PAUL SCHERRER INSTITUT

LABORATORY FOR DEVELOPMENTS AND METHODS

Electronic and ionic conductivity in metal oxides

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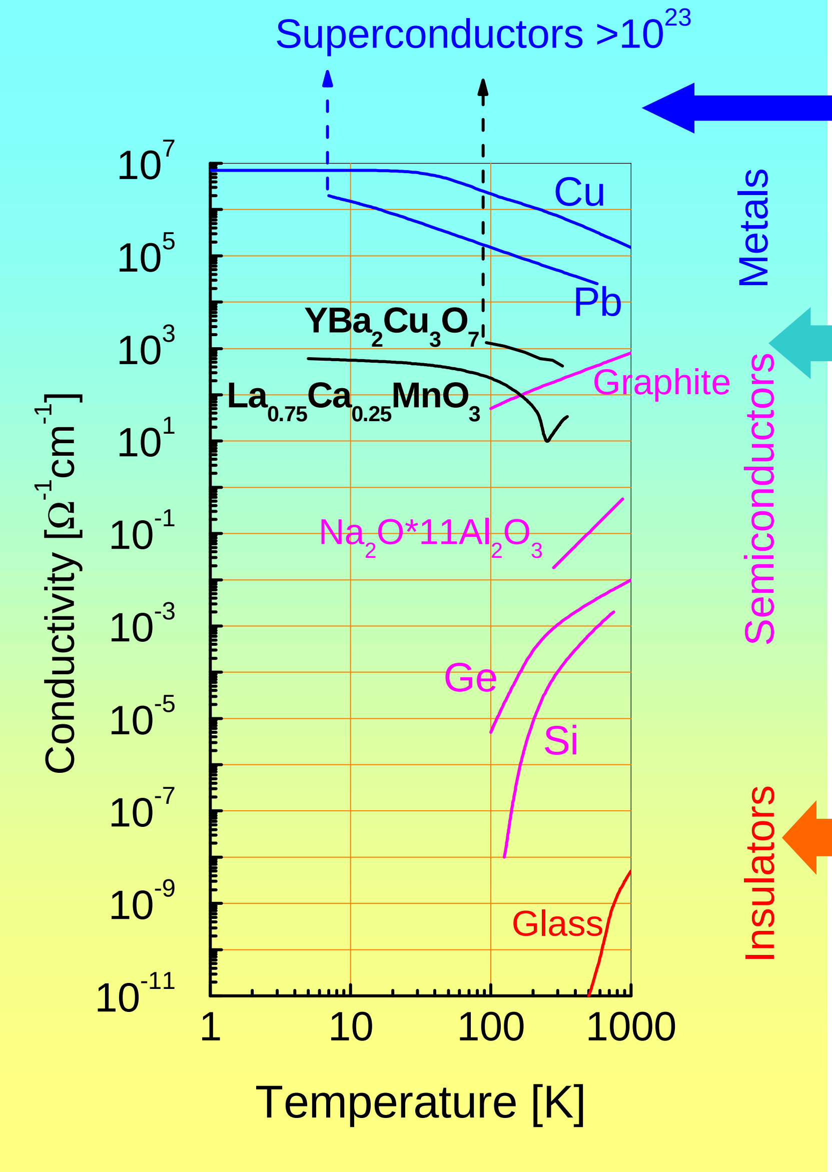
Electrical conductivity

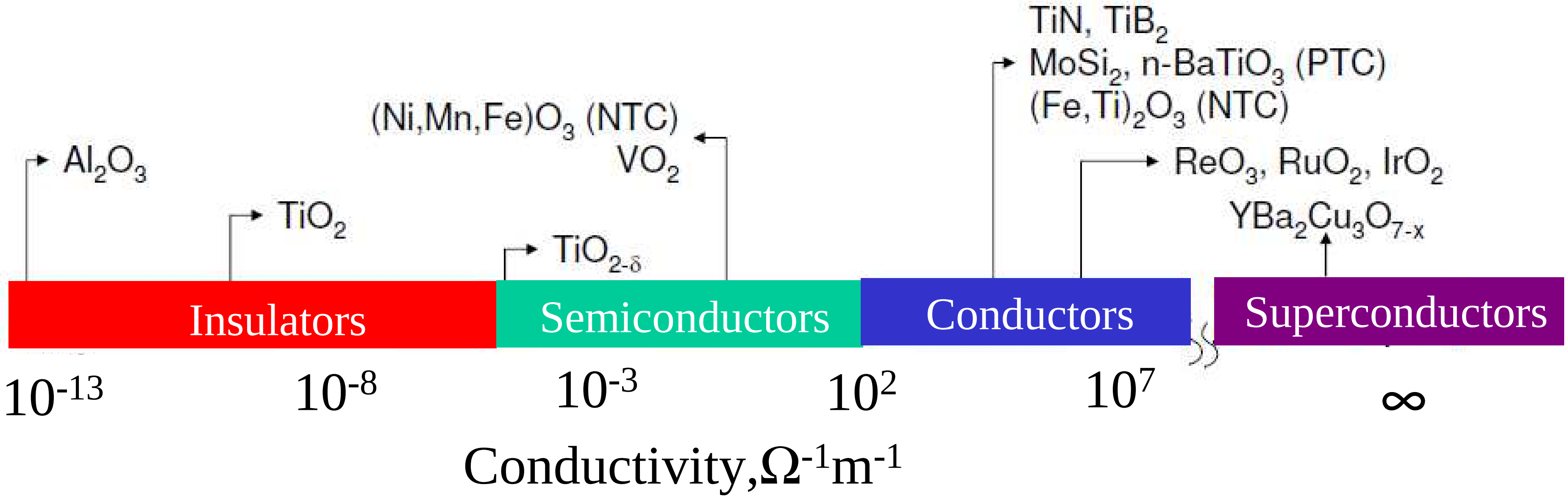


Superconductivity: by cooling resistivity drops to zero

Conductivity of metals decreases with temperature. Increased interaction of electrons with lattice!

Conductivity of insulators and semiconductors increases with temperature. Concentration of carriers increases!

Electrical resistivity of ceramic (oxide) materials – over 20 orders of magnitude



Al_2O_3

TiO_2

$TiO_{2-\delta}$

$(Ni,Mn,Fe)O_3$ (NTC)
VO_2

TiN, TiB_2
$MoSi_2$, n-$BaTiO_3$ (PTC)
$(Fe,Ti)_2O_3$ (NTC)

ReO_3, RuO_2, IrO_2

$YBa_2Cu_3O_{7-x}$

Insulators

Semiconductors

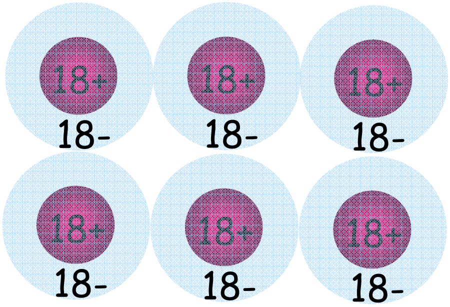
Conductors

Superconductors

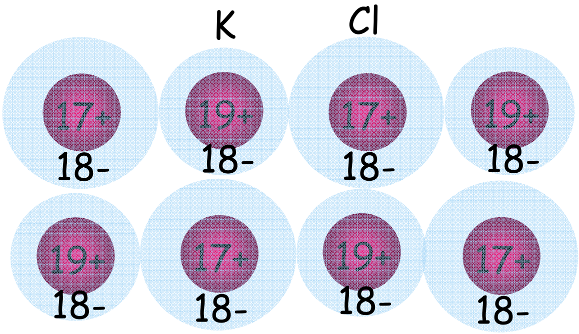
10^{-13} 10^{-8} 10^{-3} 10^{2} 10^{7} ∞

Conductivity, $\Omega^{-1}m^{-1}$

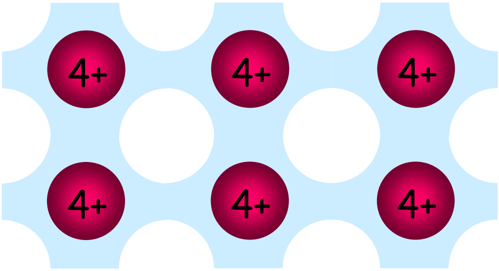
Electronic charge distribution in the basic solid types (chemical bond point of view)



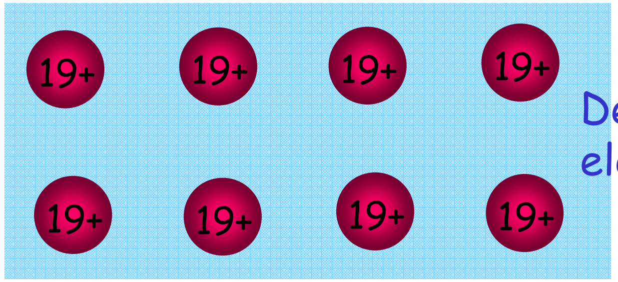
Molecular: Ar



Ionic: KCl



Covalent: C (diamond)

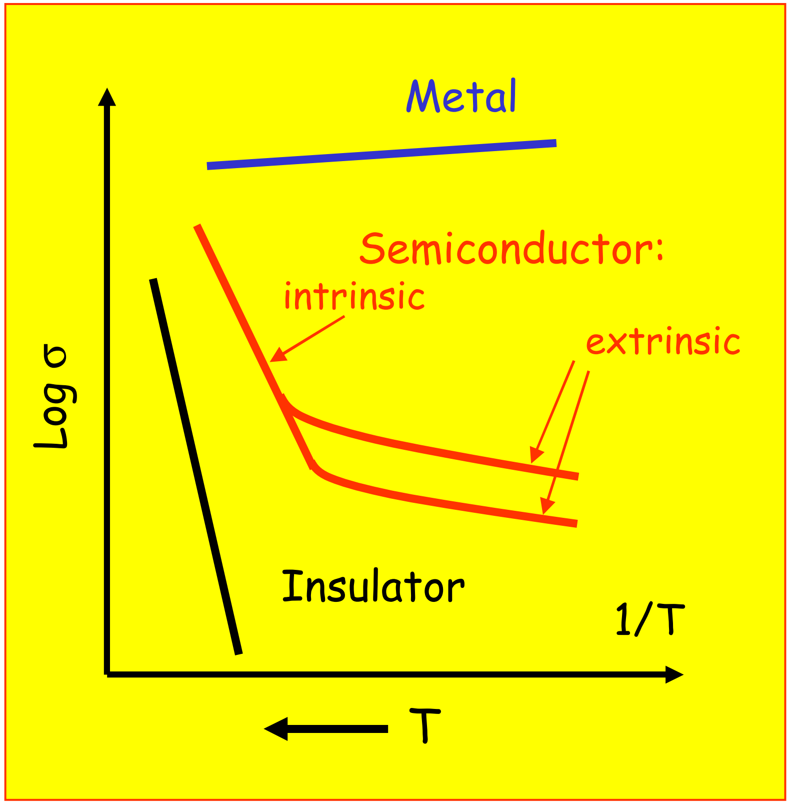


Metallic: K

After N.W. Ashcroft, N.D. Mermin, „Solid State Physics", Philadephia, 1976

Metals, semiconductors, insulators

Semiconductors: electrons are excited over the band gap and occupy energy levels in conductivity band. Holes are created in valence band. The process is thermally activated-conductivity increase with temperature.



