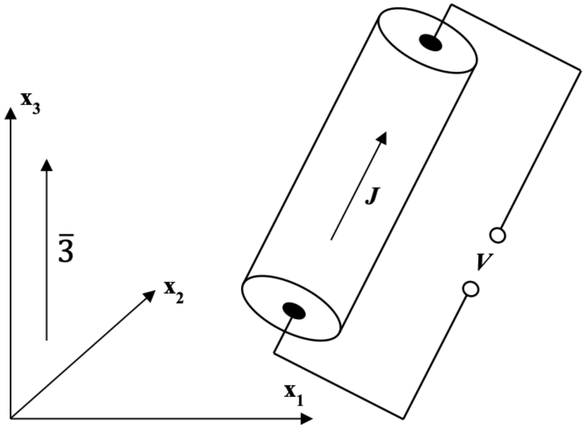
Comments: exercise 10-1



(see Symmetry Tables):

$$\tau = \begin{pmatrix} \tau_{11} & 0 & 0 \\ 0 & \tau_{11} & 0 \\ 0 & 0 & \tau_{33} \end{pmatrix}$$

$$\begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} = \begin{pmatrix} \tau_{11} & 0 & 0 \\ 0 & \tau_{11} & 0 \\ 0 & 0 & \tau_{33} \end{pmatrix} \begin{pmatrix} E_1 \\ E_2 \\ E_3 \end{pmatrix} = \begin{pmatrix} \tau_{11}E_1 \\ \tau_{11}E_2 \\ \tau_{33}E_3 \end{pmatrix}$$

In case where the vectors $\vec{J}$ and $\vec{E}$ are not parallel, i.e., where the electric field is not directed along the axis of the beam, a transverse voltage appears in the bar.

transverse voltage will not appear in the system:

i) When the electric field is directed along the principal x_3 axis, i.e. $\vec{E} = (0,0,E_3)$:

$$\vec{J} = \begin{pmatrix} 0 \\ 0 \\ \tau_{33}E_3 \end{pmatrix} = \tau_{33} \cdot \begin{pmatrix} 0 \\ 0 \\ E_3 \end{pmatrix} = \tau_{33}\vec{E}$$

ii) When the electric field is directed along any direction perpendicular to the x_3 axis, i.e. $\vec{E} = (E_1, E_2, 0)$:

$$\vec{J} = \begin{pmatrix} \tau_{11}E_1 \\ \tau_{11}E_2 \\ 0 \end{pmatrix} = \tau_{11} \cdot \begin{pmatrix} E_1 \\ E_2 \\ 0 \end{pmatrix} = \tau_{11}\vec{E}$$

Comments: exercise 10-2

$BaTiO_3$ in $4mm$ phase

The impact of mechanical conditions on the heat capacity is investigated. The parallelepiped $BaTiO_3$ sample in its tetragonal phase $4mm$ (4-fold symmetry axis is directed along the x_3 axis) is used for heat capacity measurements. The sample faces are directed along (100), (010), and (001) crystallographic directions. The faces (001) are covered with electrodes and short-circuited, the external electric field is always absent.

In measurement **(a)**, the sample is kept mechanically free.

In measurement **(b)**, the sample is kept mechanically free in x_1 and x_2 directions, while the motion in x_3 direction is blocked.

Find the relative difference between heat capacities obtained in the measurements **(a)** and **(b)** $\frac{C_{(b)}-C_{(a)}}{C_{(a)}}$. Can the impact of mechanical conditions on the heat capacity be neglected?

$$C_{(\mathrm{exp})} = \frac{\delta Q}{\delta T}$$

Comments: exercise 10-2

$$C_{(\exp)} = \frac{\delta Q}{\delta T}$$

$$\varepsilon_i = s_{ij}\sigma_j + \alpha_i \delta T,$$

$$\delta Q = T\alpha_i\sigma_i + C\delta T.$$

(a) $$C_{(a)} = \frac{\delta Q}{\delta T} = C.$$

(b) $\sigma_1 = \sigma_2 = \sigma_4 = \sigma_5 = \sigma_6 = 0$, and $\sigma_3 \neq 0$. The constitutive equation for δQ is simplified into:

$$\delta Q = T\alpha_3\sigma_3 + C\delta T.$$

To find σ_3, we use the constitutive equation for $\varepsilon_3 = 0$, which must not change during the measurement:

$$\varepsilon_3 = s_{33}\sigma_3 + \alpha_3\delta T = 0 \quad \Rightarrow \quad \sigma_3 = -\frac{\alpha_3}{s_{33}}\delta T,$$

$$\delta Q = T\alpha_3\sigma_3 + C\delta T = \left(C - T\frac{\alpha_3^2}{s_{33}}\right)\delta T,$$

$$C_{(b)} = \frac{\delta Q}{\delta T} = C - T\frac{\alpha_3^2}{s_{33}}.$$

Thus, in **(a)** and **(b)** the measured heat capacities are different. Specifically,

$$\frac{C_{(b)} - C_{(a)}}{C_{(a)}} = -\frac{T\alpha_3^2}{Cs_{33}} = -\frac{300 \cdot (3.5 \times 10^{-5})^2}{2.42 \times 10^6 \cdot 15.7 \times 10^{-12}} = -0.0097$$

<1%

Lecture 11 (week 11: 5-6 May 2025)

- Electric conduction – final part
- Point defects in crystals and ceramics
  - Introduction to the defects, point defects in crystals and ceramics
  - Formal description of defects, Kröger-Vink notation
  - Law of Mass action for defects
  - Equilibrium equations for point defects
  - prediction of defect concentration vs processing parameters
  - Ionics: applications

A good textbook: M.W. Barsoum – Fundamentals of Ceramics
IoP publishing Ltd, 2003

Models of electrical conductivity

- Model of Drude (1902): electrons represented with spheres which follow classical mechanics

- Hopping conduction in insulators/semoconductors

- Energy band model (1935): electrons are quantum objects interacting with the medium but do not affect the medium or other electrons (passive electrons)

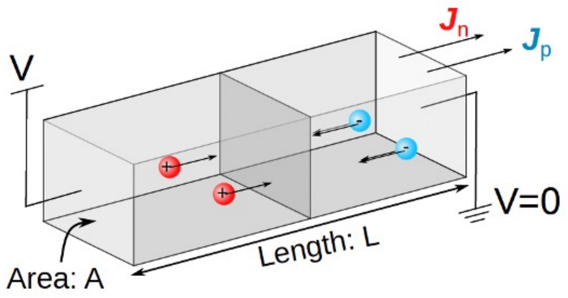
- BCS model (Bardeen, Cooper and Schrieffer;1962): electrons are quantum objects which interact with the environment (medium in which they move) and with other electrons.

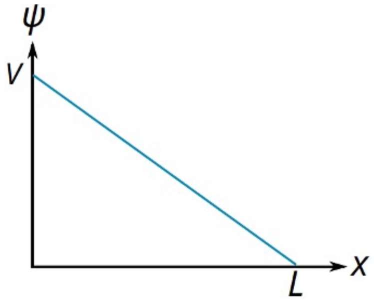
- Ionic conductivity

- Interface-controlled transport (Schottky conducrion, tunneling)
- ...

Electrical conduction: Drude model

- a widely used classical model of charge transport
  Works well for describing conductivity in semiconductors & metals



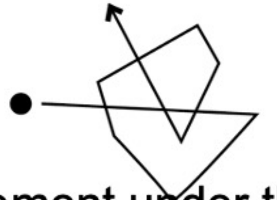


Constant voltage V

Uniform electric field E = V/L

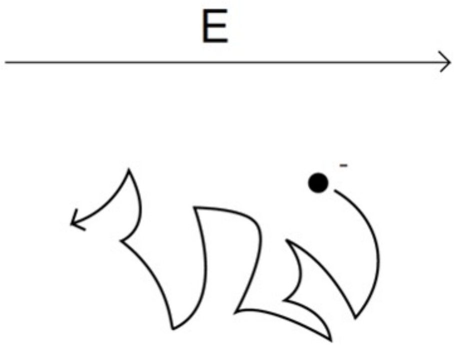
stochastic, time between scuttering events τ_c, $\lambda = v_{th}\tau_c$
mean free path λ depends on the thermal velocity

- Types of movement:
  - Thermal:



  - Drift: movement under the external electric field

Electrical conduction: Drude model

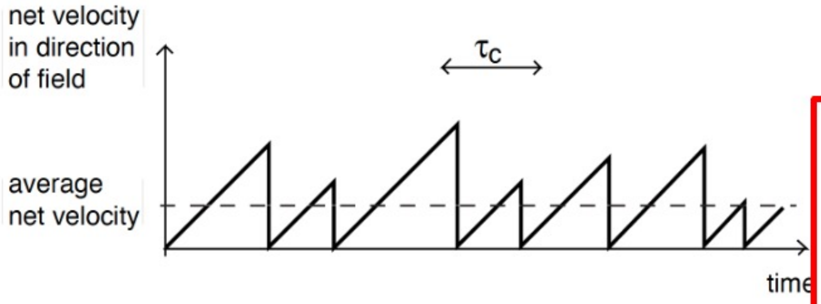


$$E \equiv electric\ field\ [V/cm]$$

$$F = \pm qE$$ *The net force acting on charge carrier*

$$v(t) = at = -\frac{qE}{m_n}t$$ *For electrons*

$$v(t) = \frac{qE}{m_p}t$$ *For holes (holes also have effective mass)*



Drift velocity:

$$\overline{v} = v_d = \pm\frac{qE}{2m_{n,p}}\tau_c = \pm\frac{q\tau_c}{2m_{n,p}}E$$

$$v_{dn} = -\mu_n E$$

$$v_{dp} = \mu_p E$$

$$\mu_{n,p} = \frac{q\tau_c}{2m_{n,p}} \equiv mobility\ [cm^2/V \cdot s]$$

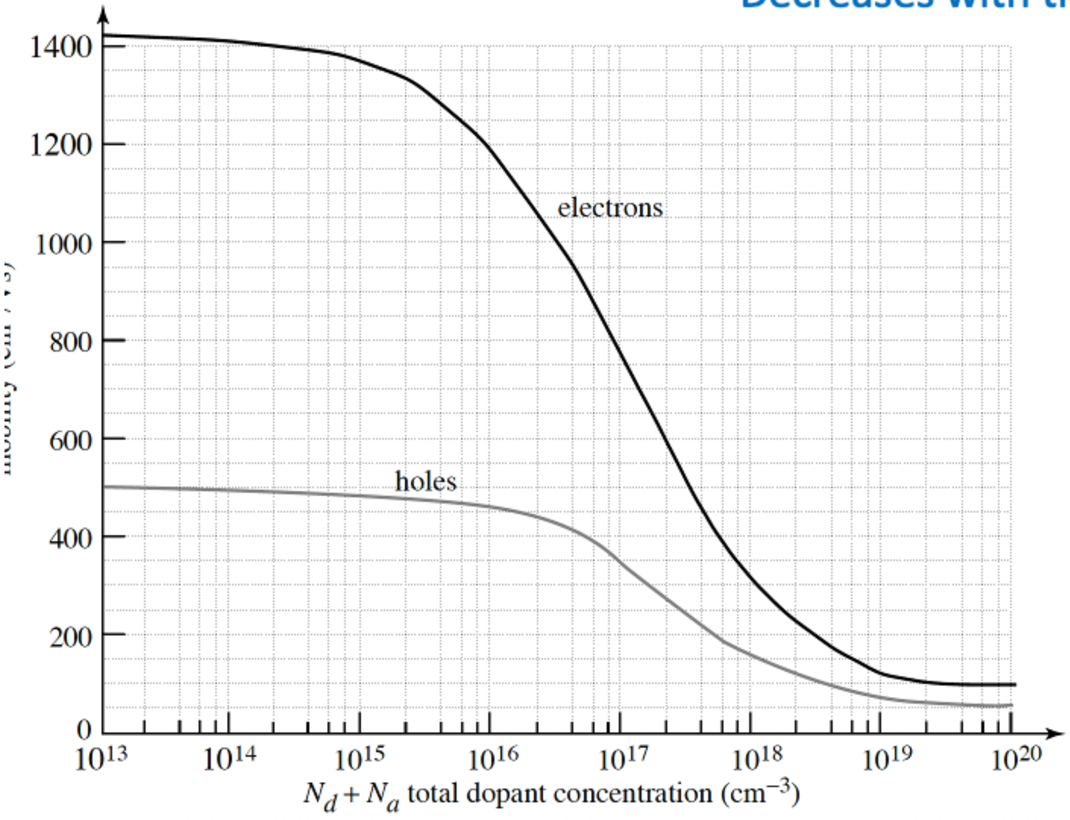
Drude model – mobility for electrons/holes in Si

$$\boxed{\begin{aligned} v_{dn} &= -\mu_n E \\ v_{dp} &= \mu_p E \end{aligned}}$$

$$\mu_{n,p} = \frac{q\tau_c}{2m_{n,p}} \equiv mobility\ [cm^2/V \cdot s]$$

Mobility is measure of *ease* of carrier drift

- Increases with longer time between collisions
- Decreases with the higher effective mass



