at 47°C in an aged solution: (a) ref. 020; (b) ref. 200; MoK $\alpha$ .

# Examples and comments

TABLE 2.4  
Segregation coefficients in alkali halides†

Host	Solute	Segregation coefficient	
		Aqueous solution	Melt
NaCl	Li	$0.007 \pm 0.004$	0.21, $0.20 \pm 0.05$ , 0.19
	K	$0.005 \pm 0.001$	0.20, $0.008 \pm 0.003$
	Br	$0.047 \pm 0.005$	0.6
	I	$< 4 \times 10^{-4}$	0.06
KCl	Na	$< 6 \times 10^{-4}$	0.03, $0.11 \pm 0.02$ , 0.31
	Rb	$0.113 \pm 0.005$	0.68, $0.6 \pm 0.1$ , 0.70
	Cs	$0.0040 \pm 0.0006$	0.16, 0.21
	Br	$0.189 \pm 0.003$	0.75, 0.71
KBr	In	$< 0.001$	0.14
	Rb	$0.334 \pm 0.004$	0.78, $0.4 \pm 0.1$ , 0.75
KI	Cl	$0.453 \pm 0.005$	0.86, 0.85
	I	$0.039 \pm 0.004$	0.5, 0.52
	Rb	$0.82 \pm 0.03$	$0.76 \pm 0.02$
	Cs	$0.03 \pm 0.01$	$0.31 \pm 0.01$
	Cl	$0.015 \pm 0.02$	$0.39 \pm 0.02$
	Br	$0.42 \pm 0.02$	$0.79 \pm 0.02$
	NO <sub>3</sub>	$0.071 \pm 0.004$	$0.43 \pm 0.01$

Segregation coefficient  $k$  depends on structure and difference in size of atoms, ions and molecules in the common crystal lattice.

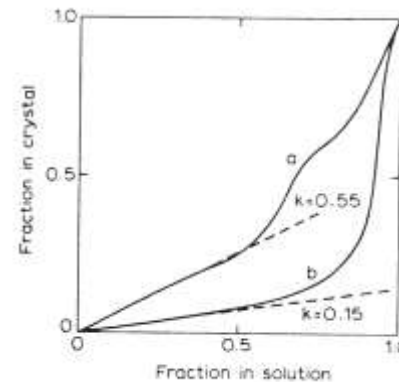


Fig. 2.20. The fractions in the solid and in aqueous solution of (a) copper sulphate and (b) ammonium sulphate in mixed crystals with potassium sulphate.

† Based on the data of Andreev (1967, 1969), Ikeya *et al.* (1968) and Gross (1970a, b).

Brice (1973)

# VII. Capture of impurities in crystals

Podstawowa literatura:

K. Sangwal, *Additives and Crystallization Processes: From Fundamentals to Applications*, Wiley, Chichester, 2007, chap. 9.

Large deformation of lattice does not favor capture of impurity atoms in it.

Impurities captured in crystal lattice are:

- 1) individual atoms, ions, molecules or complexes of molecular dimensions like dimers and trimers; **uniform impurity capture**. Solid solution is formed when  $c_{i\text{Solid}} = c_{i\text{Liquid}}$  (thermodynamically equilibrium capture of impurities) or  $c_{i\text{Solid}} \neq c_{i\text{Liquid}}$  (nonequilibrium impurity capture).
- 2) Colloidal inclusions of micrometer dimensions; **nonuniform capture of impurities**.

Concentration and distribution of uniform and nonuniform capture of an impurity are different in the crystal volume due to thermal nonequilibrium at crystal-liquid interface.

**Nonuniform capture occurs:**

- 1) in different growth sectors of a crystal (sectorial nonuniformity),
- 2) In a given growth sector (zonal nonuniformity; growth bands, impurity striations),
- 3) In the vicinity of structural defects such as dislocations and grain and twin boundaries as enrichment or depletion of impurity (structural nonuniformity).

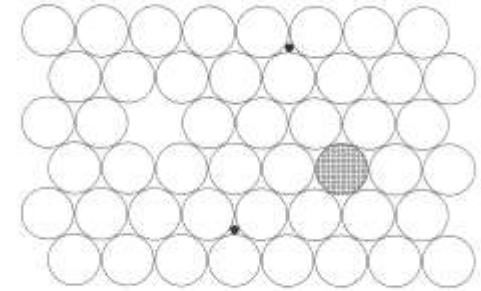


Figure 9.1 Different types of point defects involved during impurity incorporation: vacant site, substituted atom (hatched circle), and interstitial atoms (small black circles).

# Distribution coefficient of impurities

Concentrations [C] and [A] in atomic/ionic fraction, weight fraction or as mass in volume.