Conductivity can be increased by a doping. Through the doping energy levels within band gap will be created.

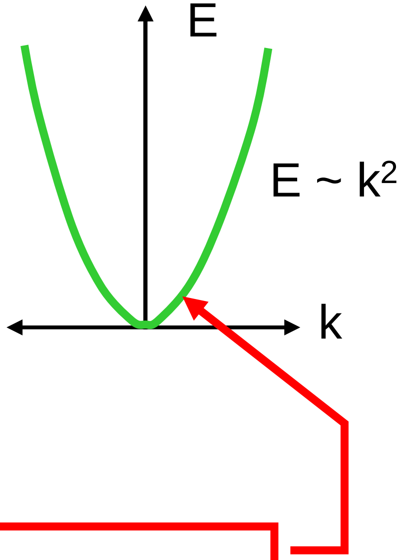
A material with an energy gap >2.5 eV is an insulator.

Electron in a (1D) solid

Energy of
an electron: $E = \hbar\omega = (\hbar k)^2/2m$

$k=2\pi/\lambda$ wave vector

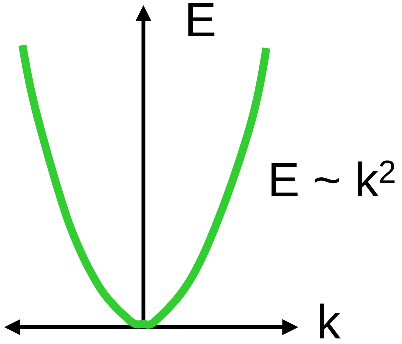
λ – wavelength
of the electron



Electrons with $\lambda \gg a$ (lattice parameter)
can travel freely through a crystal

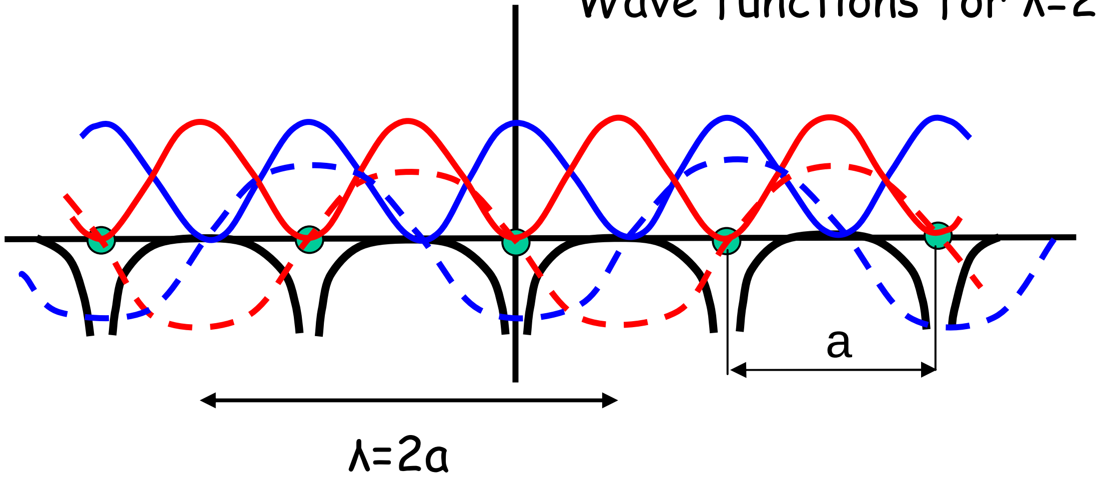
For more energetic electrons when $\lambda \to a$????

Electron in a (1D) solid



Potential energy of an electron
in a periodic array of positive ions

Wave functions for λ=2a

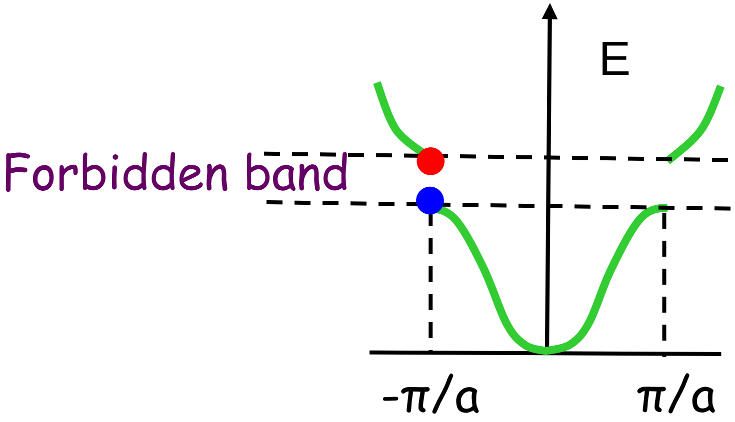


Distribution of the electron densities:

$\Psi^2 \sim \cos^2(\pi x/a)$ lower energy

$\Psi^2 \sim \sin^2(\pi x/a)$ higher energy

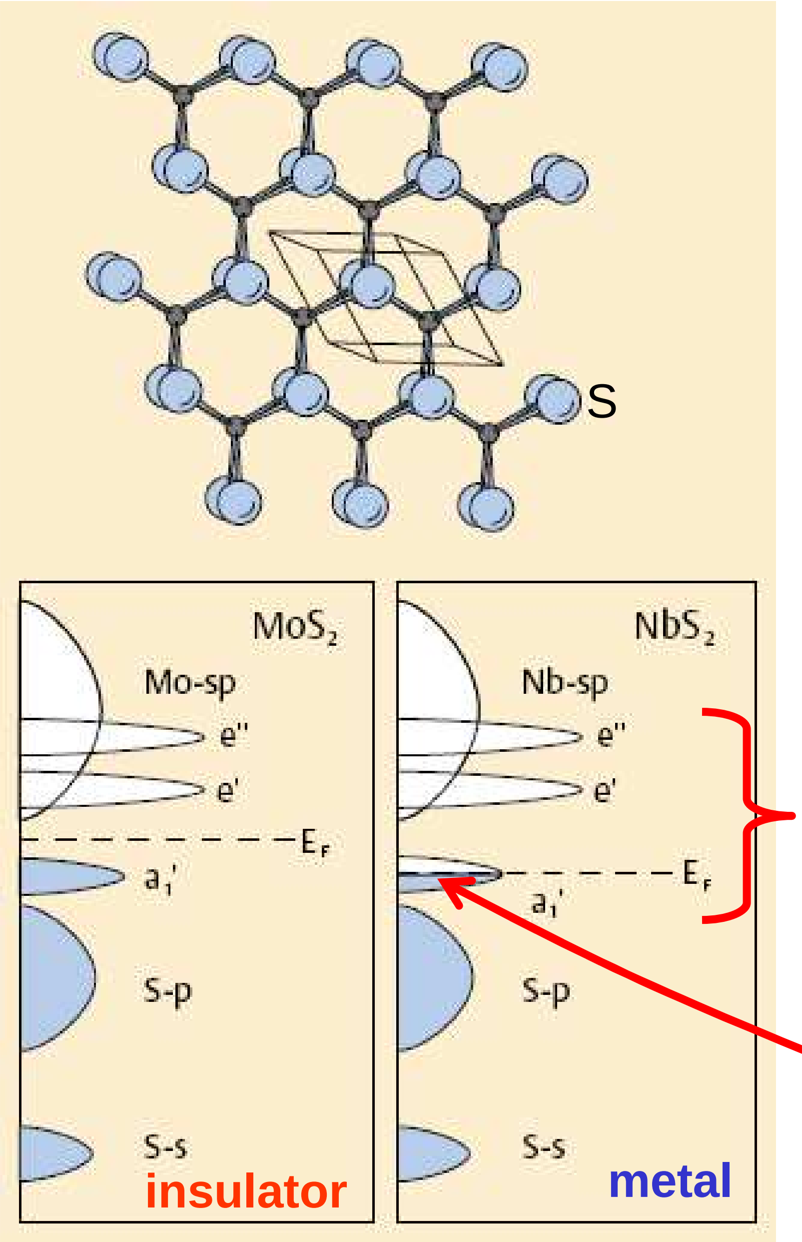
Electrons which have a wavelength commensurate with the lattice are scattered on the periodic potential



Band (Bloch-Wilson) insulators

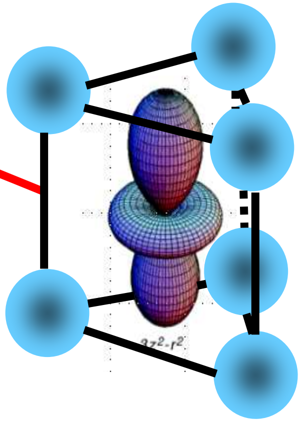
Partially filled energy band ⇨ metal

Filled energy band ⇨ insulator



$Mo^{4+}\ 4d^2$ $Nb^{4+}\ 4d^1$

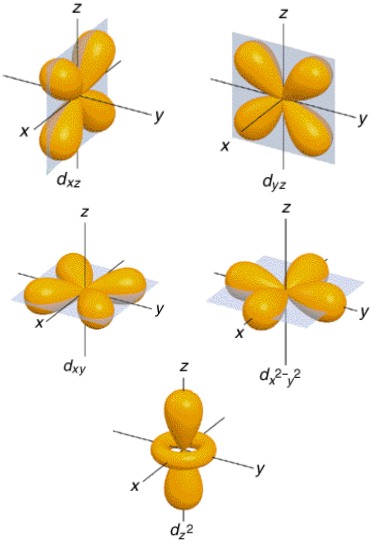
splitted d orbitals (trigonal prism coordination)