Mobility for Si at 300K

mobility depends on doping

Holes are “heavier” than electrons

$$\tau_c \simeq 10^{-14} \sim 10^{-13}\ s \quad << 1\text{ps}$$

$$v_{th} \simeq 10^7\ cm/s$$

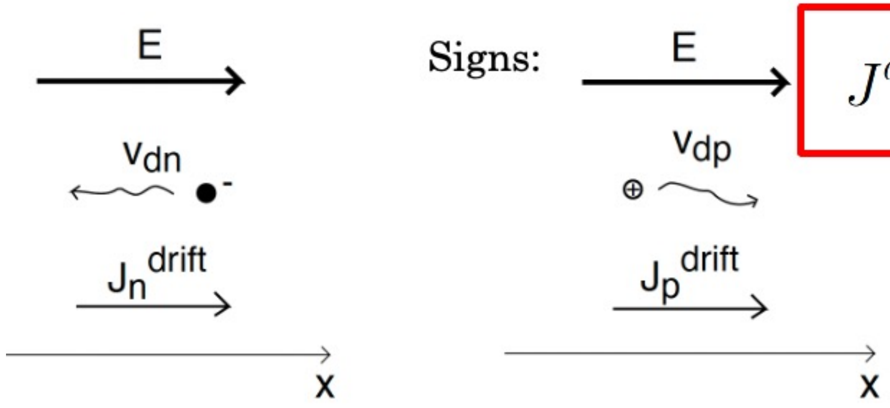
$$\Rightarrow \lambda\ \simeq 1 \sim 10\ nm$$

Drude model – mobility for electrons/holes in Si

Drift current density:

- *∝ carrier drift velocity*
- *∝ carrier concentration*
- *∝ carrier charge*

$$\boxed{\begin{aligned} J_n^{drift} &= -qnv_{dn} = qn\mu_n E \\ J_p^{drift} &= qpv_{dp} = qp\mu_p E \end{aligned}}$$



$$\boxed{J^{drift} = J_n^{drift} + J_p^{drift} = q(n\mu_n + p\mu_p)E}$$

Ohm's law:

$$J = \sigma E = \frac{E}{\rho}$$

$$\sigma \;\equiv conductivity\;[\Omega^{-1} \cdot cm^{-1}]$$

$$\rho \;\equiv resistiviy\;[\Omega \cdot cm]$$

$$\boxed{\rho = \frac{1}{\sigma} = \frac{1}{q(n\mu_n + p\mu_p)}}$$

Drude model for conductivity – simple relations, numbers

Ohm's law: $\boldsymbol{J} = \boldsymbol{\sigma} \boldsymbol{E}$ where $\boldsymbol{J}$ is the current density, E is the electric field and σ is the conductivity. In microscopic terms,

$\sigma = nq\mu$ where μ is mobility of charge carriers.

$$\overline{v} = v_d = \pm \frac{qE}{2m_{n,p}} \tau_c = \pm \frac{q\tau_c}{2m_{n,p}} E \qquad \mu_{n,p} = \frac{q\tau_c}{2m_{n,p}} \equiv mobility\ [cm^2/V \cdot s]$$

Si at 300K: what is the mean free path?

$$\tau_c \simeq 10^{-14} \sim 10^{-13}\ s \quad << 1\text{ps}$$

$$v_{th} \simeq 10^7\ cm/s$$

$$\Rightarrow \lambda \ \simeq 1 \sim 10\ nm$$

Electron mobility at 300K:
Si (300K) – about 1000 cm^2/V s
Metals like Cu, Ag – 30-50 cm^2/V s
GaAs - 10000 cm^2/V s

Ionic conducton - <1 cm^2/V s
GaAs/AlGaAs 2D gas:
Mobility below 4K can be 10^6-10^7 cm^2/V s

Limitations of the classic theory (Drude model)

- The Drude model is a useful and important tool for understanding/describing charge transport, however, it has limitations
- Electrons are considered classic particles (like a gas), and their wave nature is not taken into account – problems at short distances
- Ballistic transport (small number of scattering events) is described differently
- Transport through barriers e.g. tunneling is described differently
- Transport at high electric fields may not be accurately described with Drud etheory
- The concept of electron/hole mobility is widely used in semiconductor device physics, very often, the mobility is considered as an empirical parameter (without any relation with electron/hole mass)

Ohmic conductors and resistors

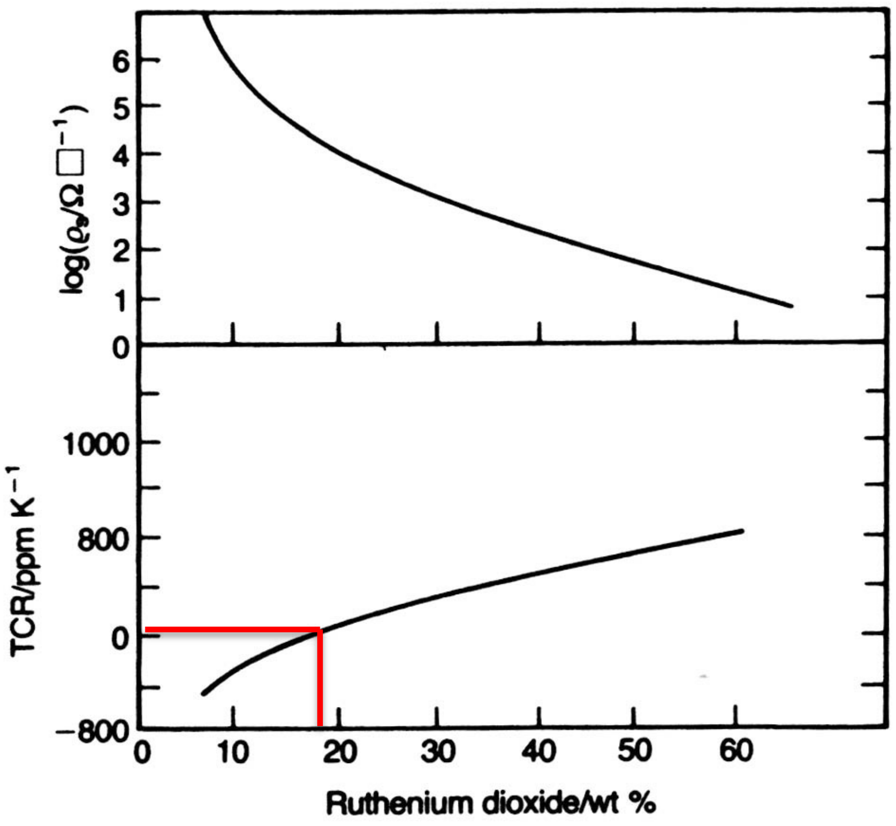
In applications in electronics there is a great demand for ohmic resistors with a low thermal coefficient of resistivity..

Typically, the resistors should have resistance on the order of 10^3-10^8 Ohm. The conductors with good properties usually exhibit too high conductivity (10^{-6} Ohm m) for fabrication of simple resistances.

10^5 Ohm over 100 mm with a mat. with resistance of 10^{-6} Ohm m requires a cross section with 10^{-12} m^2, which represents a major technological challenge..

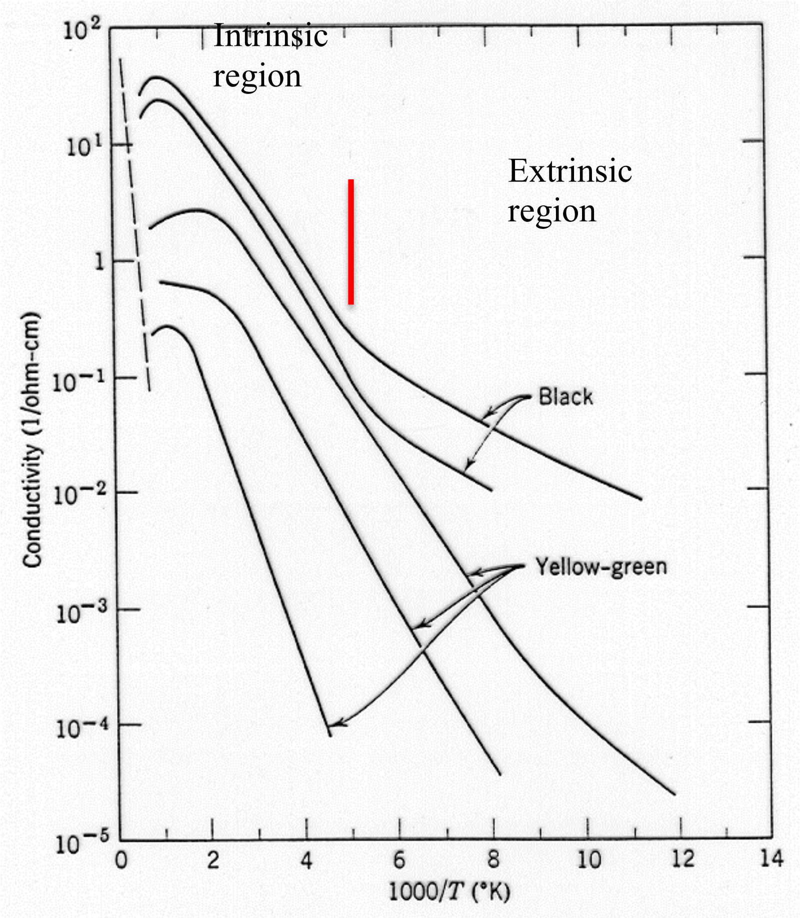
An economical and viable approach: use a conductive powder (RuO_2, PdO, ..) within a glassy resistive phase (e.g., 52PbO-35SiO2-10Bi2O3 -3Al2O3).

The first component behaves as a metal and exhibits a positive thermal coeff. of the resistivity (TCR). The second component is resistive and exhibits a negative TCR. By choosing the mixture conveniently, it is possible to modify the resistivity and its temperature coefficient..



For T-sensitive applications, pay attention to the specs of the resistor (like capacitors)

Resistors (doped SiC) for heating elements



Conductivity-temperature characteristics
of differently doped SiC

Dopants: B, Al, N

High strength, good thermal shock resistance at high temperatures (up to 1600° C)

Heat generation by Joule heating->
Resistance should not be too low.
(in SiC 0.01 to 1 Ohm-m

Electrical conductivity of oxide materials varies over many orders of

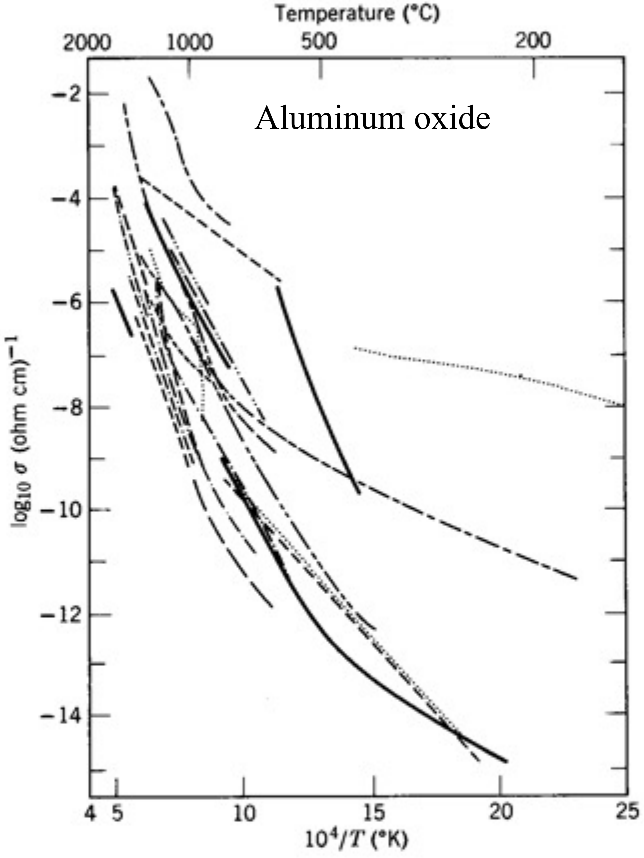


Fig. 17.38. Reported literature data for the electrical conductivity of aluminum oxide. From A. A. Bauer and J. L. Bates, *Battelle Mem. Inst. Rept.*, 1930, July 31, 1974.

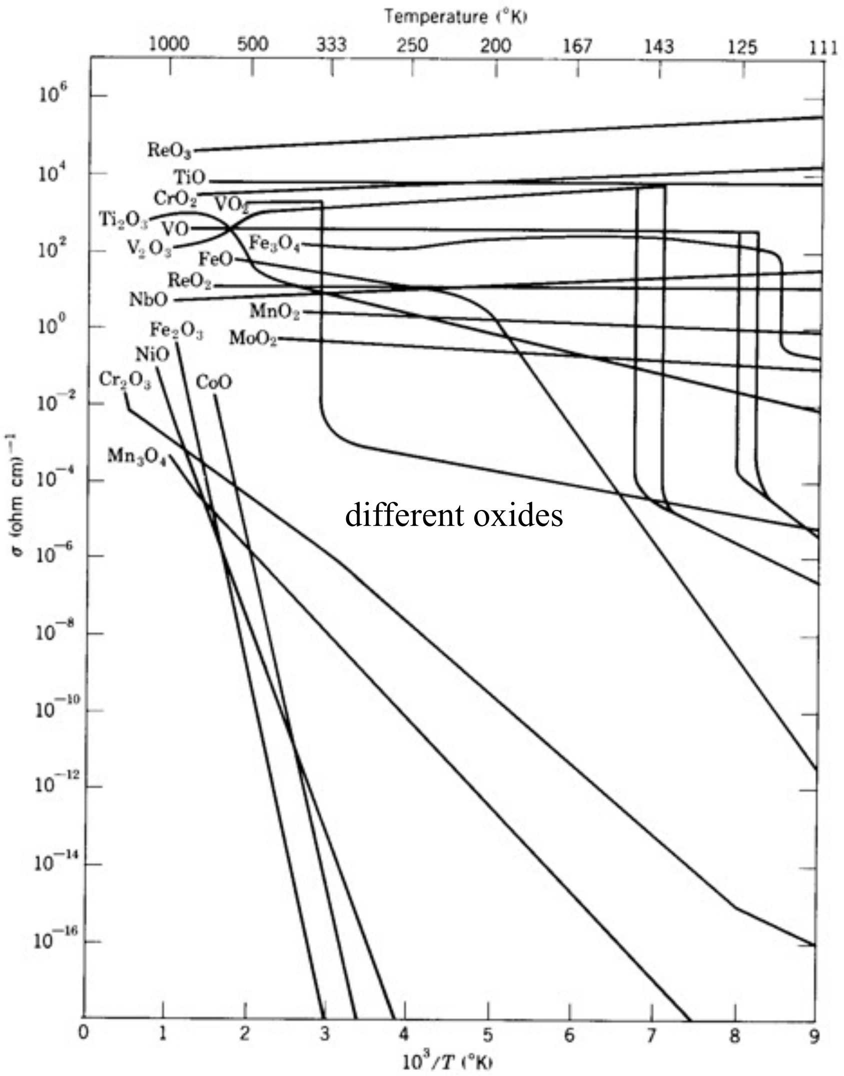


Fig. 17.11. Temperature dependence of the electrical conductivity of several electronically conducting oxides. Courtesy D. Adler.