When impurity C (i) enters the substance A (s): segregation coefficient

$$k_d = \frac{[C_{\text{solid}}]}{[C_{\text{solid}}] + [A_{\text{solid}}]} \times \frac{[C_{\text{liquid}}] + [A_{\text{liquid}}]}{[C_{\text{liquid}}]} \quad (1)$$

When  $[C] \ll [A]$ ,

$$k_d = \frac{[C_{\text{solid}}]}{[C_{\text{liquid}}]} \frac{[A_{\text{liquid}}]}{[A_{\text{solid}}]} \quad (2)$$

In the case of growth from the melt

$$k_d \approx \frac{[C_{\text{solid}}]}{[C_{\text{liquid}}]} \quad (3)$$

When concentration is in mole fraction

$$k_d = \frac{x_{iS} / x_{sS}}{x_{iL} / x_{sL}} \quad (4) \quad \begin{array}{l} \text{S - solid} \\ \text{L - liquid} \end{array}$$

$k_0$  depends on physico-chemical properties of crystal and impurity.

$k_{\text{eff}}$  depends on the nature of crystal-fluid interface;  $k_{\text{eff}}$  (smooth interface) <  $k_{\text{eff}}$  (rough interface).

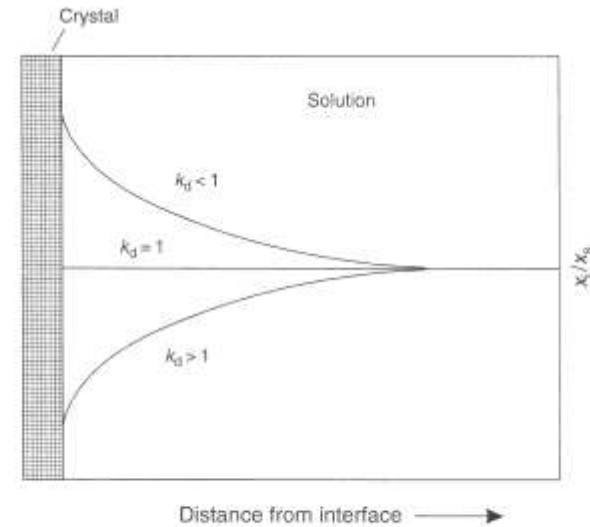


Figure 9.2 Schematic illustration of the dependence of  $x_{iL}/x_{sL}$  on distance from the crystal-solution interface, and relationship between  $x_{iL}/x_{sL}$  at the crystal-medium interface and the segregation coefficient  $k_d$ . Adapted from Rimstidt et al. (1998)

## Segregation of impurities

1. Equilibrium (supersaturation  $\sigma \Rightarrow 0$ )  
Equilibrium segregation coefficient  $k_0$
2. Nonequilibrium ( $\sigma > 0$ )  
Effective segregation coefficient  $k_{\text{eff}}$



# Equilibrium segregation coefficient

## 1) Two-component mixture approach:

For C to enter A the theoretical description is similar to that of phase diagrams for two-component systems

In the case of C in A:

$$\ln k_0 = \frac{\Delta H_m^A}{R_G} \left( \frac{1}{T} - \frac{1}{T_m^A} \right) - \frac{\Delta H_m^C}{R_G} \left( \frac{1}{T} - \frac{1}{T_m^C} \right)$$

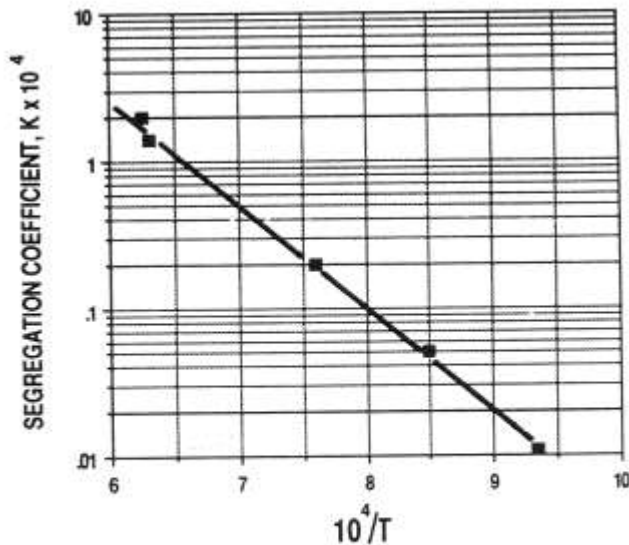


Figure 3.7 Logarithm of the segregation coefficient versus  $1/T$  for copper in silicon crystals. (Reprinted with permission from C.D. Thurmond and J.D. Struthers (1953). *J. Phys. Chem.* 57, 331-835. Copyright 1953 American Chemical Society.)

## 2) Thermodynamic approach:

$\ln k_0 = \ln k_0(0) - \Delta G / R_G T$   
 where:  $k_0(0)$  is the value of  $k_0$  when  $r_i = r_s$ , and  $\Delta G$  is the change in the difference in the free energy.