$d_{xz},\ d_{yz}$

$d_{xy},\ d_{x^2-y^2}$

d_{z^2}

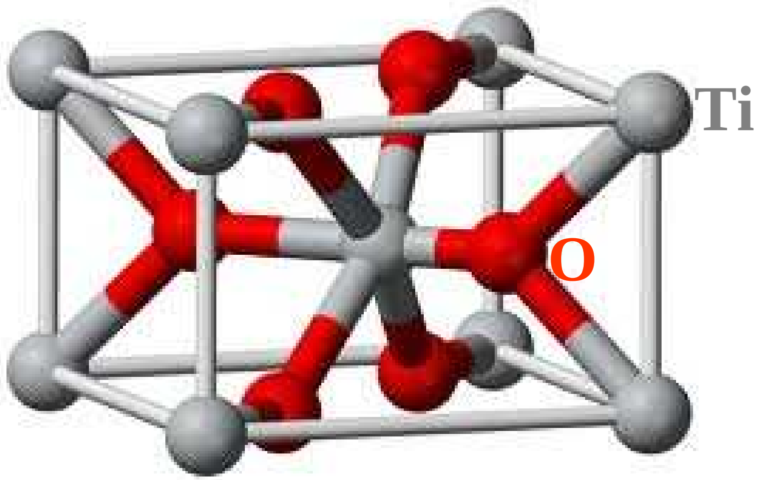


No carriers – no conductivity

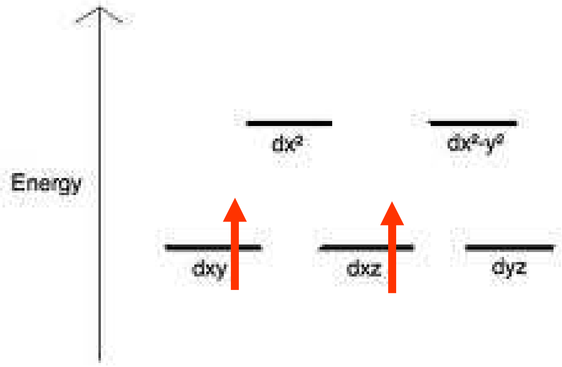
Na_2O	Na^+ $2p^63s^0$	O^{2-} $2p^6$	Noble gas configuration: insulator
MgO	Mg^{2+} $2p^63s^0$	O^{2-} $2p^6$	insulator
TiO_2	Ti^{4+} $3d^04s^0$	O^{2-} $2p^6$	insulator

Free carriers?

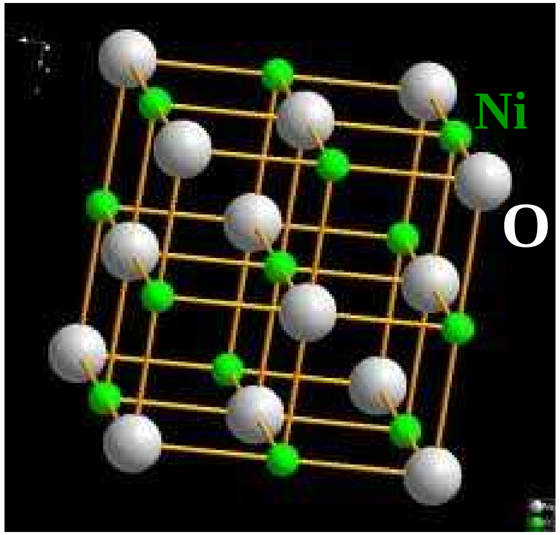
TiO	Ti^{2+} $3d^24s^0$	O^{2-} $2p^6$	Free d-electrons: metal
NiO	Ni^{2+} $3d^84s^0$	O^{2-} $2p^6$	Insulator But why???



TiO- rutile Ti $3d^2 4s^0$



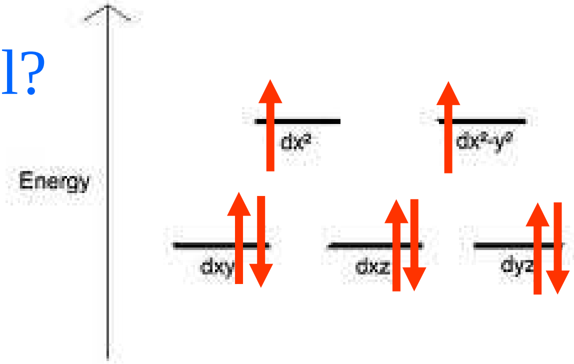
metal



NiO- NaCl structure Ni $3d^8 4s^0$

Is insulator!

Why not a metal?

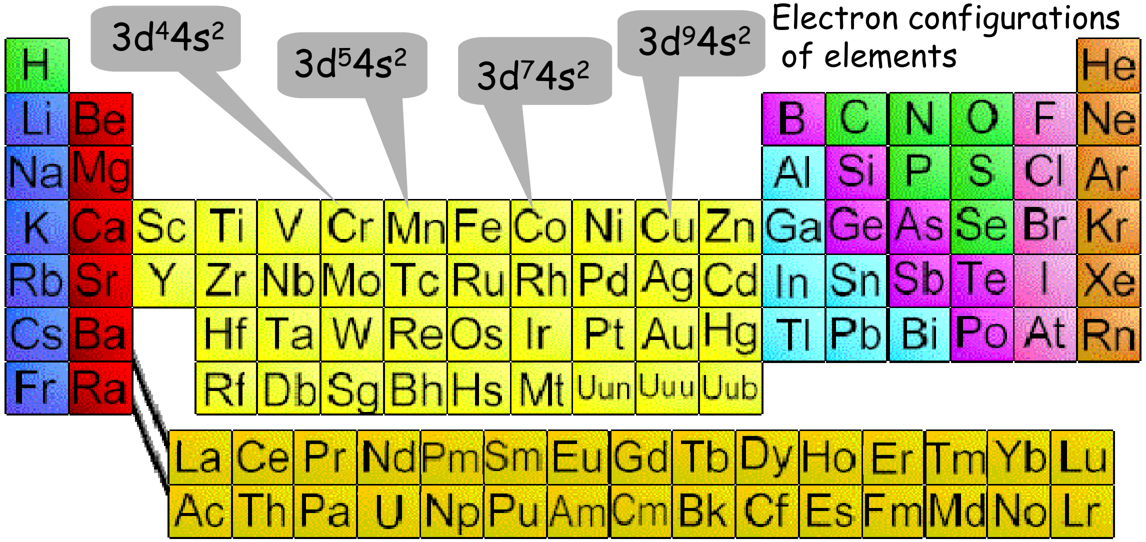


Why not metal?

CuO	Cu^{2+}	$3d^94s^0$
CoO	Co^{2+}	$3d^74s^0$
MnO	Mn^{2+}	$3d^54s^0$
Cr_2O_3	Cr^{3+}	$3d^34s^0$

Whatever is the crystal field splitting the orbitals are not fully occupied!!!

Odd number of d electrons- all this oxides should be metals but are insulators



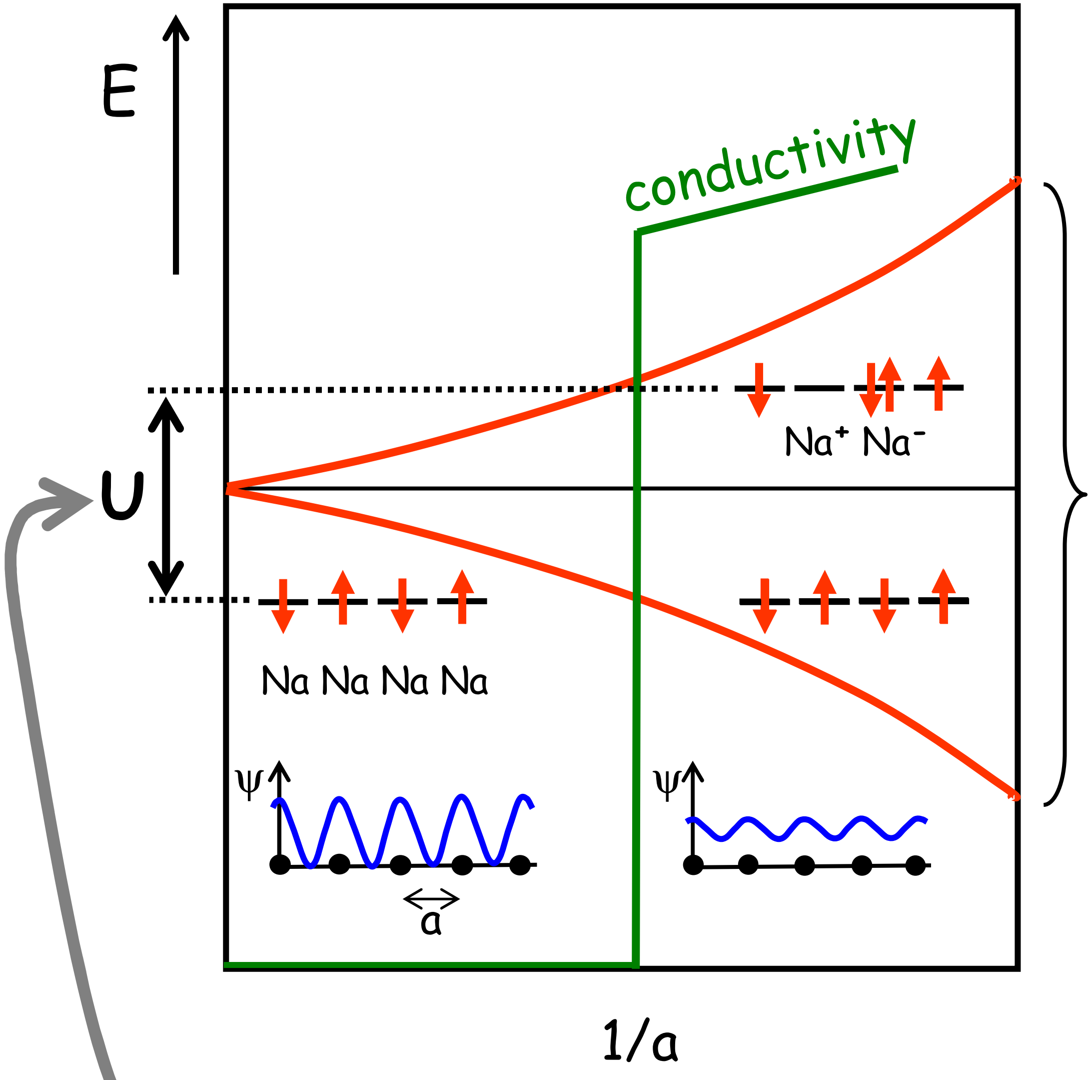
Mott-Hubbard insulators

- The d-levels in most of the transition metal oxides are partially filled, therefore, the band theory predicts electron delocalization and metallic properties.
- According to band structure calculations half of the known binary compounds should be conducting.