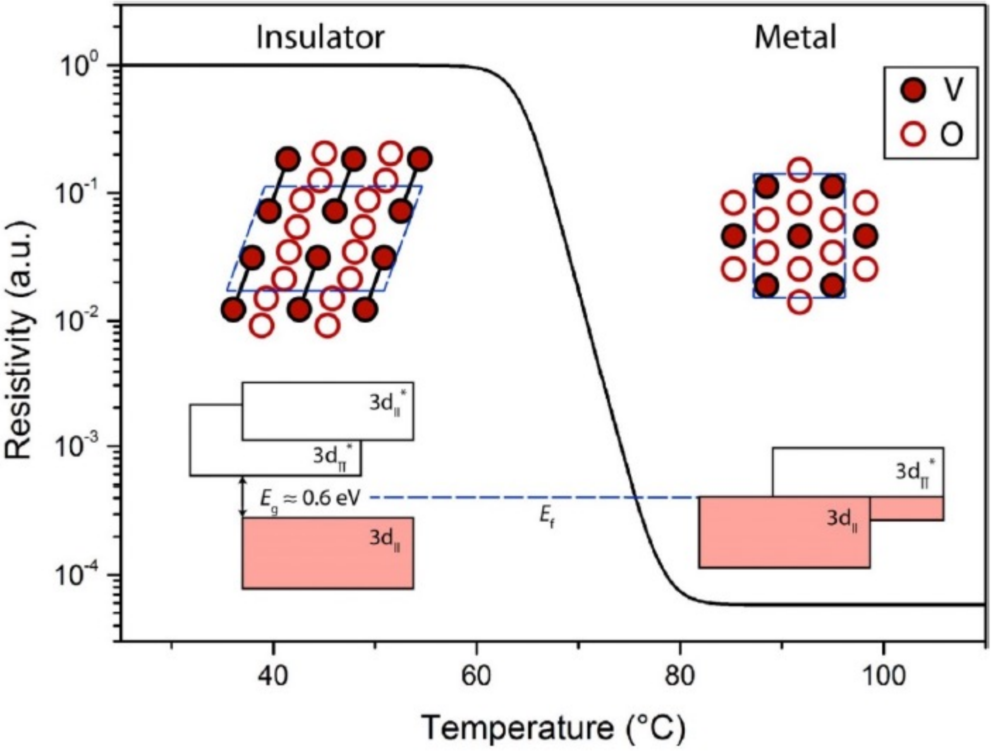
Arrhenius plots are commonly used because many mechanisms imply ***$I=A \exp(-E_A/kT)$***
Therefore plotting ***I*** (log scale) vs 1/T (or often 1000/T) makes sense

An abrupt change of the I-V or I-T characteristics signals a change of mechanism, a jump may signal a phase transition

IMT (Insulator-Metal Transition) in vanadium dioxide – VO_2

- Vanadium dioxide (VO_2) undergoes a structural phase transition at ~68 °C accompanied by a steep decrease in resistivity.
- The monoclicic phase presents a bandgap ~0.6 eV.
- The tetragonal phase presents metallic behavior.

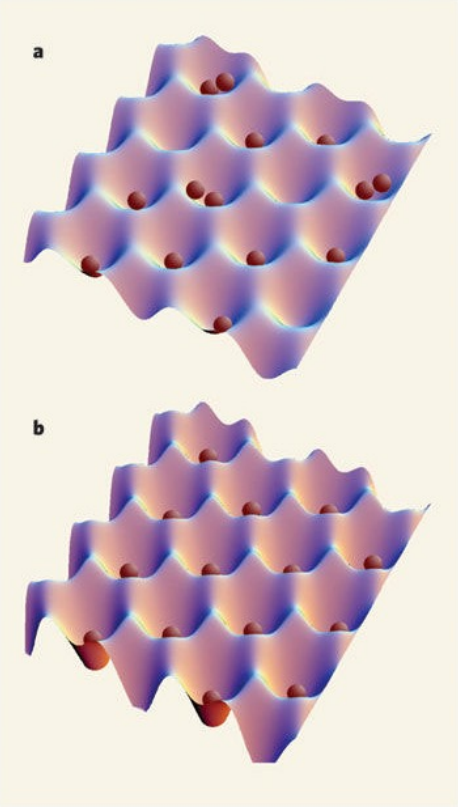
How to exploit this behavior for integrated electronic sensing and computational functions?



IMT in VO_2 - Mott-type transition (localization)

Exception to band theory

- Materials that **owe their insulating nature to correlations in the motions of different electrons**. These correlations arise from the classical Coulomb repulsion between charge particles.
- Surfaces of semiconductors: electrons are effectively confined to two dimensions.

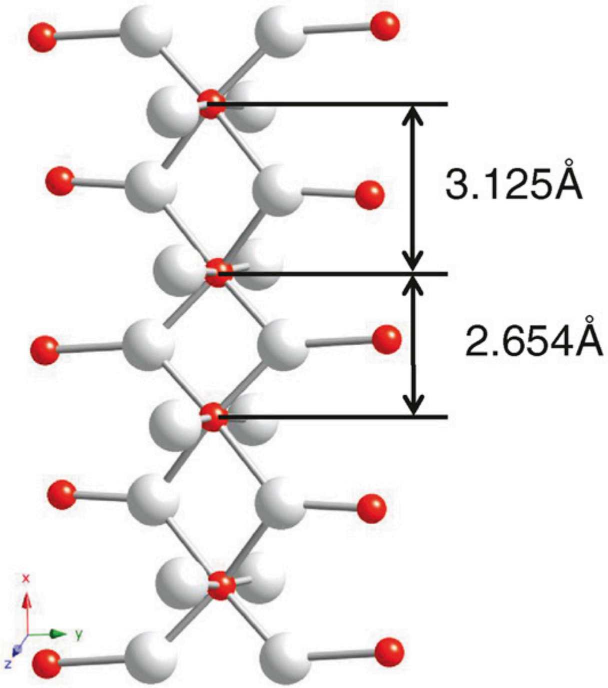


If the confining potential has deeper wells, electrons find it harder to delocalize and so do not conduct — despite what the band theory of solids predicts.

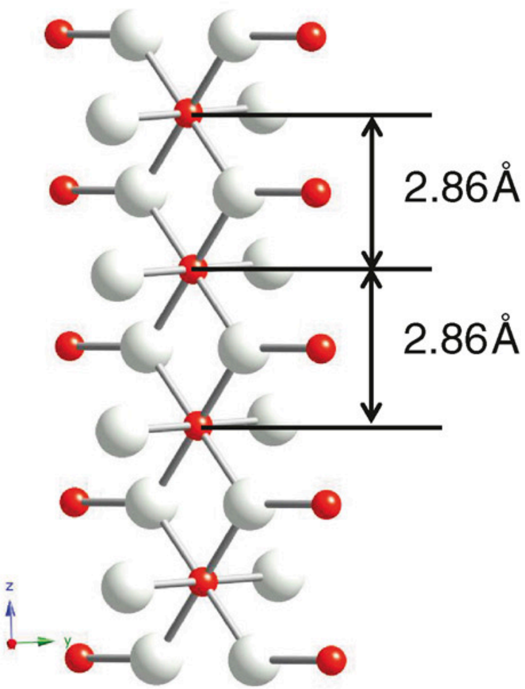
When is a metal not a metal?
Steven C. Erwin, Nature, Vol. 441, 2006.

IMT in VO_2 - insight into the structural transition

Semiconductor monoclinic phase



Rutile metallic phase

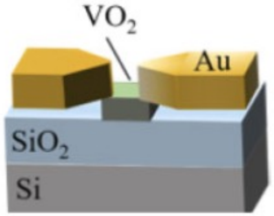


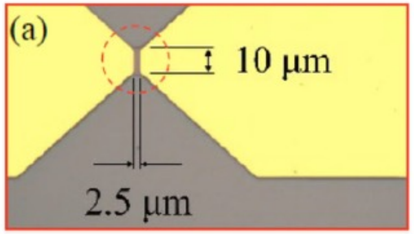
Structural change is associated with IMT:

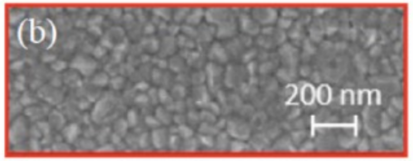
- VO2 – one remaining electron from V is available for conduction
- Room temperature - M-phase (which can be regarded as distorted R-phase. Short and long separation distances between V-atoms are alternated. Because of the rather long distances electrons are localized
- At 68C the lattice undergoes a transition to R-phase. The distances become equal and are short enough for the electronic orbitals to overlap

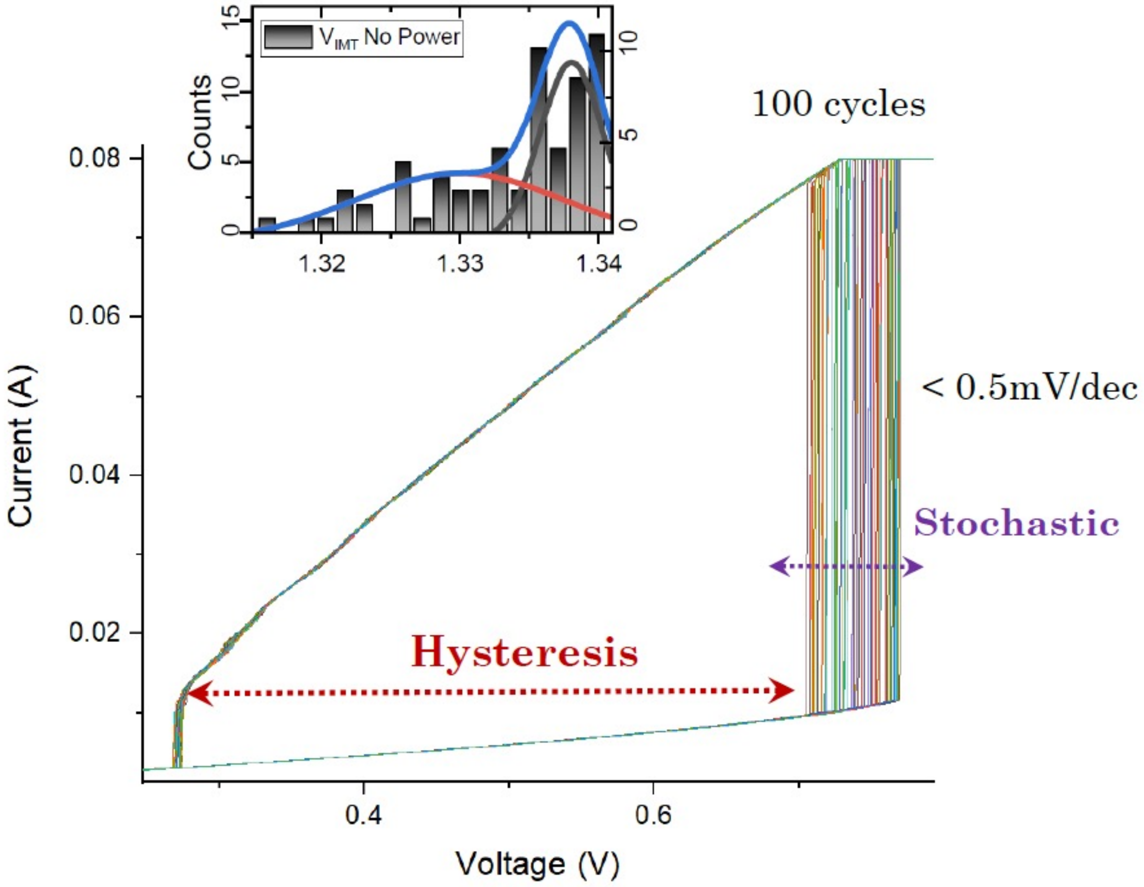
IMT in VO_2 – can be switched by current

- Highly correlated oxide: vanadium dioxide
- IMT transition supersensitive to external stimuli (!)









IMT in VO_2 – potential for applications

Electronic applications:

- Switches (very high speed of switching – can be sub-ps range !)
- radio-frequency devices (filters , phase shifters)
- memories
- New logic concepts (neuromorphic computing)
- sensors (gas, IR – high sensitivity to heat)
- usable in the from of ceramic films

Civil engineering:

- smart windows (glass gets less transparent upon heating)

Tuning of properties: phase transition can be shifted up/down by doping

- e.g. for electronic applications transition near 70° is not ideal. Above 90° is much better (avoids spontaneous transition due to the circuit heating) – Ge-doping helps increasing IMT temperature

Ionic conduction

Electrolyte conducts electricity by movement of ions.

Many electrolytes are liquid solutions or salts in the state of melting.

However, there are solid-state electrolytes, such as some glasses and crystalline materials.