**Other approaches** are based on: difference in volumes, heat of sublimation, diffusion coefficient, etc.

In the case of mismatch of volume fraction  $\Delta V/V_A$  at a given temperature:

$$\begin{aligned} \ln k_{eq} &= B_1 + B_2 \Delta V / V_A \\ &= A - B + B(r_i / r_s)^3. \end{aligned}$$

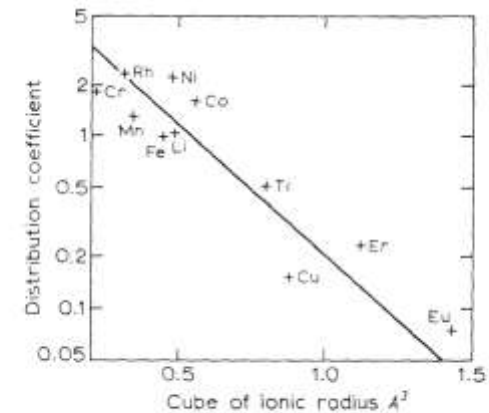
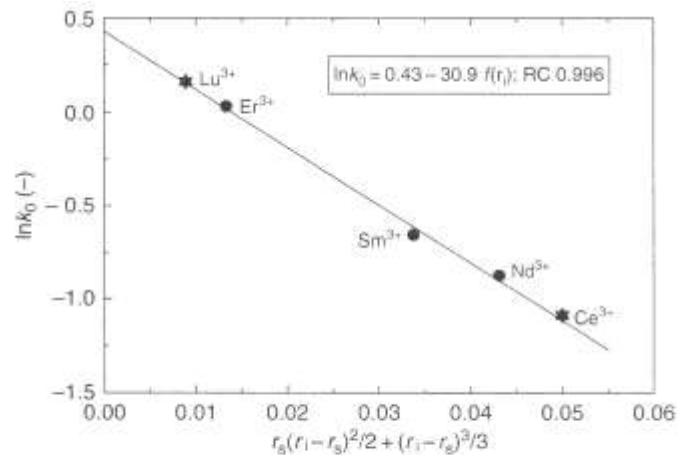


Fig. 2.21. Distribution coefficients in zinc tungstate as a function of the cube of the ionic radius.

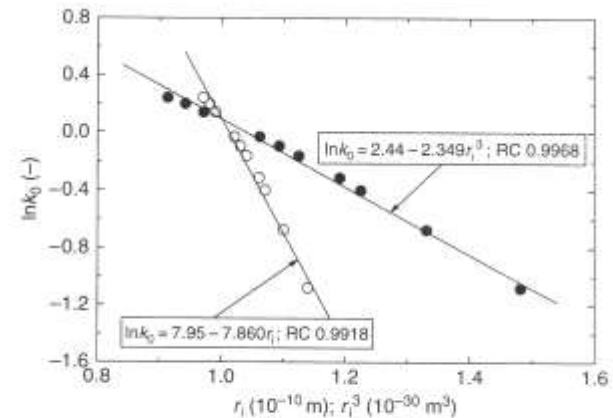
When change in free energy is due to mismatch ( $r_i - r_s$ ) of sizes of atoms/ions:

$$\ln k_0 = \ln k_0(0) - \frac{4\pi EN_A}{R_G T} \left( \frac{1}{2} r_s (r_i - r_s)^2 - \frac{1}{3} (r_i - r_s)^3 \right),$$

where  $E$  – Young's modulus.

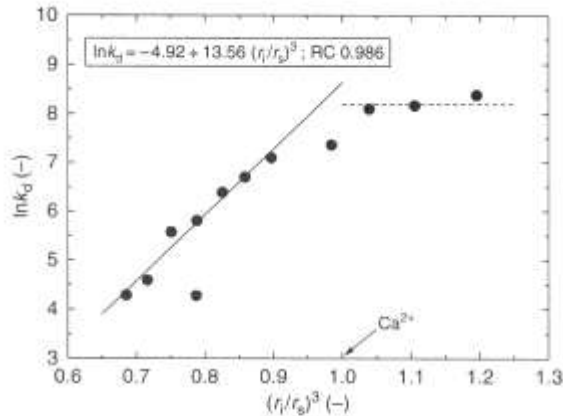


**Figure 9.5** Logarithm of equilibrium segregation coefficient  $k_0$  of various rare earths in cubic  $ZrO_2$  stabilized with  $Y_2O_3$  as a function of  $\frac{1}{2}r_s(r_i - r_s)^2 + \frac{1}{3}(r_i - r_s)^3$ . Data for  $Er^{3+}$ ,  $Sm^{3+}$ , and  $Nd^{3+}$  are experimental, whereas those for  $Lu^{3+}$  and  $Ce^{3+}$  are calculated from Equation (9.24). Adapted from Römer et al. (1994)