- In reality, many oxides show insulating behavior, implying that the d-electrons are localized.
- Short-range Coulomb repulsion of electrons can prevent formation of band states, stabilizing localized electron states.

The Nobel Prize in Physics 1977: Philip Warren Anderson, Sir Nevill Francis Mott and John Hasbrouck van Vleck *"for their fundamental theoretical investigations of the electronic structure of magnetic and disordered systems"*.

Mott considered the idealized metal-insulator transition for Na crystal by changing the interatomic spacing.



Electron hopping between atoms during conduction

$$\mathrm{Na} + \mathrm{Na} \xrightarrow{U} \mathrm{Na}^{+} + \mathrm{Na}^{-}$$

Bandwidth or band dispersion*:* *energy difference between the highest and lowest level. Bandwidth increases with better orbital overlap. Localization of electrons – narrow bands.*

Hubbard U - energy penalty for transferring an electron between two adjacent sites -assumed to be independent on *a*

After: Feng Duan, Jin Guojun, “Introduction to Condensed Matter Physics”, Vol.1, World Scientific 2005

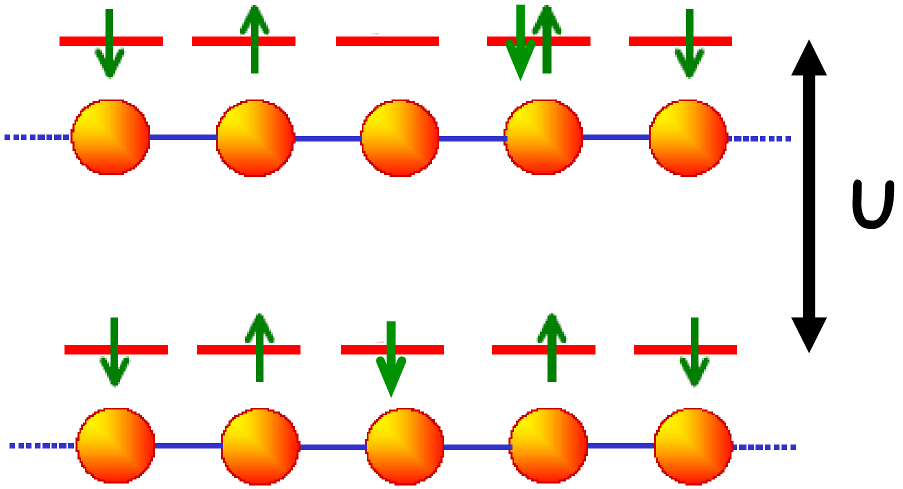
Mott-Hubbard insulators

Coulomb repulsion is described in terms of a *correlation energy*, Hubbard-*U*, which is the energy penalty for transferring an electron between two adjacent sites.

$U \sim I - A$

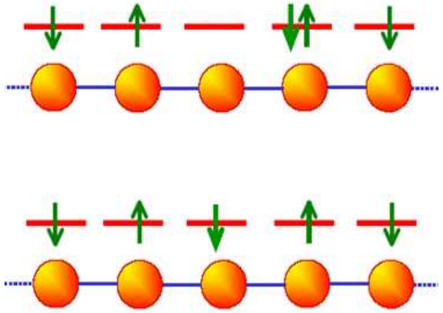
ionization energy (a few eV)

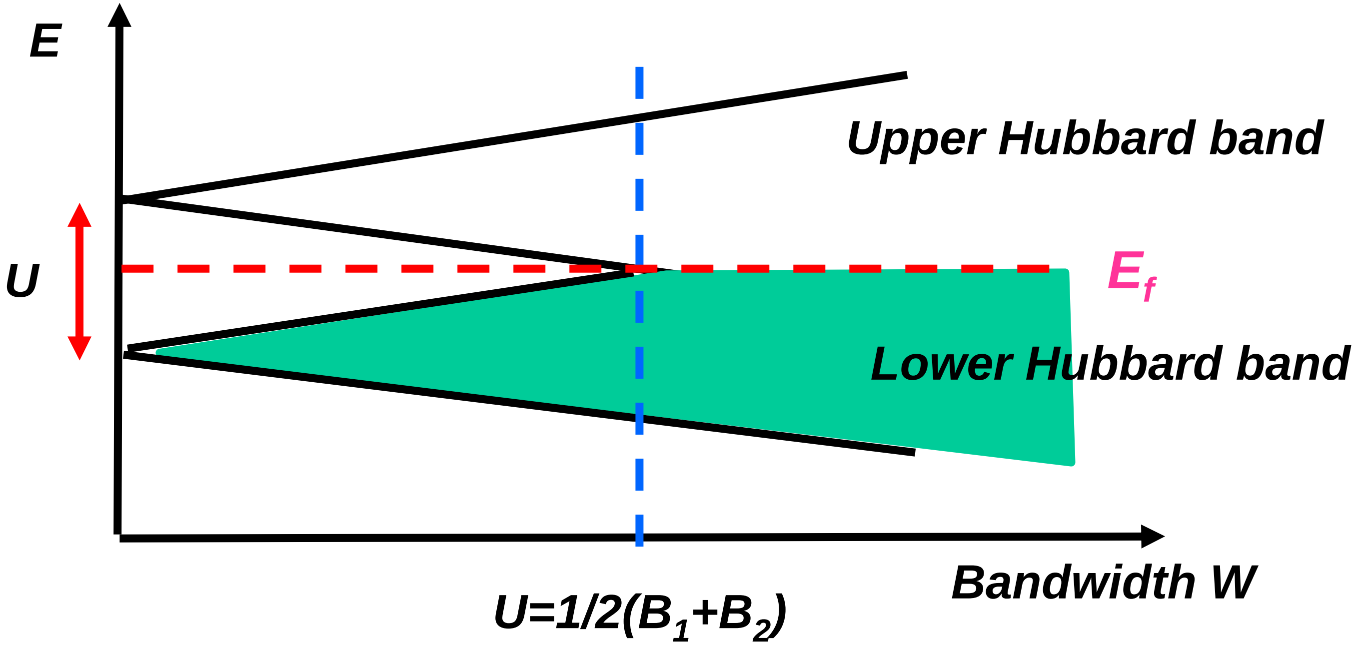
electron affinity



$Ni^{2+} + Ni^{2+} \rightarrow Ni^{3+} + Ni^{+}$

$d^8 + d^8 \rightarrow d^7 + d^9$





If $U > W$, the d band of the transition metal is splitted into sub-bands. For an electron transfer an energy barrier U must be overcome and the material is insulating.

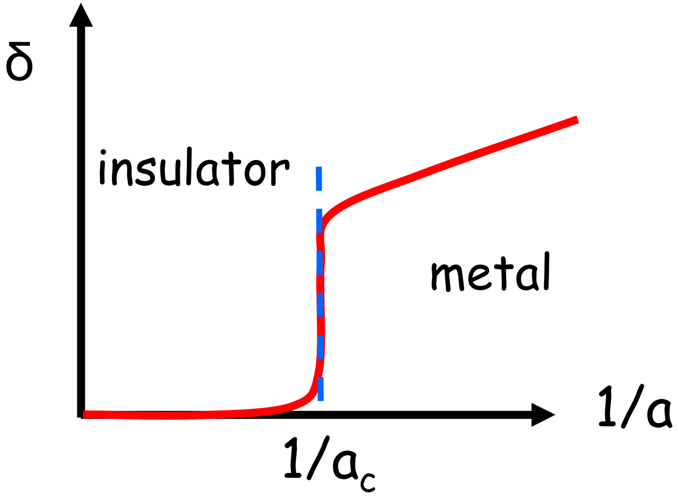
Mott-Hubbard (MH) insulator.

At the point where $W \sim U$, the bands overlap. Beyond this point, there is no energy gap and **the material is metallic**.

The effect of the electron repulsion makes even the half-filled band *insulating* when the interaction between atoms (band width W) is small.