Such materials are called:

Solid Electrolytes or

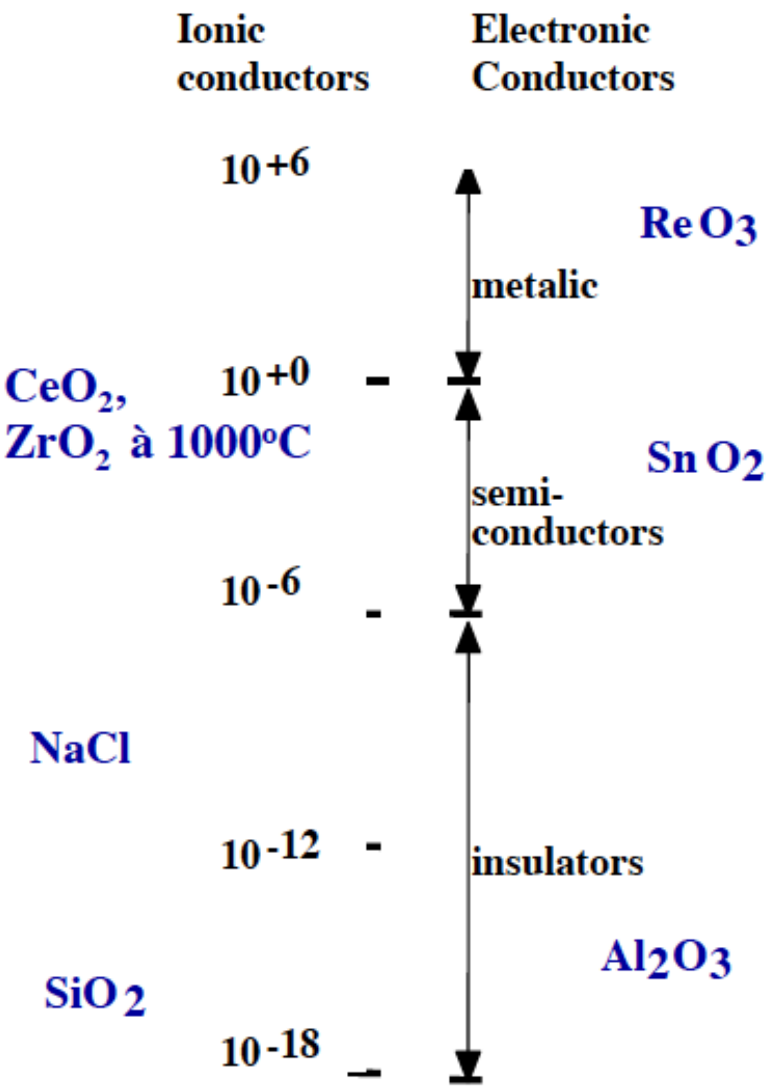
Fast Ion Conductors or

Super ionic Conductors…

Ionic vs. electronic conductors

Comparison of properties of ionic conductors and conventional electronic conductors (metals).

Metals:
Conductivity σ from 10 to 10+5 (Ωcm)-1
Electrons are responsible for charge transport
σ decreases with increasing T (collisions with phonons)
Semiconductors:
Conductivity σ from 10^{-6} to 10+0(Ωcm)-1
Electrolytic solids:
Conductivity σ from 10 $^{-3}$ to 10 (Ωcm)-1
Ions responsible for charge transport
σ increases with increasing T (activation of transport)



Ionic conductors

Electronic Conductors

10^{+6}

ReO_3

metalic

CeO_2, ZrO_2 à 1000°C

10^{+0}

SnO_2

semi-conductors

10^{-6}

NaCl

10^{-12}

insulators

Al_2O_3

SiO_2

10^{-18}

Ionic conductors

- Liquid electrolytes at ambient T ≈ 1 $(\Omega\text{-cm})^{-1}$
- ß-Alumina (20° -200° C) ≈ 10^{-1}-10^{-2} $(\Omega\text{-cm})^{-1}$
- Usual ionic materials ≈10^{-10} $(\Omega\text{-cm})^{-1}$
- ZrO_2-Y_2O_3 (1000° C) ≈10^{-1} $(\Omega\text{-cm})^{-1}$

Solid ionic conductors (due to structural disorder and defects)

1. Halides (Cl ...) et chalcogenides (S ...) (disordered cations)

AgI, Na_2S $KAg_4I_5Ag_2S$ (sublattice is conducting), CuI, Ag_3SBr, $CsAg_4I_5$

2. ß-Alumina (A_2O x nAl_2O_3) (mobile monovalent A cations, e.g., A=Na, K, Ag, Li (small, high mobility)

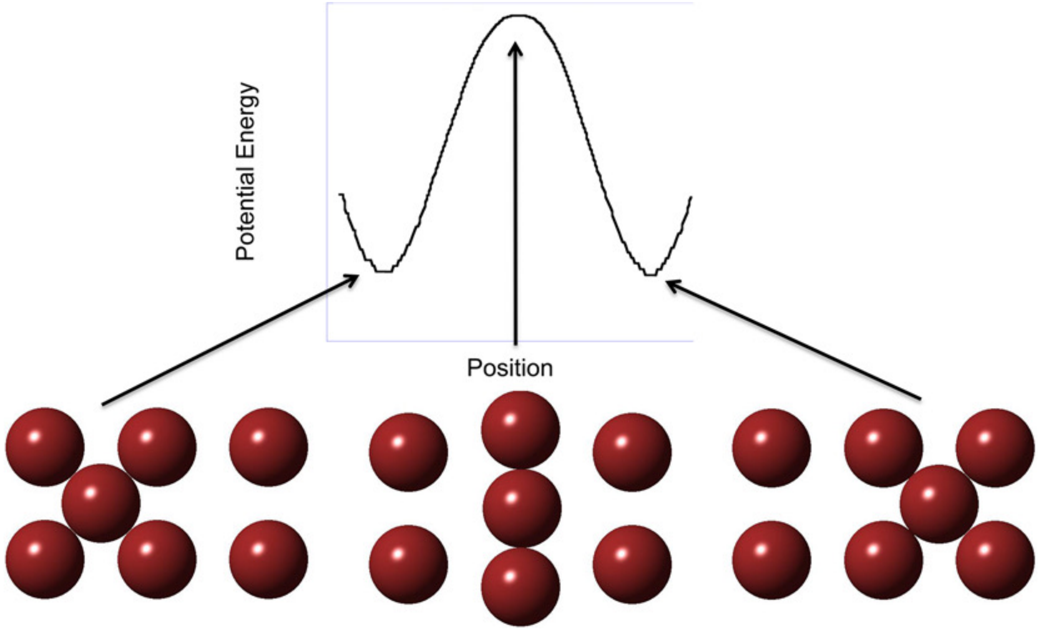
n= 5….11 e.g., Na_2O x $11Al_2O_3$ ($NaAl_{11}O_{17}$)

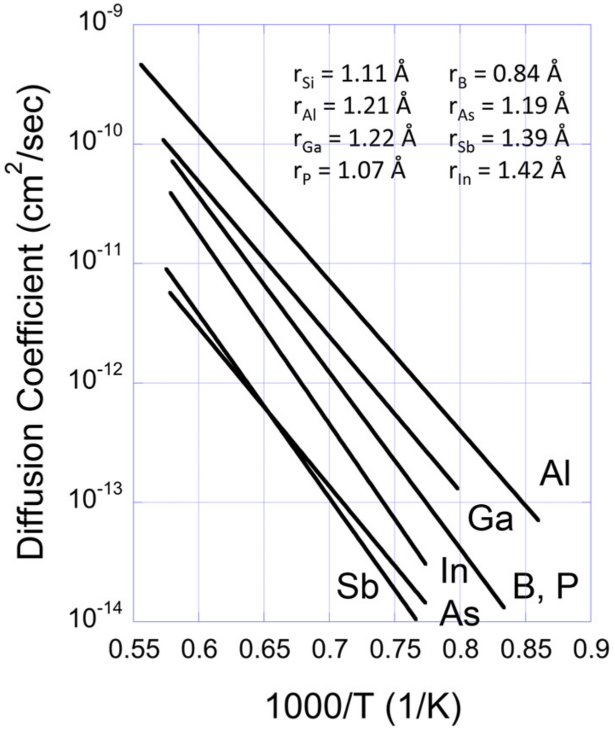
3. Oxides with O-vacancies stabilised by doping

$CaOxAO_2$, A= Zr, Hf, Th, Ce... (Fluorite: $Zr_{0.95}{}^{+4}Ca_{0.05}{}^{+2}O_{1.95}{}^{-2}$)

$M_2O_3xZrO_2$ M=La, Sm, Y, Yb, Sc...

Thermally-activated ionic transport





Potential energy vs position showing the barrier associated with squeezing atoms through interstices

$$\sigma(T) = \sigma_0 \, exp \, (E_a /kT)$$

Diffusion coefficients for various atoms in silicon: the diffusion is thermally activated

Bigger covalent radii = lower diffusion

Description of ionic conductivity

What influences motion of ions:

- **Diffusion due to chemical gradient and thermal activation**
- **Electrical field**

- **Diffusion, Fick's law:** $$j_D(x) = -D\frac{\partial c(x)}{\partial x}$$
- **Drift current:** $$j_{drift} = \sigma E$$

- **Einstein equation:** $$D = kT\frac{\mu}{ez}$$

- **In equilibrium: total current is 0**

In contrast to purely electronic current transport, there is always a chemical reaction tied to the current flow that takes place wherever the ionic current is converted to an electronic current - i.e. at the contacts or electrodes.

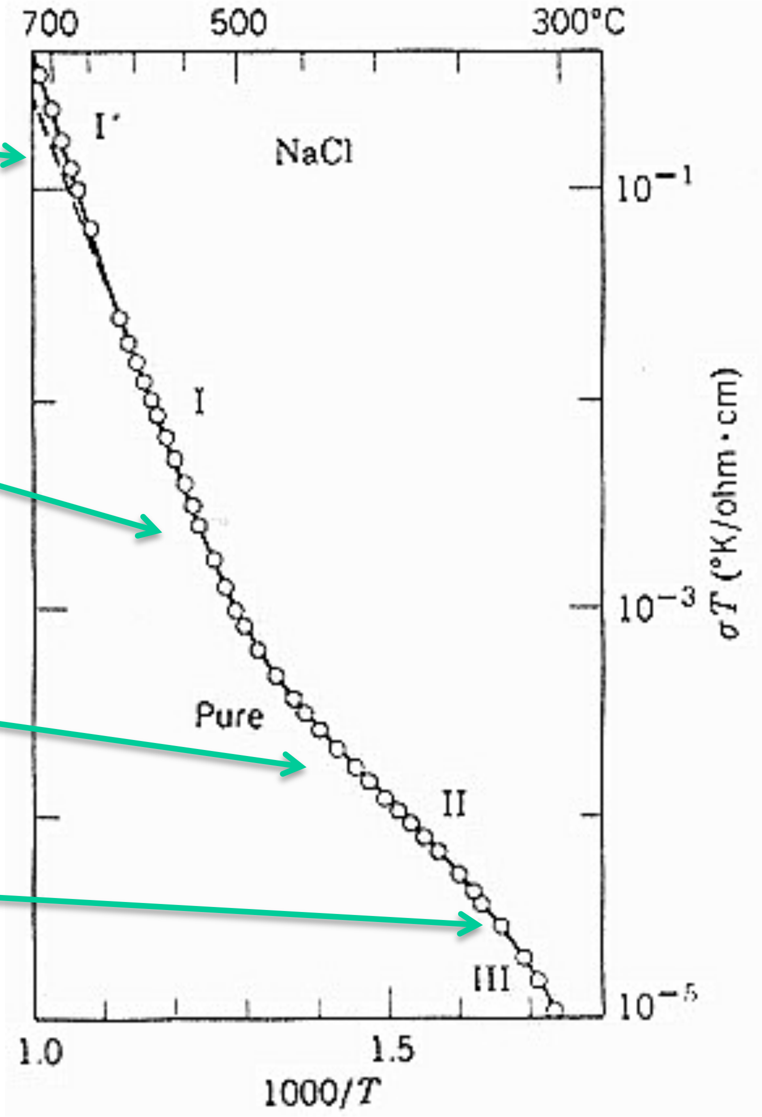
Example of ionic conductivity

Region I’: close to melting, conductivity of Cl and Na

Region I: conductivity by Na+1 hopping from one vacancy to another. Concentration of vacancies depends on temperature

Region II: conductivity of impurities (extrinsic region)

Region III: association of impurities and vacancies reduces diffusion.