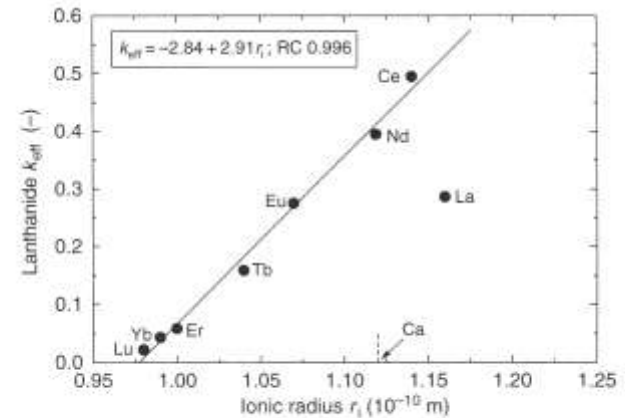


**Figure 9.6** Logarithm of equilibrium segregation coefficient  $k_0$  of various rare earths in cubic  $ZrO_2$  stabilized with  $Y_2O_3$  against additive cationic radii  $r_i$  and  $r_i^3$ . The cationic radii  $r_i$  and  $r_i^3$  are due to Shannon, with coordination number 8. Data from Römer et al. (1994)

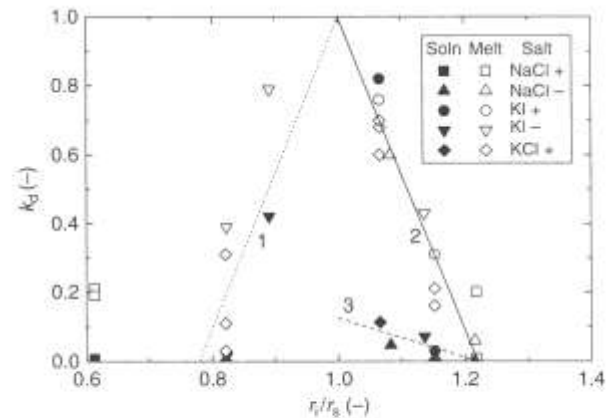
# Some more examples



**Figure 9.8** Logarithm of  $k_d$  for various trivalent rare earth metal ions in calcite as a function of  $(r_i/r_8)^3$ . The effective ionic radius, due to Shannon, is in six-fold coordination. The extremely deviating point for  $(r_i/r_8)^3 = 0.78$  was excluded while fitting the data. Data from Rimstidt et al. (1998)



**Figure 9.9** Plot of  $k_{gf}$  for various lanthanide ions in gypsum crystals against their radii  $r_i$ . Data from de Vreugd et al. (1994)



**Figure 9.10** Dependence of segregation coefficient  $k_d$  of cations and anions in different alkali metal halides grown from aqueous solutions and from the melt on their Shannon radii  $r_i$ , with coordination number 8 or 9. Data from Brice (1973). Additive cations and anions are denoted by + and -, respectively, in the inset

# Effective segregation coefficient

1) Bulk diffusion model of Burton et al. (1953):

$$k_{eff} = \frac{k_0}{k_0 + (1 - k_0) \exp(-R\delta / D)}, \quad (1)$$

where:  $\delta$  - thickness of diffusion layer,  
 $D$  – diffusion coefficient of impurity in the solution.

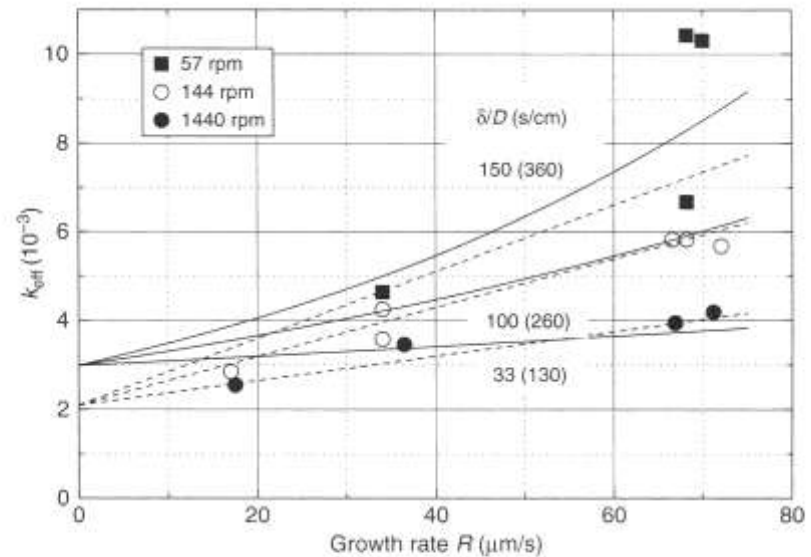
For  $k_0 \ll 1$

$$k_{eff} = k_0 \exp(R\delta / D) \quad (2)$$

From the plots

$\delta/D = 30 - 150$  s/m.

Since  $D = 10^{-12} - 10^{-9}$  cm<sup>2</sup>/s,  
 $\delta = 0.3 - 1.5$  nm.