Pressure and temperature dependence

- Every material under high pressure will have metallic properties
- Insulator-Metal transition can be achieved increasing temperature (thermally induced carriers) or doping



Phase diagram of V_2O_3

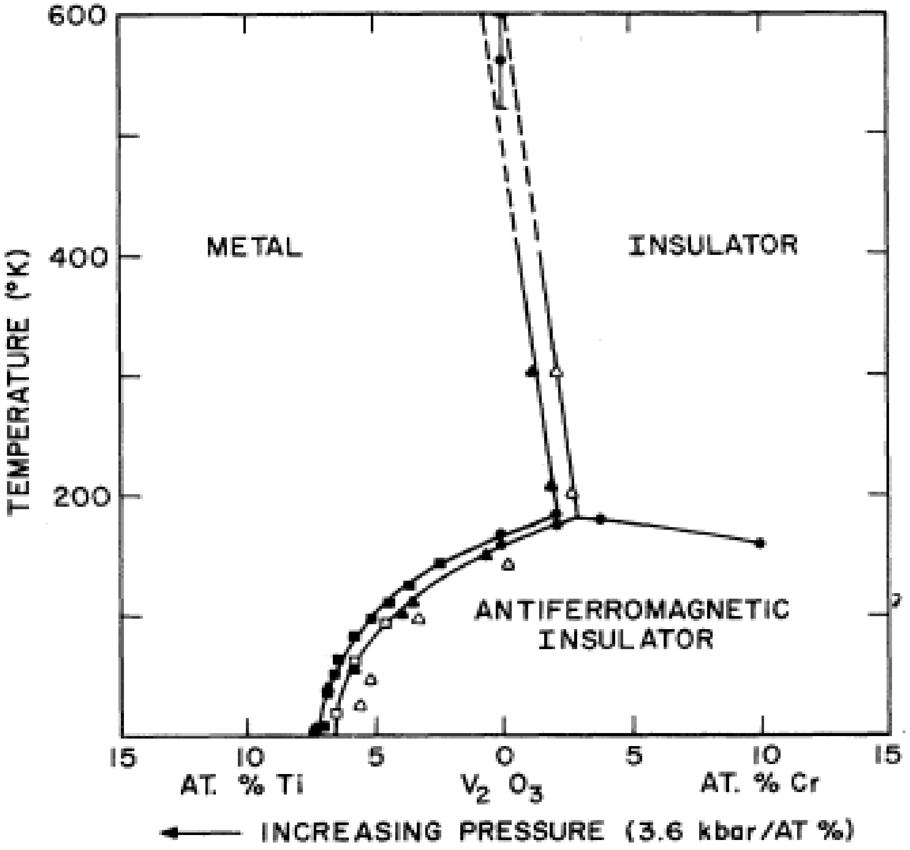


FIG. 3. Generalized phase diagram of transition temperature versus both pressure and at.% Cr and Ti in V_2O_3: Closed circles are from mixed oxides at 1 atm; solid and open squares are V_2O_3 on increasing and decreasing pressure, respectively; solid and open triangles are $(V_{0.96}Cr_{0.04})_2O_3$ on increasing and decreasing pressure. There are large experimental uncertainties (±2 kbar) in the pressure calibration below 10 kbar and therefore in the M–I phase boundary.

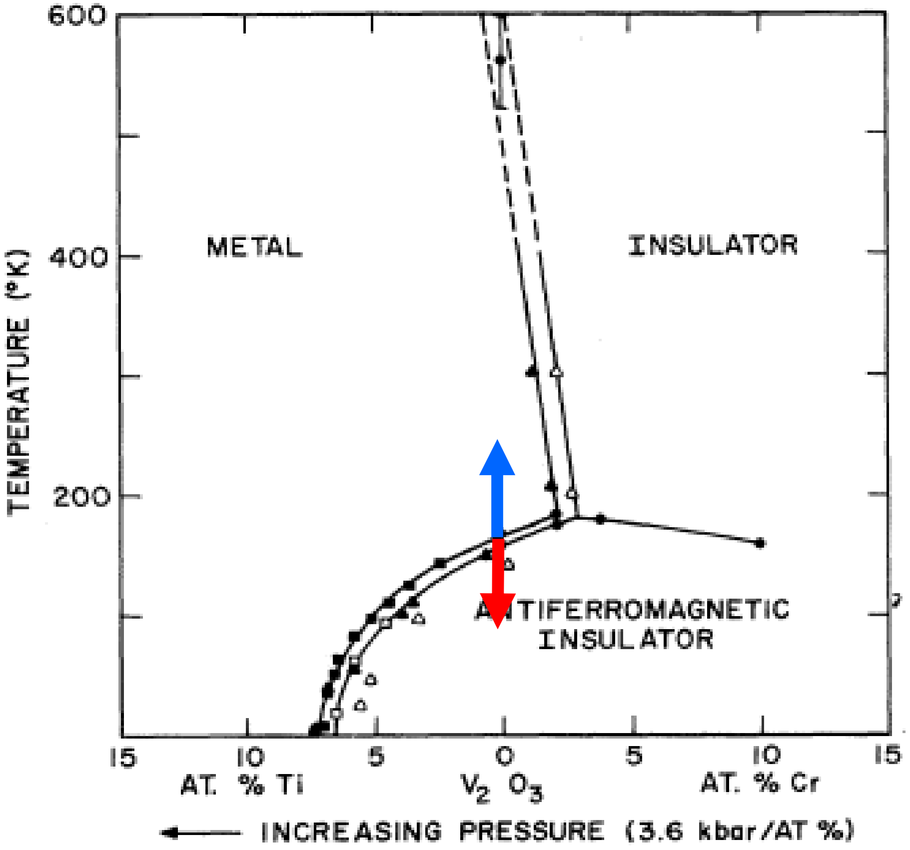
- Mixed oxides (chemical pressure)

Ti^{3+} 0.81 Å; V^{3+} 0.78 Å; Cr^{3+} 0.755 Å

- Pressure experiments for V_2O_3 and $(V_{0.96}Cr_{0.04})_2O_3$

D.B. McWhan et al., PRL, 23 (1969) 1384

V_2O_3 metal-insulator transition



D.B. McWhan et al., PRL, 23 (1969) 1384

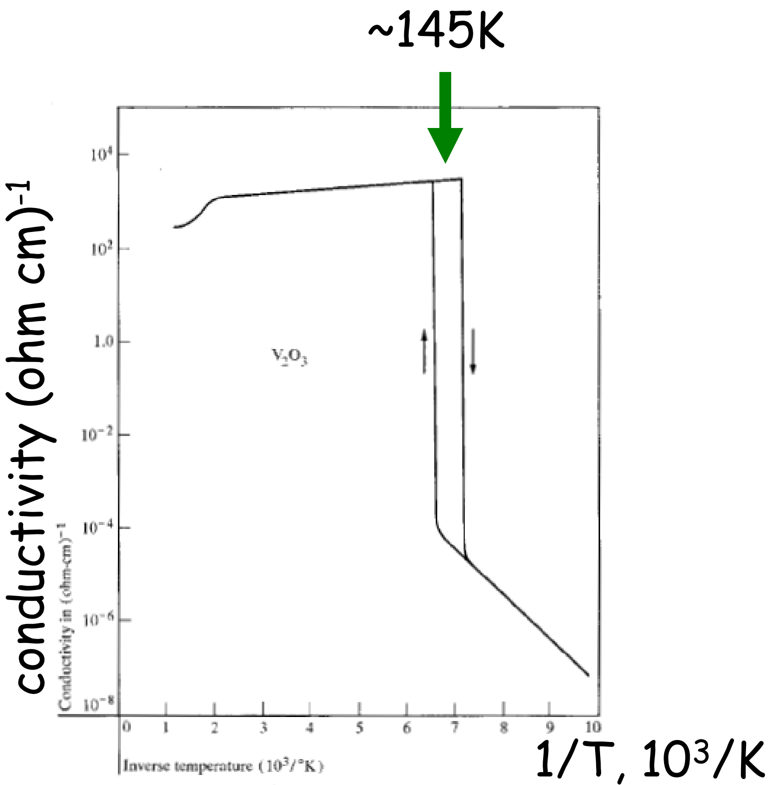
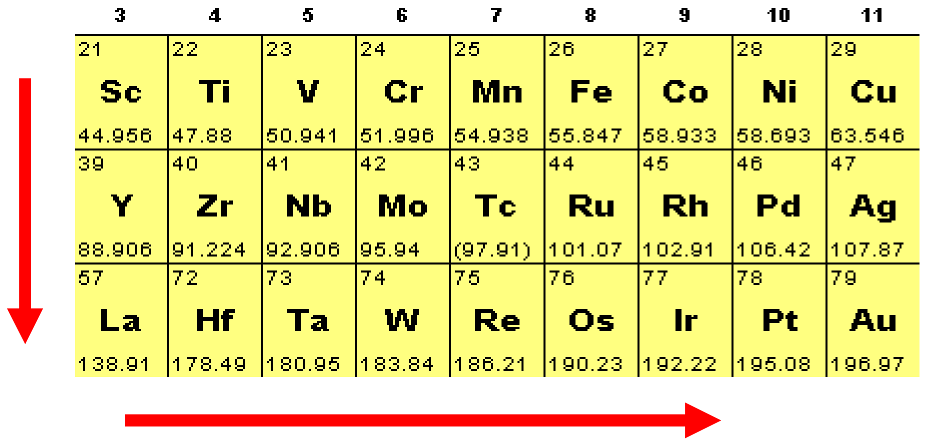


Figure 1 The conductivity of pure V_2O_3 at 1 atm as a function of temperature (from Ref. 15).

J. Feinleib and W. Paul, *Phys. Rev.* 155(1967) 841

General rules

Transition metals TM



3	4	5	6	7	8	9	10	11
21 **Sc** 44.956	22 **Ti** 47.88	23 **V** 50.941	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.847	27 **Co** 58.933	28 **Ni** 58.693	29 **Cu** 63.546
39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.94	43 **Tc** (97.91)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87
57 **La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97

↑W ↓U Larger d orbitals

↑W

- low oxidation state (more electrons) for early TM (good M-M overlap)
- high oxidation state for late TM (good M-O-M overlap: covalent bond)
- for covalent bonds: low electronegativity anions

  halides, O, S, Se, Te, phosphides.....

NiS, CoS and CuS-metals
NiO, CoO and CuO- **(MH) insulators**

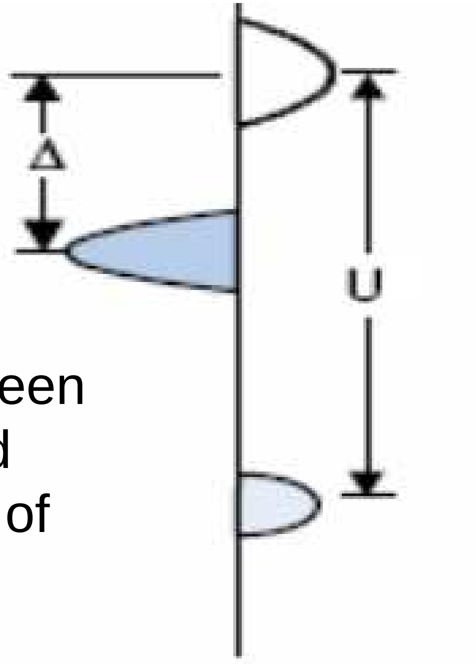
↑U

- electron configuration e.g. Mn^{2+} $3d^5$ has half-filled shell
- other cations in the structure (as e.g. in perovskites ABO_3)

- •Mott-Hubbard models assumes that the band gap is within d-band.
- In many cases one has to consider ligands- e.g. oxide anions in oxides.
- •Additionally to W and U a third parameter has to be considered: Δ gap.