Ionic conduction: examples of applications

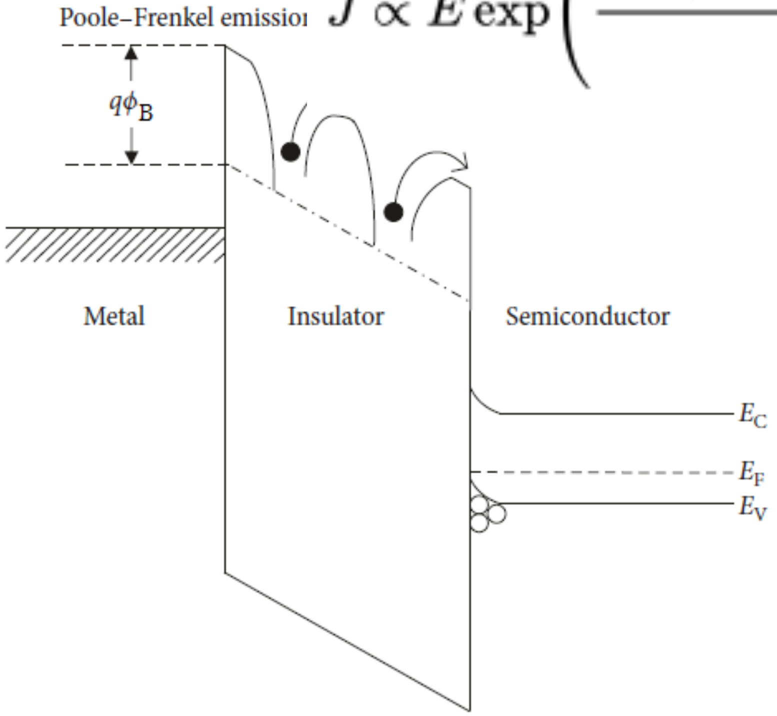
- **Batteries (regular and rechargeable)**
- **Fuel cells (electrochemical conversion systems that convert fuel directly, efficiently, and cleanly to electrical/thermal energy)**
- **Solid state sensors (e.g. gas sensors)**
- **Electrochromic windows**
- **Engineering properties of crystals/ceramics**
- **Sensors (will see examples later)**

Hopping conduction: Pool-Frenkel emission

The electrical conductivity of dielectrics/semiconductors in presence of high electric field (e.g. 105 V/cm) is often described by Pool-Frenkel law

The underlying mechanism is hopping between the trap states (empty states) lowered by electrostatic attraction between the ionic trap site and the conduction electron

$$J \propto E \exp\left(\frac{-q\left(\phi_B - \sqrt{qE/(\pi\epsilon)}\right)}{k_B T}\right)$$



Example: Poole-Frenkel electron emission from the traps in AlGaN/GaN transistors (J. Appl. Phys. 95, 6414, 2004)

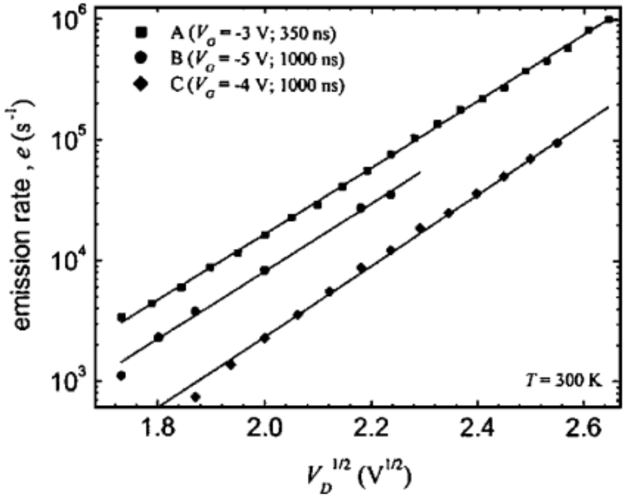


FIG. 3. Emission rate as a function of the square root of the applied voltage

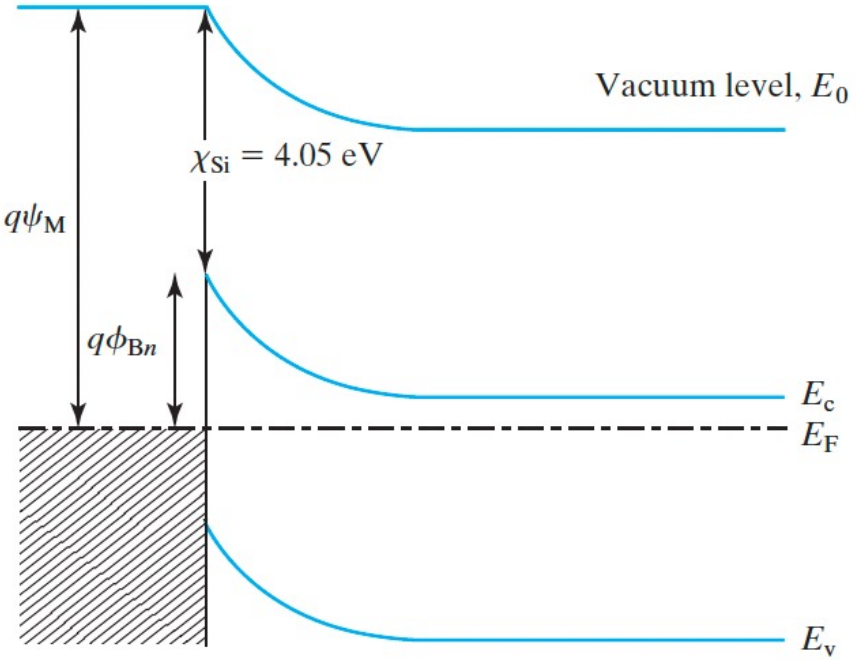
Metal-semiconductor junction

A metal electrode deposited on a semiconductor/insulator does not necessary result in a good ohmic contact

Two kinds of metal-semiconductor contacts: Ohmic or blocking contacts:

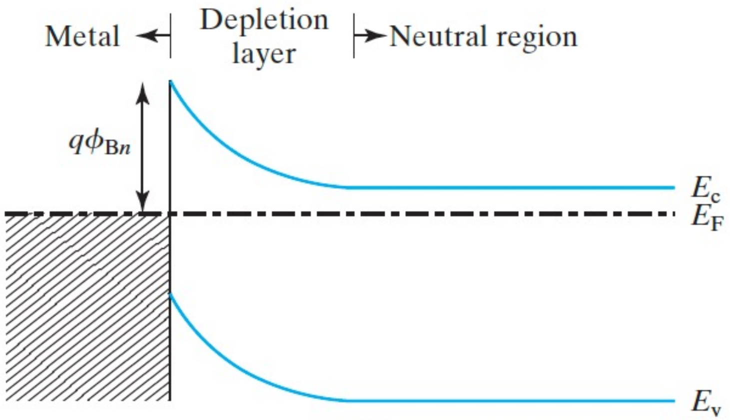
Example of silicon:

- **metal on lightly doped silicon – rectifying Schottky diodes**
- **metal on heavily doped silicon – low-resistance ohmic contacts**



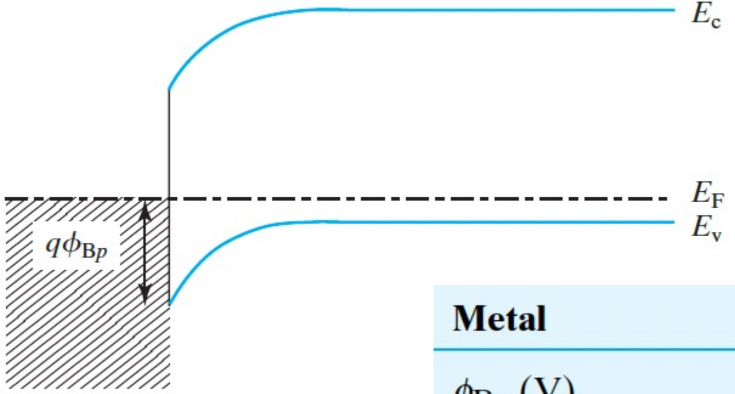
Metal-semiconductor junction

the barrier against electron flow between the metal and the n-type semiconductor



(a)

the barrier against hole flow (p-type)



Both p-type and n-type semiconductors tend to form Schottky barriers.
A perfect Ohmic contact between a metal and semiconductor do not exist, for a good contact a metal with lower Schottky barrier is preferred

Work function matching and barriers for n- and p- type silicon

Metal	**Mg**	**Ti**	**Cr**	**W**	**Mo**	**Pd**	**Au**	**Pt**
ϕ_{Bn} (V)	0.4	0.5	0.61	0.67	0.68	0.77	0.8	0.9
ϕ_{Bp} (V)		0.61	0.50		0.42		0.3	
Work Function	3.7	4.3	4.5	4.6	4.6	5.1	5.1	5.7

Schottky effect: identification of Schottky conduction mechanism from the «square root law»

$$I = I_0 \left(e^{\frac{qV}{nkT}} - 1 \right)$$

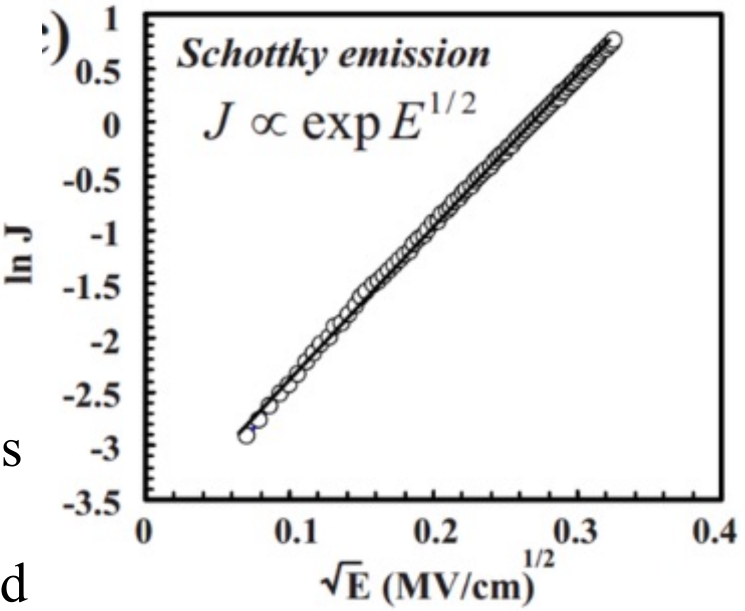
$$I_0 = AA^* T^2 e^{-\frac{q\Phi_B}{kT}}$$

Barrier lowering effect:

$$\Phi'_B = \Phi_B - \sqrt{\frac{qE}{4\pi\epsilon}}$$

the Schottky barrier is lowered: $\Delta\Phi_B = \sqrt{\frac{qE}{4\pi\varepsilon}}$

Example:SnO2 with Ti electrode



When an electron is near a conductor (metal), it induces an **opposite charge** in the metal. This creates an **attractive Coulombic force** pulling the electron toward the junction, effectively **lowering the barrier**.

- I-V plot: the straight line in lnJ vs. sqrt (E) coordinates attests to the Schottky mechanism
- Can be easily confused with the Pool-Frenkel (hopping) conduction mechanism

Conduction: final remarks

- **Different mechanisms, their identification is important, addressing some key are essential for its understanding**
- **Type of material: metal/dielectric/semiconductor**
- **What limits the conduction: the interfaces of bulk**
- **Type of charge carriers: electrons/holes/ions/defect associates**
- **Possible crossover between conduction mechanisms vs T**
- **Polycrystalline materials: grains and grain boundaries (different conduction mechanisms)**

Point defects in crystals and ceramics

- Introduction to the defects, point defects in crystals and ceramics
- Formal description of defects, Kröger-Vink notation
- Law of Mass action for defects
- Equilibrium equations for point defects
- prediction of defect concentration vs processing parameters
- Ionics: applications

A good textbook: M.W. Barsoum – Fundamentals of Ceramics
IoP publishing Ltd, 2003

Colors

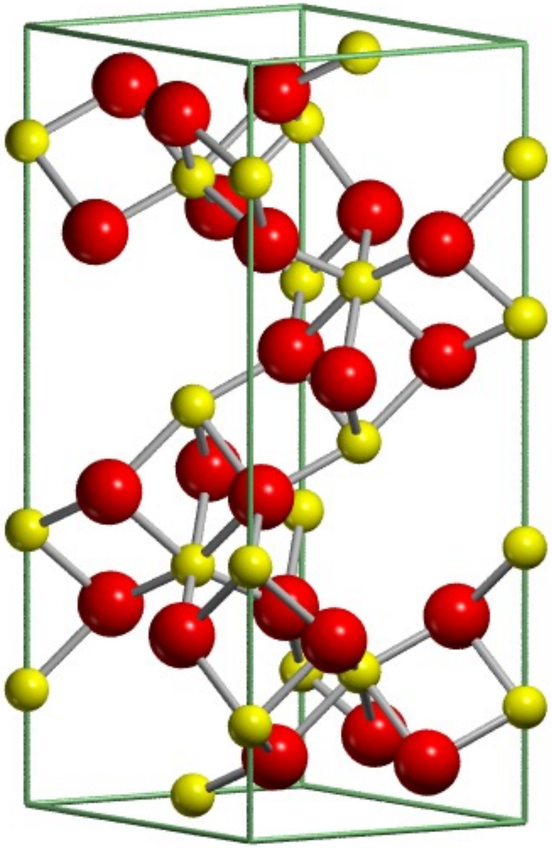
Blue saphir

In sapphire (Al_2O_3), the neighbouring impurities of Fe^{+2} et Ti^{+4} ions absorb photons with wave length corresponding to the red light.
During this absorption electrons are transferred from Fe to Ti ions:
$Fe^{+2} + Ti^{+4} \rightarrow Fe^{+3} + Ti^{+3}$

Absorption of red!