**Figure 9.11** Dependence of segregation coefficient  $k_{eff}$  of Sb in Ge crystals on growth rate  $R$  for different stirring conditions. Solid curves were drawn according to the BPS Equation (9.26) due to Burton et al. (1953), and dashed lines are according to the linear dependence in Equation (9.28). The values of  $\delta/D$  for the linear dependence are given in parentheses. Adapted from Burton et al. (1953)

## 2) Approach involving diffusion-relaxation

Hall (1953), Kitamura and Sunagawa (1977), and Chernov (1984):

$$k_{eff} = k_0 + (k_{ads} - k_0) \exp(-R_i / R), \quad (1)$$

with

$$R_i = h / \tau$$

where:

$h$  – thickness of step on growing surface,

$\tau$  - time interval for the growth of successive

layers,

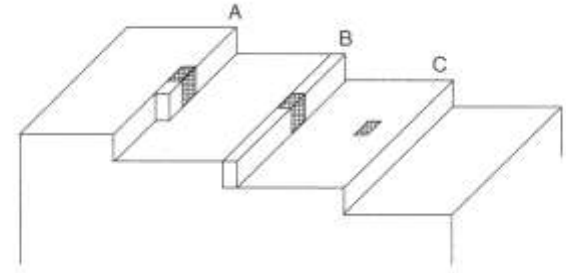
$k_{ads}$  – segregation coefficient of the impurity in the adsorption layer.

When  $k_0 \ll 1$ ,

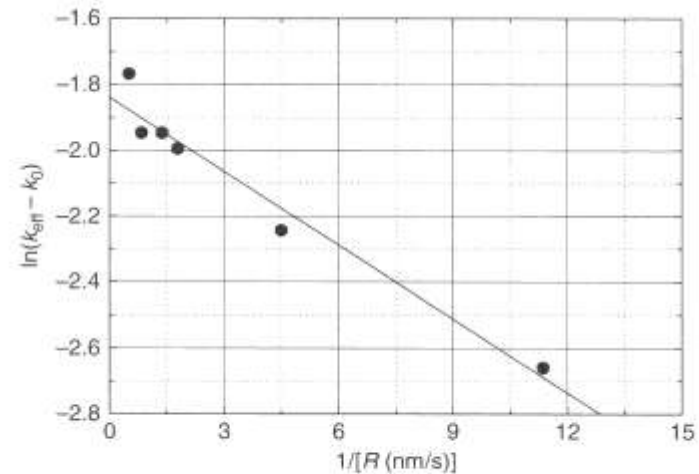
$$k_{eff} = k_{ads} \exp(-R_i / R), \quad (2)$$

and when  $R_i/R \ll 1$ ,

$$k_{eff} = k_{ads} - k_{ads} (R_i / R). \quad (3)$$



**Figure 9.12** Different positions of trapped impurity particles: (A) trapped in a kink, (B) trapped in a step ledge by solute particles from both sides, and (C) trapped in the surface terrace



**Figure 9.13** Plot of  $\ln(k_{eff} - k_0)$  of  $Pb^{2+}$  ions in  $BaNO_3$  crystals against  $1/R$ ; impurity concentration  $c_i$  in the solution about 10 mol%. Adapted from Tsuchiyama et al. (1981)

### 3) Approach based on statistical selection

Voronkov, Chernov (1967):

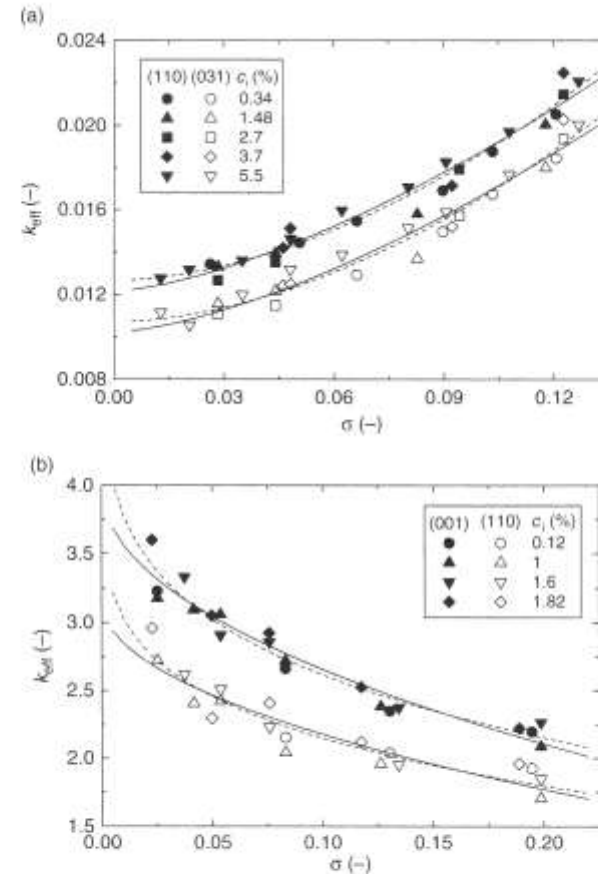
$$k_{eff} = \frac{k_0}{1 + \sigma / \sigma_{const}}, \quad (1)$$

where:  $\sigma_{const}$  – constant.