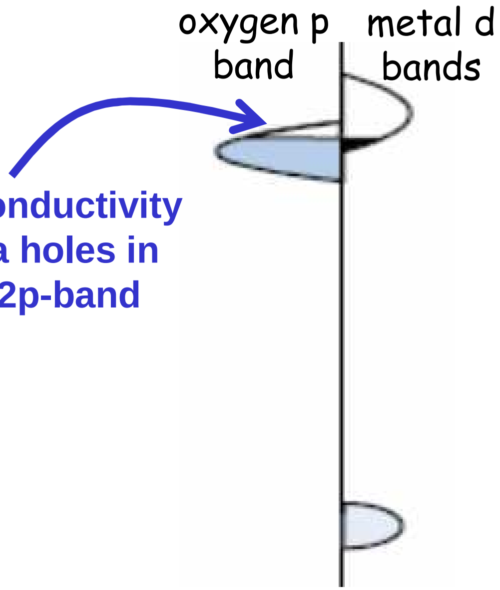
Oxygen p bands

Metal d bands



Δ is a gap between *2p* oxygen band and the *d-band* of the metal.

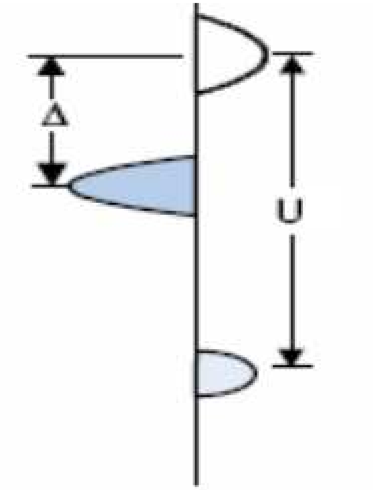
(Semi)Metal



Conductivity via holes in O 2p-band

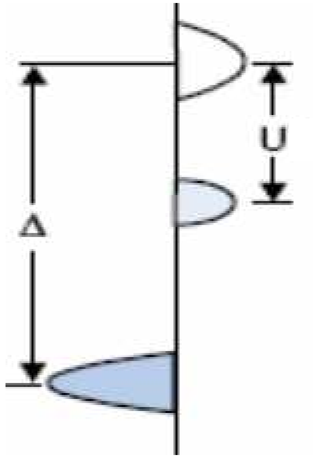
LaCuO$_3$ is a metal
Cu 3d-band and O 2p-band overlap.

Charge-transfer-insulator (semiconductor)



$E_{gap} \approx \Delta$
U is large

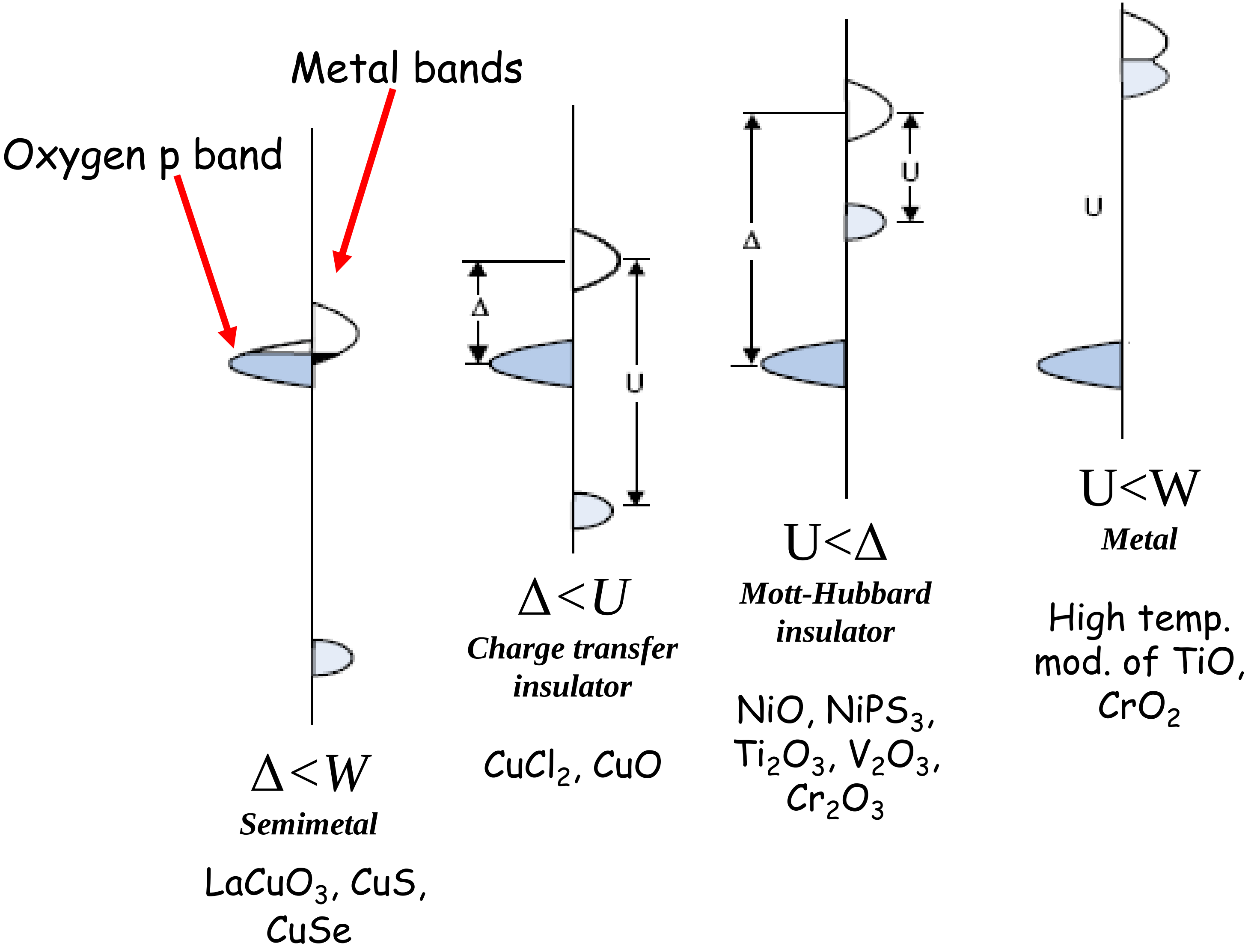
Mott-Hubbard-insulator



$E_{gap} \approx \Delta$

Different Δ/U ratio!