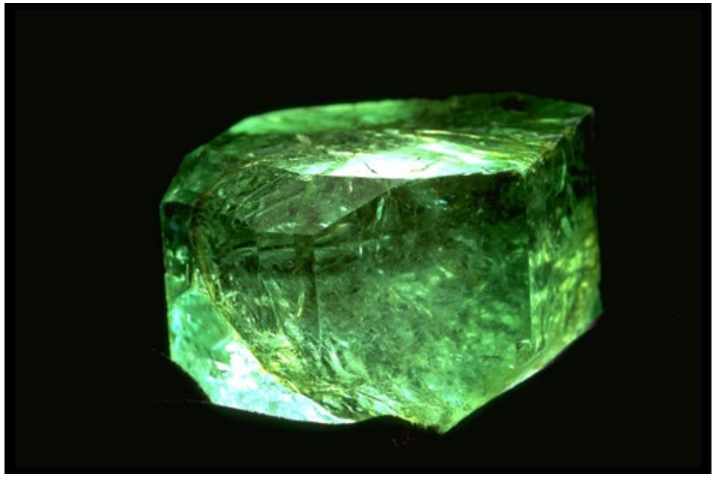
Red sapphire (rubin)

The color due to the presence presence of Cr^{+3}



Al_2O_3 corundum / sapphire

Colors



beryl (emerald)
$Be_3Al_2Si_6O_{18}$

Cr^{+3}

The environment of Cr+3 in sapphire and beryl is different

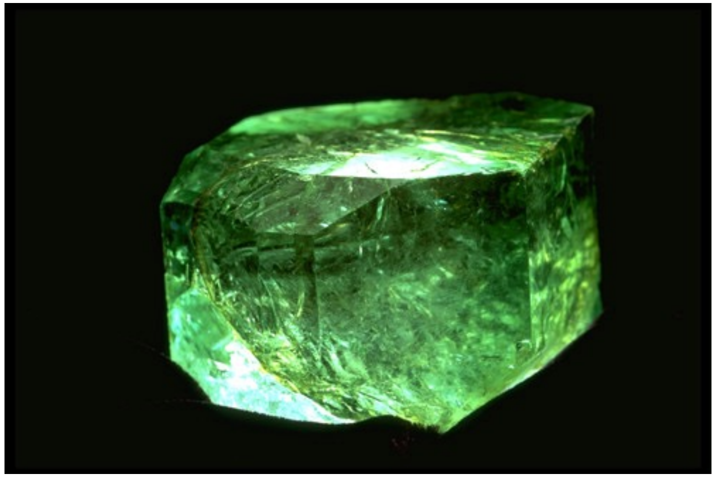
Red beryl
$Be_3Al_2Si_6O_{18}$

Mn^{+3}

Diamond Hope -
Blue diamond

Impurities of boron create energy levels in the forbidden band (close to the valence band).
During absorption of red light, electrons jump to those sites.

Colors



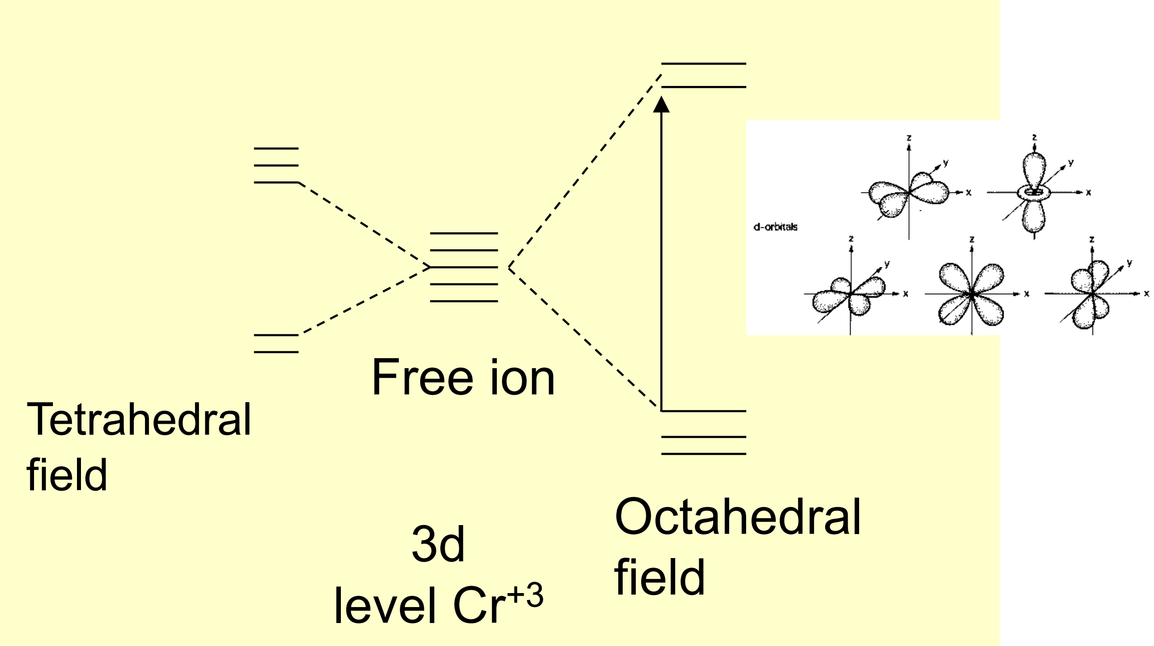
Beryl (emerald)
$Be_3Al_2Si_6O_{18}$

Cr^{+3}

Coordination number of the defect is essential!

Red beryl
$Be_3Al_2Si_6O_{18}$

Mn^{+3}



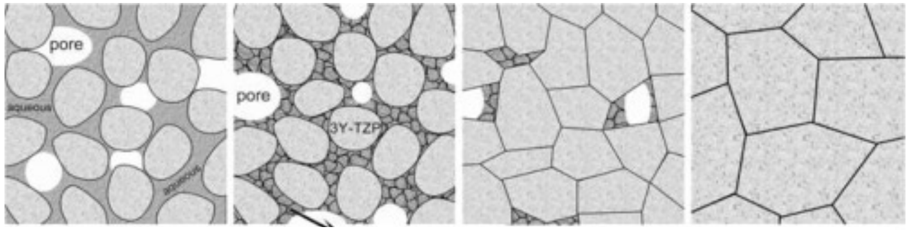
Tetrahedral field

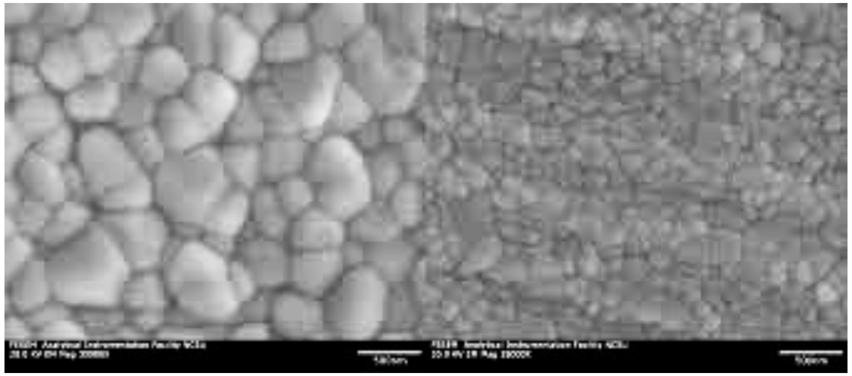
Free ion

Octahedral field

3d
level Cr^{+3}

Examples of importance of defects in ceramics





- Preparation
  - sintering
- Functionality
  - Conductive ceramics
  - Insulating ceramics
  - SiO_2 and HfO_2 in transistors for high density memories
  - Piezoelectric ceramics
  - Ferrites (magnetic ceramics)
  - Ceramic sensors
  - Varistors
  - Color
  - Luminescent materials

Structural defects in ceramics

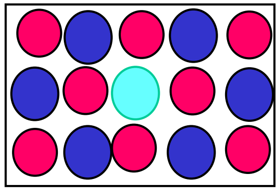
Our focus:

- **Learn about different types of structural defects in ceramics, understand their origin and ways to control them**
- **Understand effects of external parameters (temperature, partial pressure of oxygen,…) on concentration of defects.**
- **Describe quantitatively effect of those parameters on concentration of defects**

Clasification of defects

- All materials possess defects
- Defects influence properties
- In some cases, defects can be used to obtain better properties (or new properties)

- 0-dimensional defects Point defects: e.g., vacancies and imurities (foreign atoms).
- 1-D defects: Linear defects: e.g., dislocations (key for stress relaxation in thin films)
- 2-D defects: Surface defects: e.g. grain boundaries (energy barriers, GB transport, gas exchange)
- 3-D defects: Volume defects: secondary phases, porosity (dielectric response, breakdown strength, interfaces)



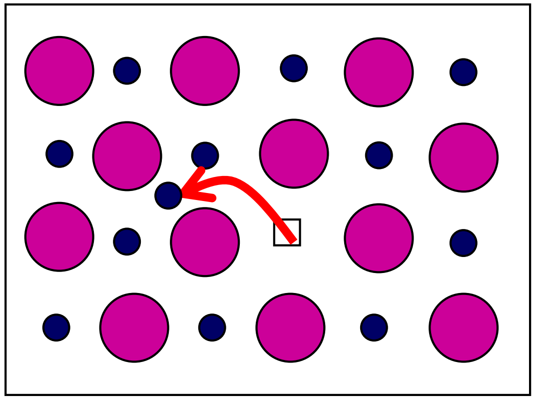
Point defects in ceramics

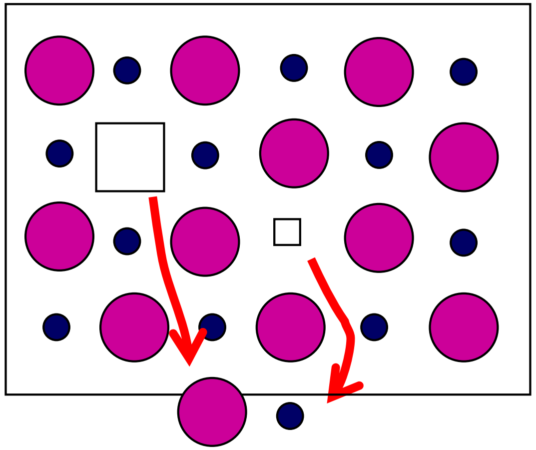
(compare with metals)

- Can be situated at several sites
- Combination of cations and anionic defects.
- Atomic defects can be compensated by electronic defects.
- The type and concentration of defects are most often related to sintering conditions (temperature, pO2,…)
- can have same materials of p-type or n-type depending on conditions
- Defects can be associated or dissociated

Intrinsic ionic defects

- **Intrinsic defects do not involve foreign atoms**
- **Can be interstitials and vacancies**
- **Two types of vacancies: Frenkel defects and Schottky defects.**





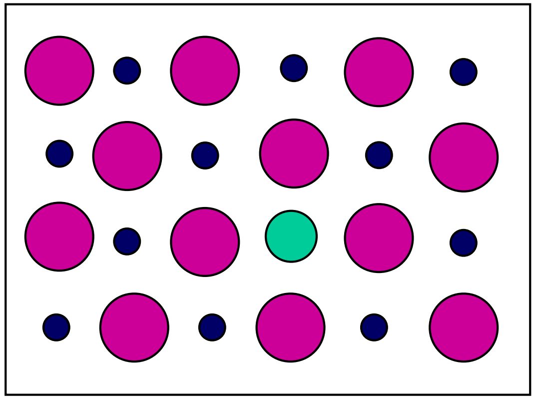
Frenkel defects are formed from

one vacancy and one interstitial

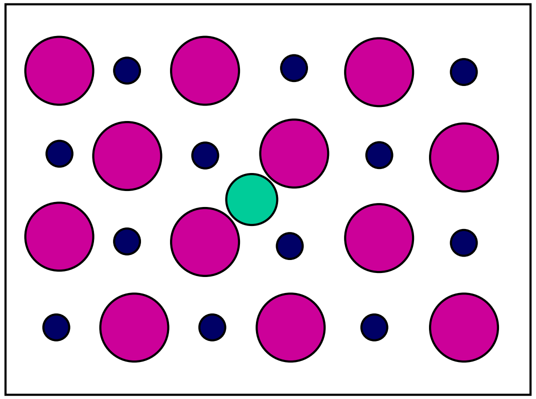
Schottky defects
Are formed from two types of vacancies.

Extrinsic ionic defects

- **Extrinsic defects come from impurities**
- **Can be formed in the lattice as substituent or interstitial atoms**
- **In all cases, electrical neutrality must be preserved**