When  $\sigma / \sigma_{const} \ll 1$ ,

$$k_{eff} = k_0 - k_0 \sigma / \sigma_{const} \quad (2)$$

Natural statistical selection depends on kinetics of attachment and detachment of impurity particles at kinks in steps.



**Figure 9.15** Dependence of effective segregation coefficient  $k_{eff}$  of additive ions for two different faces of crystals grown from aqueous solutions on supersaturation  $\sigma$ : (a)  $\text{CrO}_4^{2-}$  ions in the (110) and (031) faces of  $\text{K}_2\text{SO}_4$  crystals and (b)  $\text{Ni}^{2+}$  ions in the (001) and (110) faces of  $\text{ZnK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  crystals. Curves were drawn according to Equation (9.43) with different values of  $n_2$ : (a)  $n_2 = -0.5$  (continuous curve) and  $-0.8$  (dashed curve), and (b)  $n_2 = 0.5$  (continuous curve) and  $0.8$  (dashed curve). Original data are from Zhmurova and Khaimov-Mal'kov (1970b). Adapted from Sangwal and Palczyńska (2000)

## 4) Approach based on surface adsorption

### Assumptions:

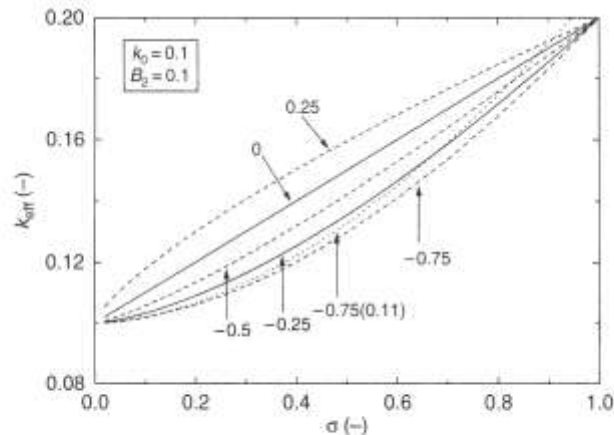
- 1) Impurity particles compete with particles of crystallizing substance.
- 2) Increase in supersaturation  $\sigma$  leads to increase in the density of kinks in steps.
- 3)  $k_{\text{eff}} = k_0 + f(\text{kink density})$   
 $= k_0 + f_{\text{kink}}(1-\theta)/\theta$  (1)

where:

$f_{\text{kink}}$  – fraction of kink sites on the surface of a crystal growing at supersaturation  $\sigma$ ;

$\theta$  - total surface coverage

$$(\theta = \theta_{\text{solute}} + \theta_{\text{imp}}).$$



**Figure 9.16** Illustrative plots of the dependence of  $k_{\text{eff}}$  of additive in an imaginary crystal on supersaturation  $\sigma$  predicted from Equation (9.43) for different values of  $n_2$  with constant  $B_2 > 0$ . This case represents  $k_0 < 1$ . Adapted from Sangwal and Pałczyńska (2000)

For Langmuir adsorption isotherm:

$$k_{\text{eff}} = k_0 + \frac{B_1 \sigma^{1-n_2}}{K_s c_s + K_L c_i} \quad (2)$$

$$\frac{1}{k_{\text{eff}} - k_0} = C_0 + C_1 c_i \quad (3)$$

For Freundlich adsorption isotherm

$$k_{\text{eff}} = k_0 + B_2 \sigma^{1-n_2} / c_i^m, \quad (4)$$

where:

$B_1, B_2, m, C_0$  and  $C_1$  – constants;

$K_s, K_i$  – Langmuir constants;

$n_2$  – a measure of barrier associated with the effect of supersaturation  $\sigma$ .

$$k_{\text{eff}} = k_0 + \frac{B_1 \sigma^{1-n_2}}{K_s c_s + K_L c_i} \quad (2)$$

$$k_{\text{eff}} = k_0 + B_2 \sigma^{1-n_2} / c_i^m, \quad (4)$$

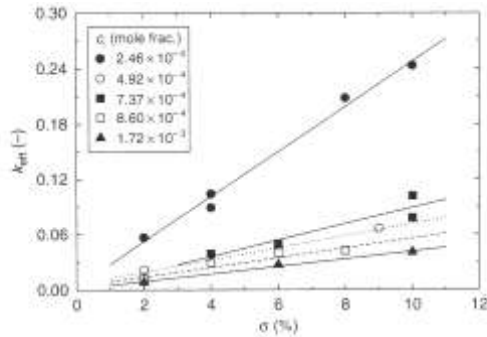


Figure 9.17 Segregation coefficient  $k_{\text{eff}}$  of  $\text{Cu}^{2+}$  ions in AO crystals as a function of supersaturation  $\sigma$  for different impurity concentrations  $c_i$ . Reproduced from E. Mielniczek-Brzóska, K. Gołzak-Koćwin, and K. Sangwal, J. Cryst. Growth **272**, 532. Copyright (2000), with permission from Elsevier