Examples



Oxygen p band

Metal bands

$\Delta < W$

Semimetal

$LaCuO_3$, CuS, CuSe

$\Delta < U$

Charge transfer insulator

$CuCl_2$, CuO

$U < \Delta$

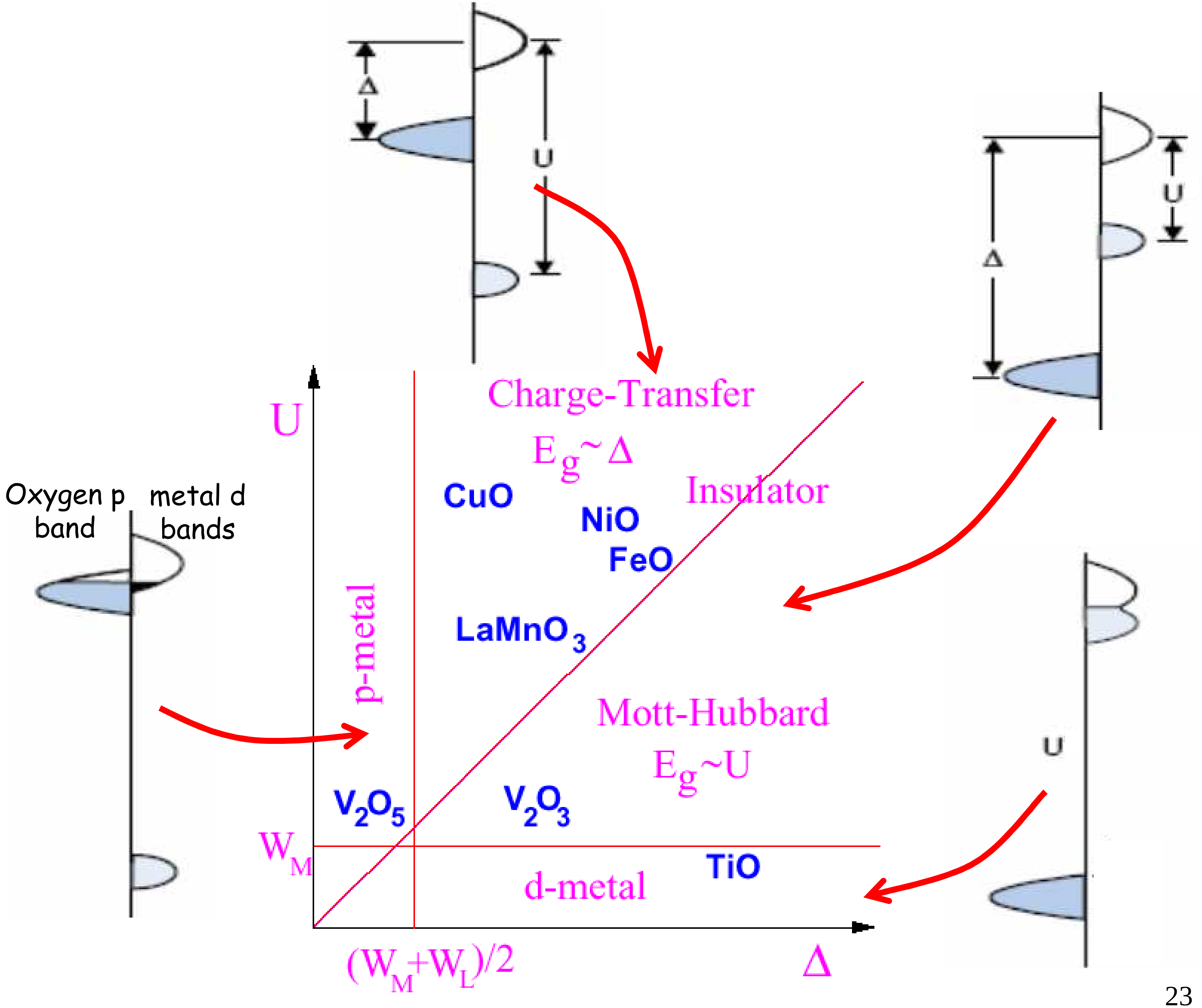
Mott-Hubbard insulator

NiO, $NiPS_3$, Ti_2O_3, V_2O_3, Cr_2O_3

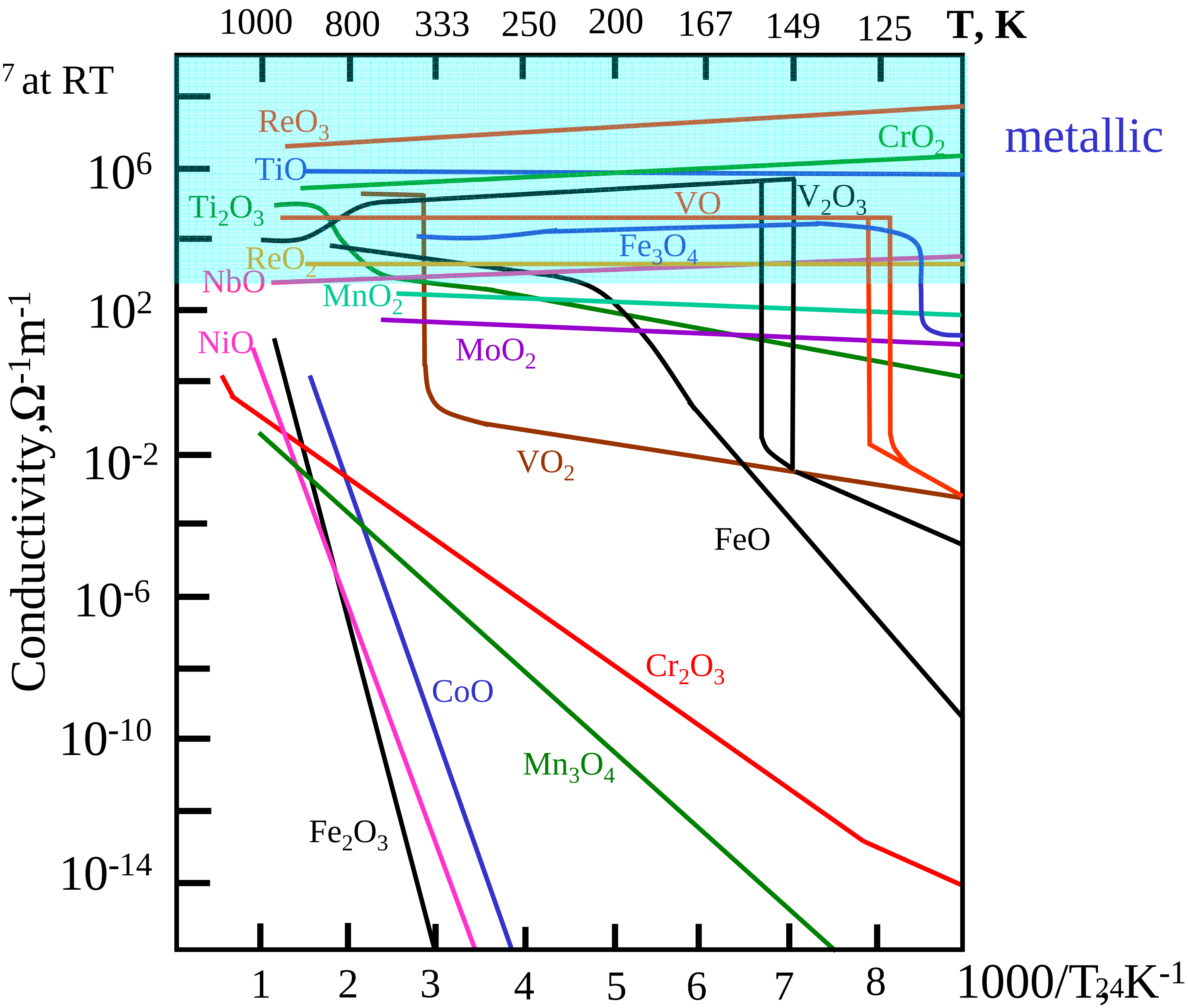
$U < W$

Metal

High temp. mod. of TiO, CrO_2

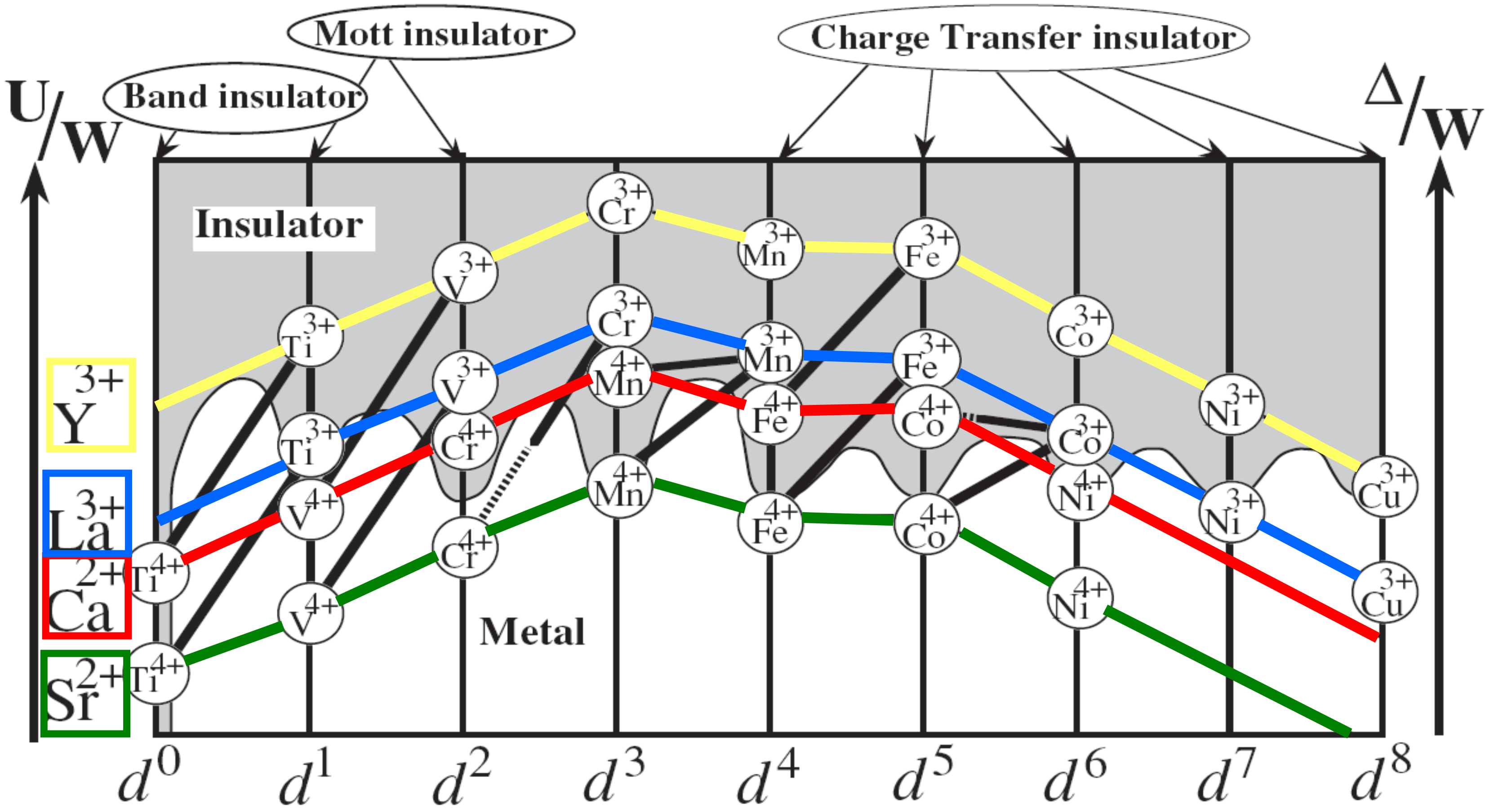

Δ
U
Δ
U
Charge-Transfer
$E_g \sim \Delta$
Insulator
CuO
NiO
FeO
$LaMnO_3$
p-metal
Mott-Hubbard
$E_g \sim U$
V_2O_5
V_2O_3
W_M
TiO
d-metal
$(W_M+W_L)/2$
Δ
U
Oxygen p band
metal d bands
U

Cu $5.9\ 10^7$ at RT



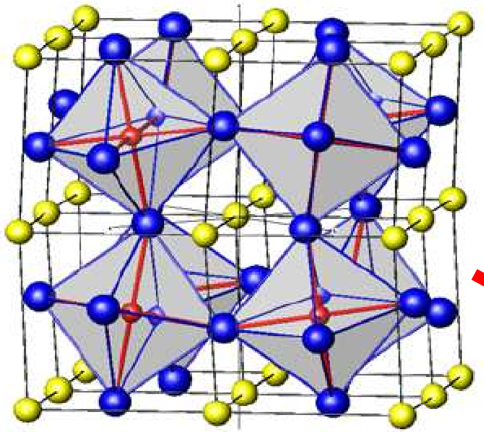
After: Schaumberg, Keramik

Perovskites

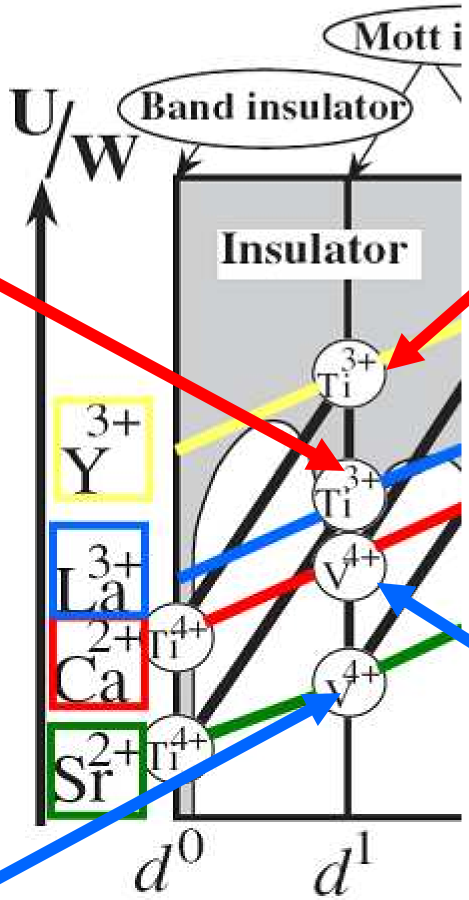


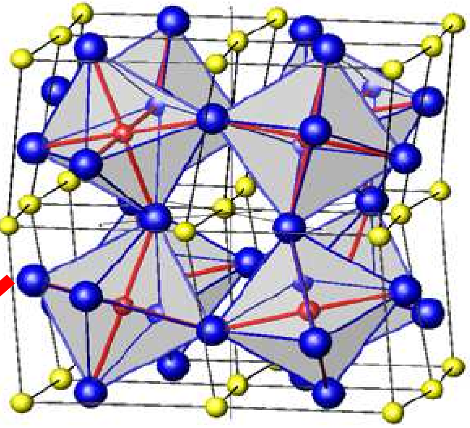
after I. H. Inoue, Semicond. Sci. Technol., 20 (2005) S112