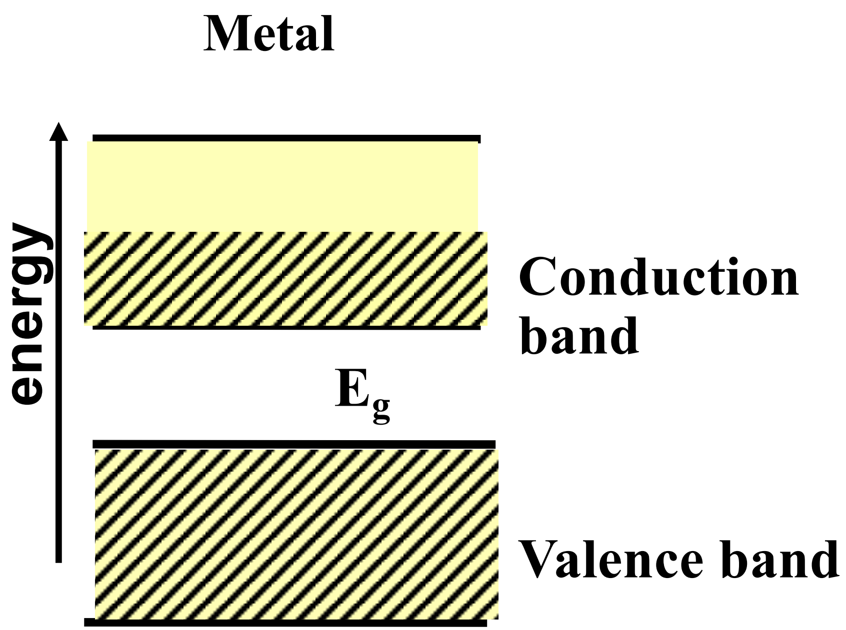
Substituent



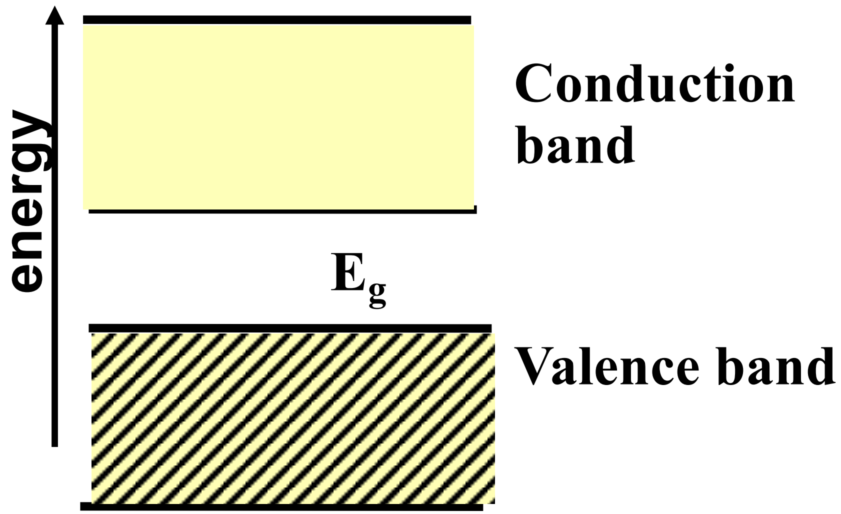
Interstitial

Electronic defects and band structure

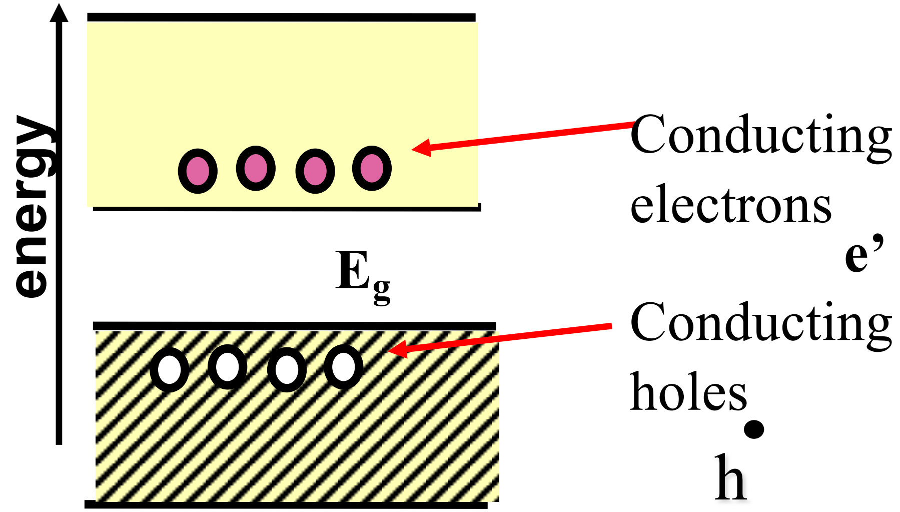
- Electrons and holes also take part in the balance of defects



metals



Insulators and semiconductors at T=0 K



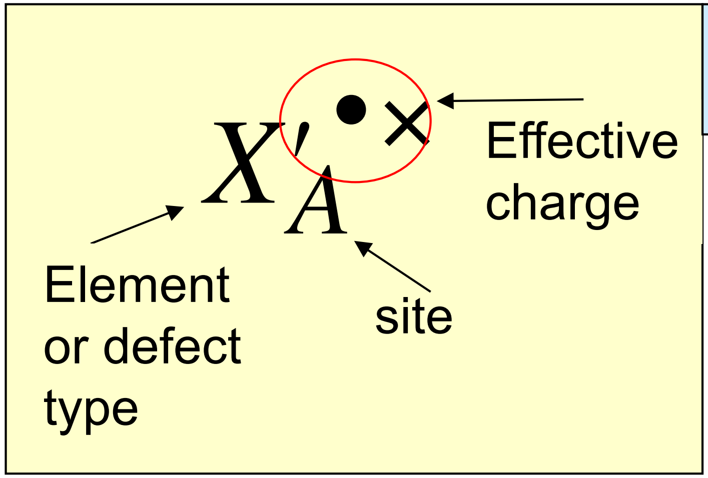
Insulators and semiconductors at T=0 K

Identification of point defects

- The identification can be made by different indirect methods, measuring properties which are influenced by defects: density, optical absorption, diffusion, electrical conductivity and melting temperature (all depend on concentration and type of defects)

- If the crystal structure is known, it is possible to make an idea of possible type of defects e.g. a small cation can occupy interstitial sites

Description of defects: Notations of Kröger and Vink



$X_A^{\prime\bullet\times}$

Effective charge

Element or defect type

site

Exponent shows charge of the defect relative to the site of the perfect crystal

V	vacancy
X_i	interstitial
$\bullet$	positive effective charge
$'$	negative effective charge
$\times$	zero effective charge

$V_O^{\bullet\bullet}$, $V_O^{\times}$ -vacany on oxygen site

$M_i^{\times}$ -atom M on interstitial site

$M_i^{\bullet\bullet}$-cation M^{+2} on interstitial site

$(V_M - V_O)$ – association of vacancies on M and O sites

$(V_M - M_i)$ – association of vacancy on M site and M interstitial

e' - free electron

$h^{\bullet}$ - free hole

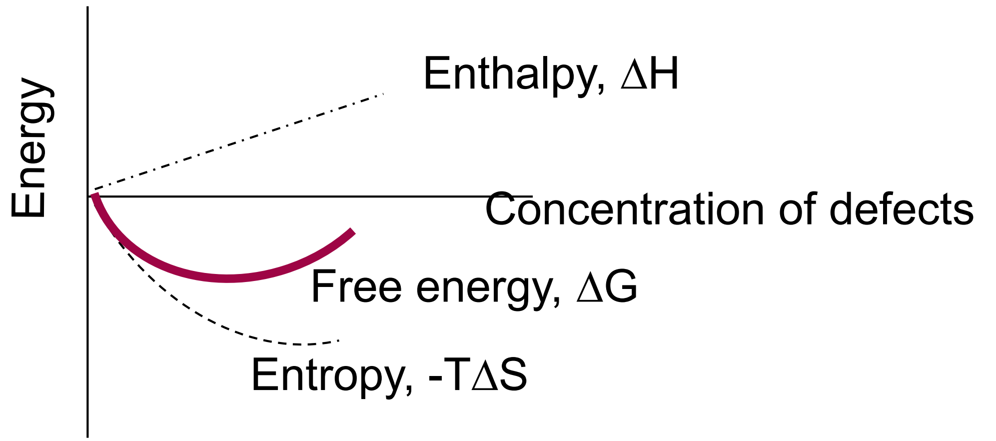
$\left[X\right]$ - indicates concentration

$n, \left[e'\right], p, \left[h^{\bullet}\right]$ – concentration of electrons and holes

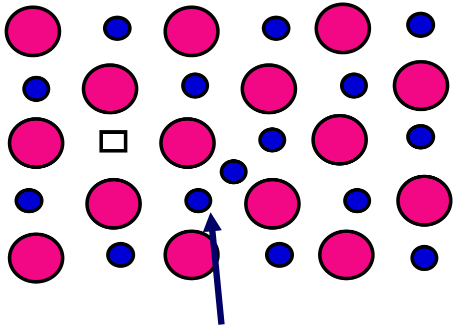
e.g.

Y'_{Zr} - indicates substition of Zr^{+4} by trivalent Y^{+3}cation

Concentration of intrinsic defects in pure materials



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



Energy must be used to displace defect.
At the same time, entropy increases.

Configurational entropy due to defects:

$$S_c = k \ln W$$

W- number of different ways to arrange defects
k – Boltzmann constant

There are always defects in equilibrium state

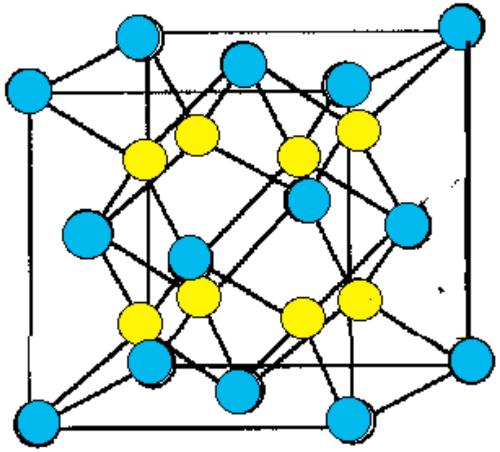
Table 2.1 Defect Concentration at Different Temperatures

$$\frac{n}{N} = \exp\left[-\frac{\Delta g}{2kT}\right]$$

Defect Concentration	1eV[a]	2eV	4eV	6eV	8eV
n / N at 100°C	2×10^{-7}	3×10^{-14}	1×10^{-27}	3×10^{-41}	1×10^{-54}
n / N at 500°C	6×10^{-4}	3×10^{-7}	1×10^{-13}	3×10^{-20}	8×10^{-27}
n / N at 800°C	4×10^{-3}	2×10^{-5}	4×10^{-10}	8×10^{-15}	2×10^{-19}
n / N at 1000°C	1×10^{-2}	1×10^{-4}	1×10^{-8}	1×10^{-12}	1×10^{-16}
n / N at 1200°C	2×10^{-2}	4×10^{-4}	1×10^{-7}	5×10^{-11}	2×10^{-19}
n / N at 1500°C	4×10^{-2}	1×10^{-4}	2×10^{-6}	3×10^{-9}	4×10^{-12}
n / N at 1800°C	6×10^{-2}	4×10^{-3}	1×10^{-5}	5×10^{-8}	2×10^{-10}
n / N at 2000°C	8×10^{-2}	6×10^{-3}	4×10^{-5}	2×10^{-7}	1×10^{-9}

[a] 1eV = 23.05 kcal/mole.

Compound	**Reaction**	**energy of formation (Δh, eV)**
KCl	$nul \leftrightarrow V_K^{'} + V_{Cl}^{\bullet}$	2.6
CaO	$nul \leftrightarrow V_{Ca}^{''} + V_O^{\bullet\bullet}$	≈ 6
MgO	$nul \leftrightarrow V_{Mg}^{''} + V_O^{\bullet\bullet}$	7.7
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
	$nul \leftrightarrow V_{Ca}^{''} + 2V_F^{\bullet}$	≈ 5.5



Law of mass action for point defects

- **Chemical reactions: Law of mass actions determines the chemical reaction rate vs. concentration of reactants**

- **Law of mass action is applicable for the analysis of the dynamic equilibrium of a reversible reaction *under equilibrium conditions***

- ***Law of mass action can be derived thermodynamically (e.g. in the textbook of Barsoum, also in many online sources)***

- ***Law of mass action is applicable for point defects or electron-hole pairs – a key instrument for analysis of defect chemistry in equilibrium***

- ***Law of mass action is applicable for elementary reactions***

Law of mass action and equilibrium constant

It is possible to consider formation of defects like a chemical reaction

For a general chemical reaction

$$\alpha A + \beta B \leftrightarrow \gamma C + \delta D \qquad (1)$$

$$\text{e.g.,} N_2(g) \; + \; 3H_2(g) \; \leftrightarrow 2NH_3(g) \; + \Delta H_o$$

The equilibrium constant is given by

$$K = \frac{[C]^{\gamma}[D]^{\delta}}{[A]^{\alpha}[B]^{\beta}} \quad , \text{eg. } K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3} \qquad (2)$$

The concentrations [A], [B], [C], [D] represent activities (or conc., or partial pressure) of different species, and exponents are their stoichiometric coefficients, respectively $\alpha, \beta, \gamma, \delta$.

Equation (2) is known as the »*Law of mass action"* for the chemical reaction (1).

The equilibrium constant of defects is calculated in the same way for reactions among defects

*We always assume a small concentration of defects (<<1%) – no interaction

Reaction among defects: balancing

- It is possible to consider formation of defects like a chemical reaction, the concentrations of involved defects are interrelated (at a given T)

- the Law of mass action produces the equilibrium constant for the reaction

- Like in a “normal” chemical reaction the conservation laws have to be respected:
  - mass conservation
  - charge conservation

- In addition to these principles, in defect reactions the number of sites has to be preserved, the balance between cationic and anionic sites should be unchanged

Stoichiometric reactions among defects:

In addition to mass and charge, the number of sites must be conserved

A Schottky type reaction in $M^{+2}O^{-2}$:

$$M_M + O_O \xleftrightarrow{MO} V_M'' + V_O^{\bullet\bullet}$$

Metal and oxygen – both leave the system

$$K = \frac{[V_M''][V_O^{\bullet\bullet}]}{[M_M][O_O]}$$

$$Nul \xleftrightarrow{MO} V_O^{\bullet\bullet} + V_M''$$

$$K_S = \left[V_O^{\bullet\bullet}\right]\left[V_M''\right] = \exp(-\Delta g_S / kT)$$

$$but\ [M_M]\ et\ [O_O] \approx 1$$

$$[V_M''] = [V_O^{\bullet\bullet}] = \sqrt{K}$$

$$or\ \ n_V = N\sqrt{K}$$

Schottky type reaction in $M^{+3}{}_2O^{-2}{}_3$:

$$Nul \xleftrightarrow{M_2O_3} 3V_O^{\bullet\bullet} + 2V_M'''$$

$$K_S = \left[V_O^{\bullet\bullet}\right]^3\left[V_M'''\right]^2 = \exp(-\Delta g_S / kT)$$

Charge neutrality and number of sites respected

*terms in square brackets are concentrations.

Stoichiometric reactions among defects: electrons and holes

Formation of electronic intrinsic defects – generation of electron – hole pair

$$Nul \leftrightarrow e' + h^{\bullet}$$

$$K_i = \left[h^{\bullet}\right]\left[e^{'}\right] \equiv pn = N_V N_C \exp(-\Delta E_g / kT)$$

Concentration per cm^3

N_c et N_V densities of states per unit volume in the conduction and valence band, respectively (instead of density of sites).