AO – ammonium oxalate monohydrate

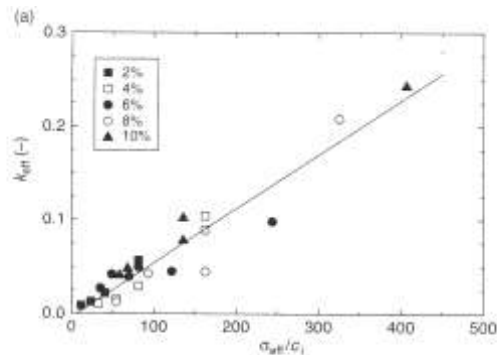


Figure 9.21 Plots of  $k_{\text{eff}}$  for (a)  $\text{Cu}^{2+}$  and (b)  $\text{Fe}^{2+}$  in AO crystals against  $\sigma_{\text{eff}}/c_i^m$ . Reproduced from K. Sangwal, E. Mielniczek-Brzóska, and J. Borc, J. Cryst. Growth **244**, 183. Copyright (2002), with permission from Elsevier

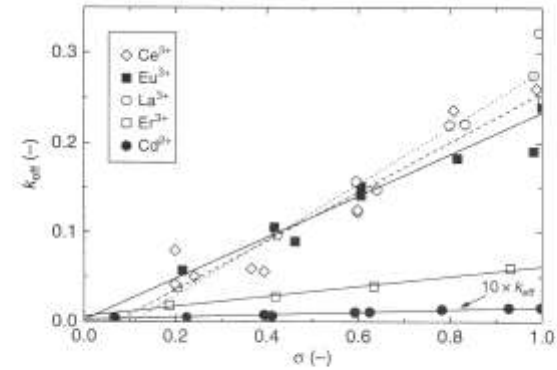
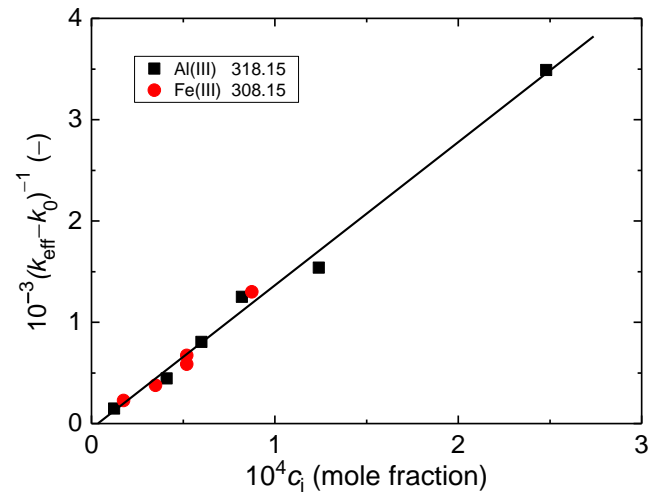


Figure 9.18 Segregation coefficient  $k_{\text{eff}}$  of various lanthanides in gypsum crystals as a function of supersaturation  $\sigma$ . Impurity concentration:  $3 \times 10^{-4} \text{ M}$  lanthanides and  $4.4 \times 10^{-4} \text{ M}$   $\text{Ca}^{2+}$ . Adapted from de Vreugd et al. (1994)

$$\frac{1}{k_{\text{eff}} - k_0} = C_0 + C_1 c_i \quad (3)$$



ADP – ammonium dihydrogen phosphate; antisolvent crystallization; unpublished results



# Relationship between $k_{\text{eff}}$ and face growth rate $R$

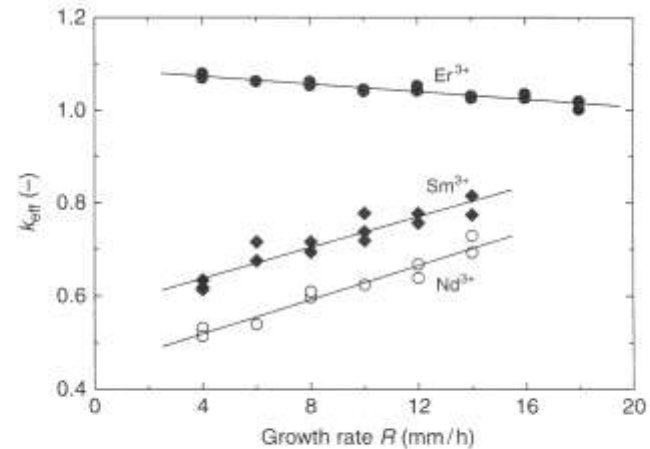
From the relation

$$R \approx A(\sigma - \sigma_c)^n,$$

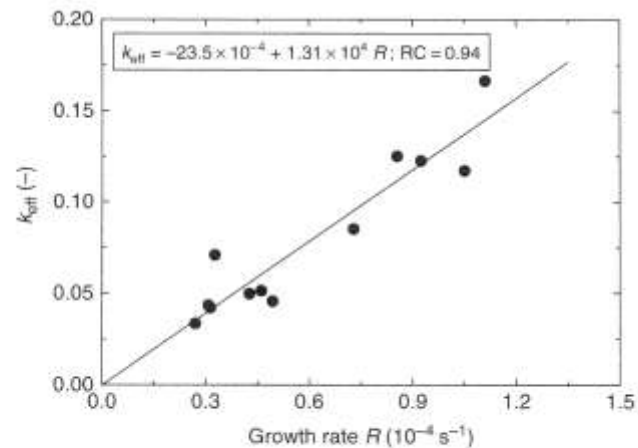
$$k_{\text{eff}} = k_0 + B_2 \sigma^{1-n_2} / c_i^m,$$

one obtains

$$k_{\text{eff}} = \left( k_0 + \frac{B_2 \sigma_c}{c_i^m} \right) + \frac{B_2}{A^{1/n} c_i^m} R^{1/n}.$$



**Figure 9.22** Dependence of effective segregation coefficient  $k_{\text{eff}}$  of three rare earth ions in cubic zirconium dioxide crystals on growth rate  $R$ . The crystals were grown by the skull melting technique. Data from Römer et al. (1994)



**Figure 9.23** Dependence of  $k_{\text{eff}}$  of  $\text{La}^{3+}$  ions in gypsum crystals on growth rate  $R$ . Original data from de Vreugd et al. (1994)

# Threshold supersaturation for capture of impurities during growth

From the plots  $k_{\text{eff}}(\sigma)$ , one obtains  $\sigma_0$ :

$$k_{\text{eff}} = p(\sigma - \sigma_0).$$

From the theory of inhibition of face growth rate by impurity, we have the dependence:

$$\frac{1}{\sigma^*} = \frac{1}{\sigma_1} \left( 1 + \frac{1}{Kc_i} \right),$$

where:  $\sigma_1$  – constant,  $K$  – Langmuir constant.

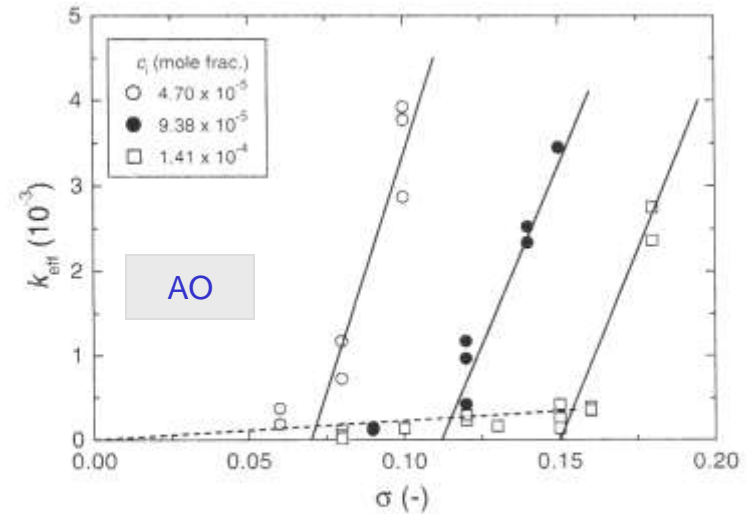
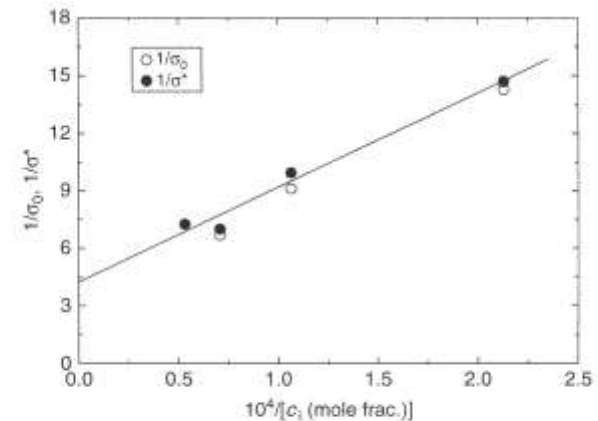


Fig. 1. Plots of  $k_{\text{eff}}$  of Mn(II) ions against  $\sigma$  for different  $c_i$ . Note two distinct linear dependences in the ranges of  $k_{\text{eff}} < 5 \times 10^{-4}$  and  $> 5 \times 10^{-4}$ .



**Figure 9.26** Dependence of  $1/\sigma_0$  and  $1/\sigma^*$  on  $1/c_i$  of  $\text{Mn}^{2+}$  impurity according to Equation (9.53). The plot was drawn for  $\sigma^*(c_i)$  data. Reproduced from K. Sangwal and E. Mielniczek-Brzóska, J. Cryst. Growth **257**, 185. Copyright (2003), with permission from Elsevier

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