ΔE_g is the forbidden energy gap between the conduction and valence bands

Stoichiometric reactions among defects

In the reactions among defects, the number of sites must be conserved, in addition to the mass and charge

Schottky reaction in MO	$\text{null} \leftrightarrow V_O^{\bullet\bullet} + V_M''$	$K_s = \left[V_O^{\bullet\bullet}\right]\left[V_M''\right] = \exp(-\Delta g_s / kT)$
Schottky reaction in $M_2^{+3}O_3$	$\text{null} \leftrightarrow 3V_O^{\bullet\bullet} + 2V_M'''$	$K_s = \left[V_O^{\bullet\bullet}\right]^3\left[V_M'''\right]^2 = \exp(-\Delta g_s / kT)$
Frenkel reaction in $M^{+2}O$	$M_M^{\times} \leftrightarrow M_i^{\bullet\bullet} + V_M''$	$K_F = \left[M_i^{\bullet\bullet}\right]\left[V_M''\right] = \exp(-\Delta g_F / kT)$
Formation of intrinsic electronic defects	$\text{null} \leftrightarrow e' + h^{\bullet}$	$K_I = \left[e'\right]\left[h^{\bullet}\right] \equiv np$ $K_I = N_c N_v \exp(-\Delta g_I / kT)$

If you know the equilibrium constant, you can thus calculate concentrations of defects:

- **Schottky defects in MO:**

$$\mathrm{Nul} = [V_O^{\bullet\bullet}] + [V_M'']$$

$$K_s = [V_O^{\bullet\bullet}][V_M''] = \exp(-\Delta g_s/kT)$$

$$\left[V_O^{\bullet\bullet}\right] = \left[V_M''\right] = \sqrt{K_S} = \exp\left[-\frac{\Delta g_S}{2kT}\right]$$

- **Frenkel defects in MO:**

$$M_M = [V_M''] + [M_i^{\bullet\bullet}]$$

$$K_F = [M_i^{\bullet\bullet}][V_M''] = \exp(-\Delta g_s/kT)$$

$$\left[M_i^{\bullet\bullet}\right] = \left[V_M''\right] = \sqrt{K_F} = \exp\left(-\frac{\Delta g_F}{2kT}\right)$$

- **Electron-hole pair**

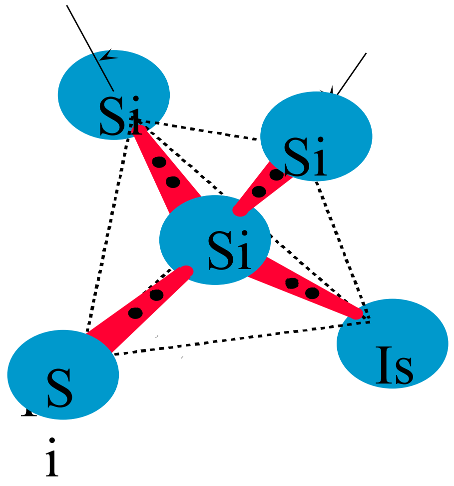
$$\mathrm{Nul} = [e'] + [h^\bullet]$$

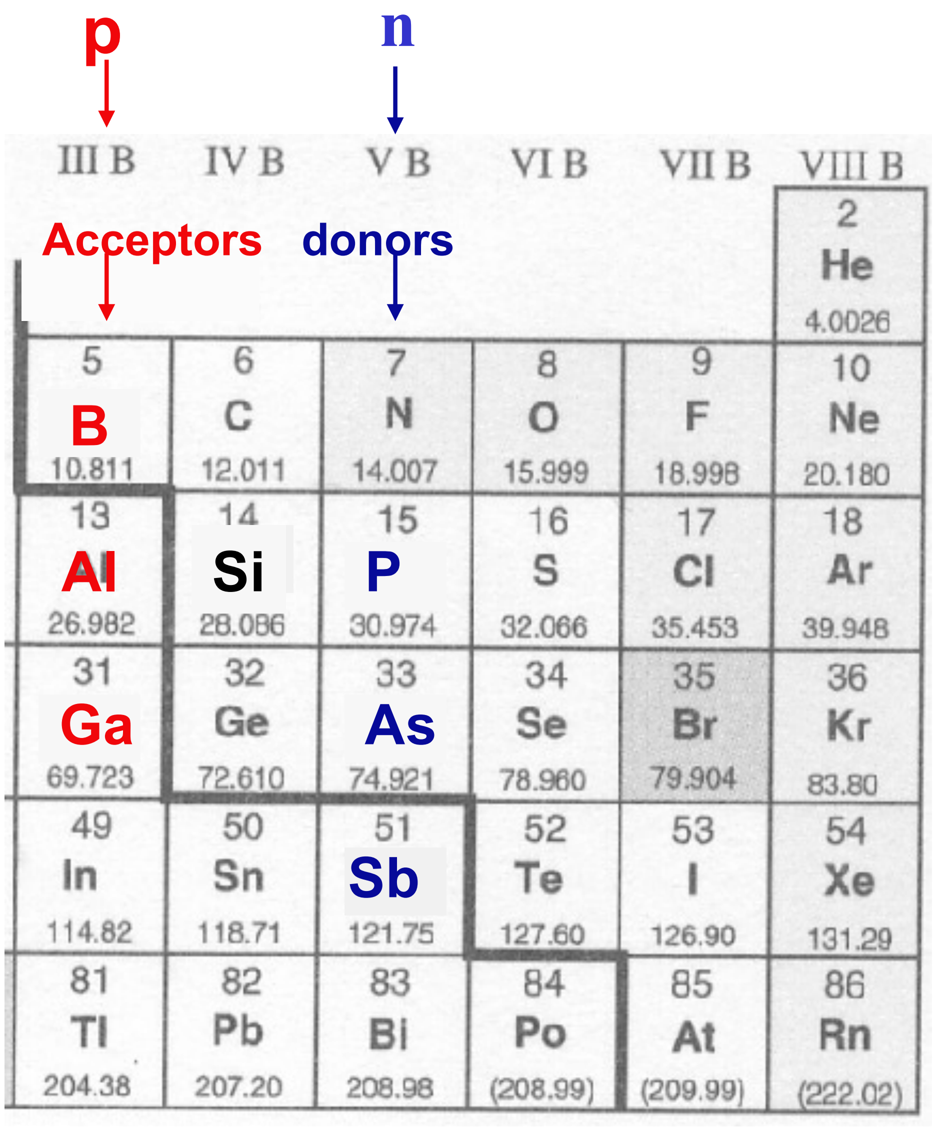
$$K_I = [e'][h^\bullet] = \exp(-\Delta g_I/kT)$$

$$\underset{\uparrow\, p}{\left[h^\bullet\right]} = \underset{\uparrow\, n}{\left[e'\right]} = \sqrt{K_I} = (N_C N_V)^{1/2} \exp\left[-\frac{E_g}{2kT}\right]$$

Extrinsic defects - dopants, impurities
Dopants in semiconductors

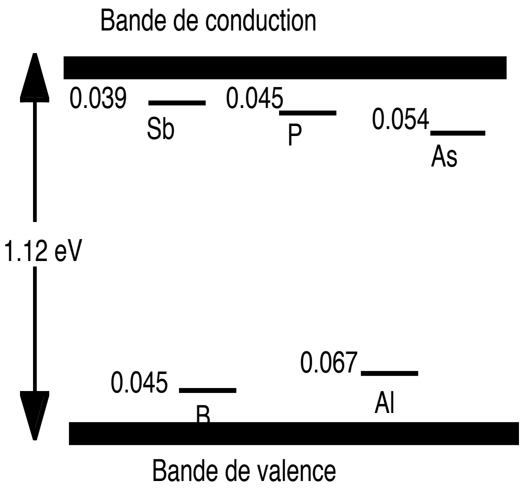
p and n dopants in silicon



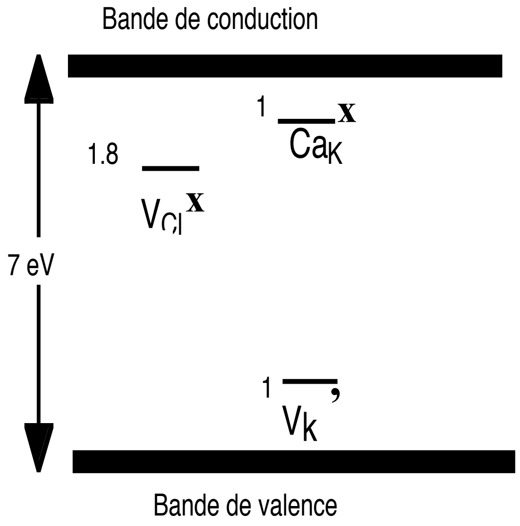


III B	IV B	V B	VI B	VII B	VIII B
					2 He 4.0026
5 **B** 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
13 **Al** 26.982	14 **Si** 28.086	15 **P** 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948
31 **Ga** 69.723	32 Ge 72.610	33 **As** 74.921	34 Se 78.960	35 Br 79.904	36 Kr 83.80
49 In 114.82	50 Sn 118.71	51 **Sb** 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
81 Tl 204.38	82 Pb 207.20	83 Bi 208.98	84 Po (208.99)	85 At (209.99)	86 Rn (222.02)

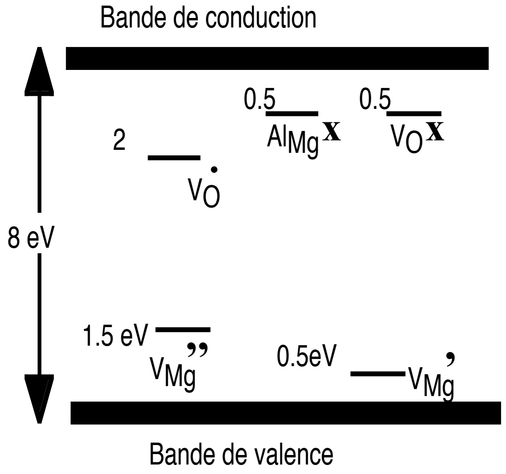
Donor and acceptor doping in functional ceramics



(a) Si



(b) KCl



(c) MgO

A defect whose energy level is close to the conduction band and which can contribute electrons to the conducting band is called a donor

A defects whose energy level is close to the valence band and can accept electrons is called an acceptor.

La^{+3} is a donor in $BaTiO_3$ because it occupies A site, while Fe^{+3}, which occupies the B site is an acceptor.

Y^{+3} can occupy either A or B site and can thus be either a donor or an acceptor.

Stoichiometric reactions among defects: electrons and holes

Formation of electronic intrinsic defects –
generation of electron – hole pair

$$Nul \leftrightarrow e' + h^{\bullet}$$

$$K_i = [h^{\bullet}][e'] \equiv pn = N_V N_C \exp(-\Delta E_g / kT)$$

This relation between electrons and holes holds for extrinsic dopants:
at a constant temperature, the product of the number of electrons in the conduction band and the number of holes in the valence band remains constant, regardless of the quantity of donor and acceptor impurities added

E.g. for Silicon $n_i = 10^{10}$ cm^{-3} at 300K; $K_i = 10^{20}$

If you introduce a shallow donor $N_D = 10^{15}$ cm^{-3},
$[h^{\bullet}] = 10^5$ cm^{-3} (in the equilibrium)

Charge neutrality is preserved!

Extrinsic defects - dopants, impurities

- **The dopants and impurities are incorporated in the crystal lattice by substitutions or as interstitials.**
- **The corresponding reaction is described by equations in which the mass, charge, and the number of sites in the lattice are conserved.**
- **Example: Introduction of a donor Ca^{+2} on K^+ site in KCl**

$$CaCl_2 \xleftrightarrow{KCl} Ca_K^{\bullet} + V_K^{'} + 2Cl_{Cl}$$

$$CaCl_2 \frac{2KCl}{\leftrightarrow} Ca_K^{\bullet} + V_K' + 2Cl_{Cl}$$

We create 2 new unit cells

- **The charged dopants are used to modify the properties either by their charges or by associated vacant sites.**
- **The charged impurities in the lattice change its properties also by the effect of associated point defects**

Extrinsic defects - dopants, impurities

- **Example:** Introduction of donor Ca^{+2} on the K^{+} site in KCl

$$CaCl_2 \xleftrightarrow{KCl} Ca_K^{\bullet} + V_K^{'} + 2Cl_{Cl}$$

- **Questions:** - is there another way to accommodate Ca^{+2} in the KCl lattice?
- - Write equations for the other reactions, e.g. avoid V_K’
- - Which reaction is the most likely? – look at partial pressure of Cl

$$2CaCl_2 \xrightarrow{2KCl} 2Ca_K^{\bullet} + 2e' + 2Cl_{Cl} + Cl_2$$

Extrinsic defects - dopants, impurities (cont.)

- **Example:** Introduction of Cr^{+3} on Ti^{+4} site in $BaTiO_3$
- (assume a mixture of $BaO+TiO_2$ when TiO_2 contains impurities of Cr^{+3} (for calcination and sintering of $BaTiO_3$)

$$2BaO + Cr_2O_3 \xrightarrow{BaTiO3} 2Cr'_{Ti} + V_O^{\bullet\bullet} + 2Ba_{Ba}^{X} + 5O_O^{X}$$

- Write equations for incorporation of impurities of La^{+3} in $PbTiO_3$ ($La_2O_3 + TiO_2$)

$$La_2O_3 + TiO_2 \xrightarrow{PbTiO3} 2La^{\bullet}_{Pb} + V''''_{Ti} + Ti^{x}_{Ti} + 5O^{x}_{O} + V^{\bullet\bullet}_{O}$$

another example:

$$Cr_2O_3 \xrightarrow{MgO} 2Cr^{\bullet}_{Mg} + 3O^{x}_{O} + V''_{Mg}$$