d^1 perovskites

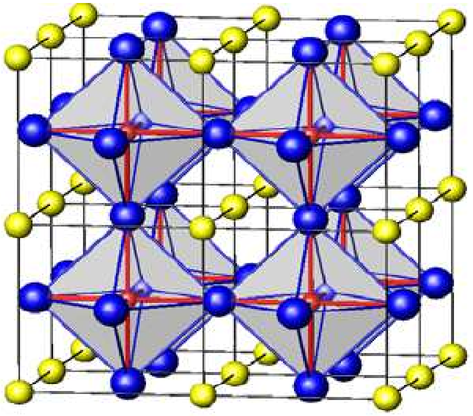


LaTiO$_3$ insulator
gap 0.2eV

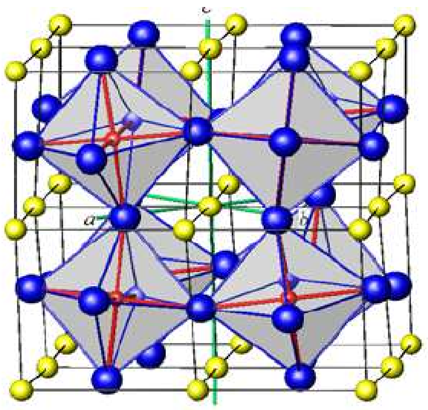




YTiO$_3$ insulator
gap 1.0 eV



SrVO$_3$ metal



CaVO$_3$ metal

Oxygen nonstoichiometric 3d oxides

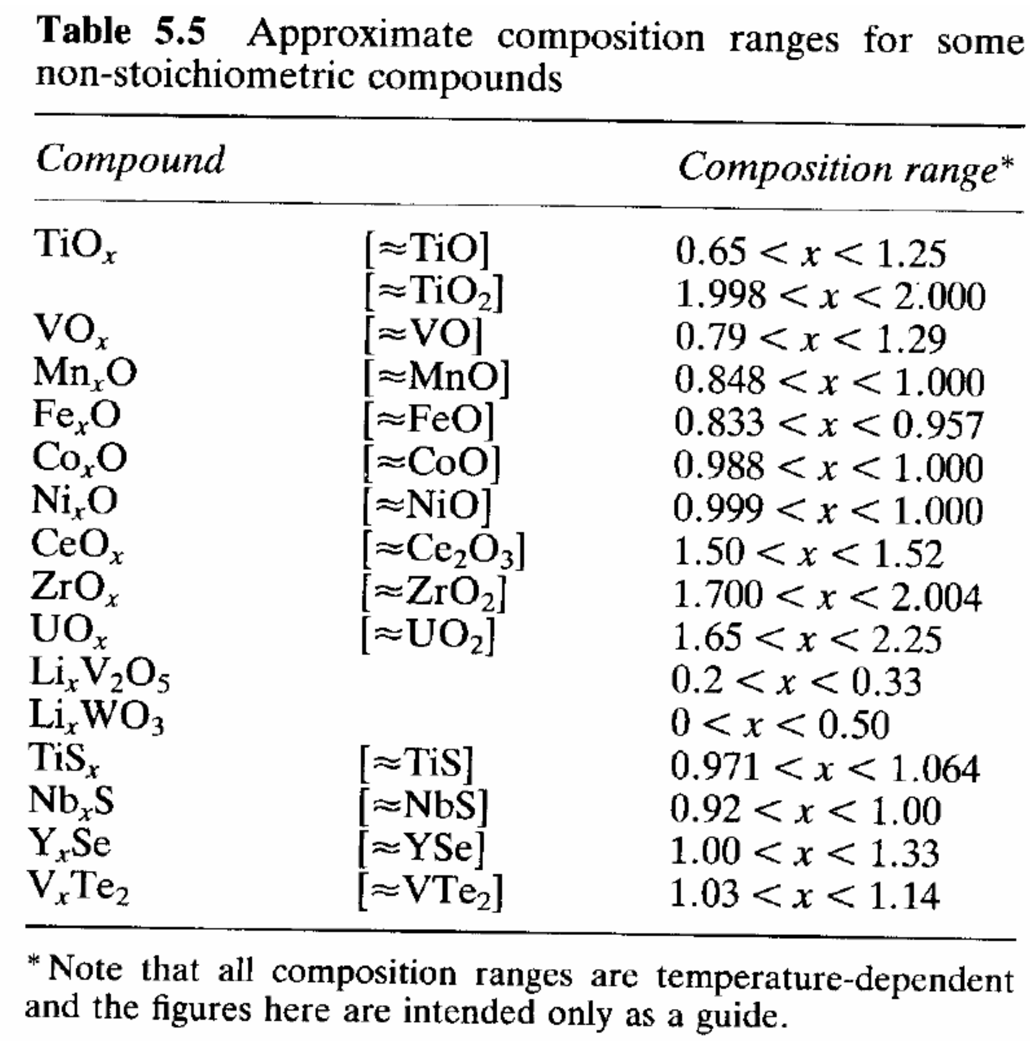


Table 5.5 Approximate composition ranges for some non-stoichiometric compounds

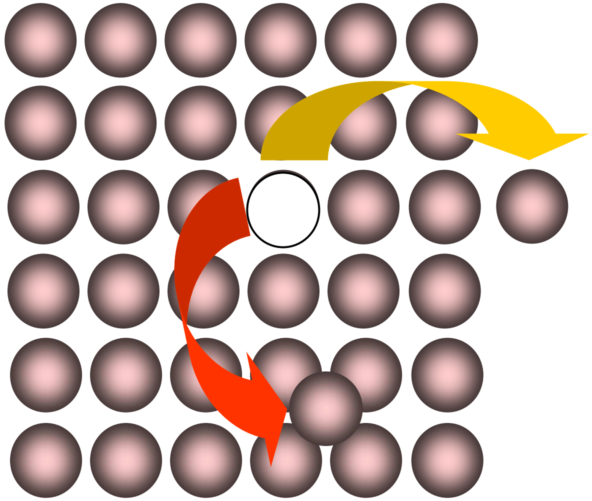
Compound		*Composition range**
TiO_x	[$\approx$TiO]	$0.65 < x < 1.25$
	[$\approx TiO_2$]	$1.998 < x < 2.000$
VO_x	[$\approx$VO]	$0.79 < x < 1.29$
Mn_xO	[$\approx$MnO]	$0.848 < x < 1.000$
Fe_xO	[$\approx$FeO]	$0.833 < x < 0.957$
Co_xO	[$\approx$CoO]	$0.988 < x < 1.000$
Ni_xO	[$\approx$NiO]	$0.999 < x < 1.000$
CeO_x	[$\approx Ce_2O_3$]	$1.50 < x < 1.52$
ZrO_x	[$\approx ZrO_2$]	$1.700 < x < 2.004$
UO_x	[$\approx UO_2$]	$1.65 < x < 2.25$
$Li_xV_2O_5$		$0.2 < x < 0.33$
Li_xWO_3		$0 < x < 0.50$
TiS_x	[$\approx$TiS]	$0.971 < x < 1.064$
Nb_xS	[$\approx$NbS]	$0.92 < x < 1.00$
Y_xSe	[$\approx$YSe]	$1.00 < x < 1.33$
V_xTe_2	[$\approx VTe_2$]	$1.03 < x < 1.14$

* Note that all composition ranges are temperature-dependent and the figures here are intended only as a guide.

Does the electrical conductivity depend on oxygen content and cation doping?

Lattice defects

Schottky- und Frenkel-defects in crystals

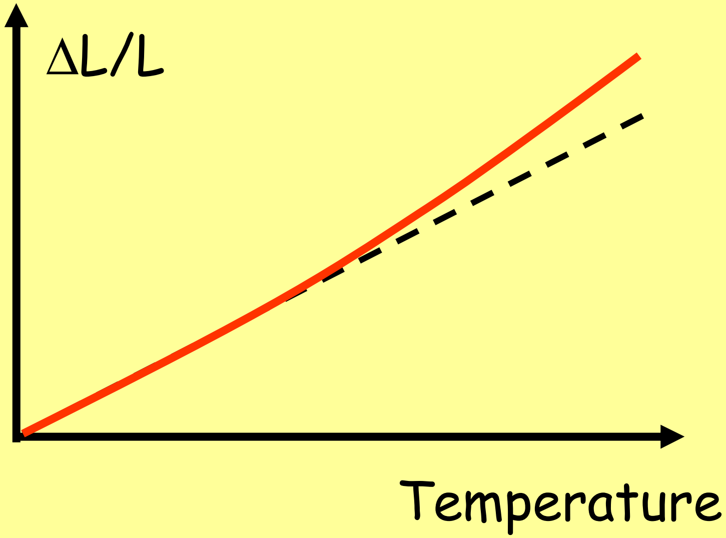


Schottky-defekts:
The volume of the crystal will increase

Frenkel-defekts:
The volume of the crystal stays constant

Dilatometer

Schottky-defects



Defect concentration n/N_0

$$\frac{n}{N_0} \cong \exp\left(\frac{-E_V}{kT}\right)$$

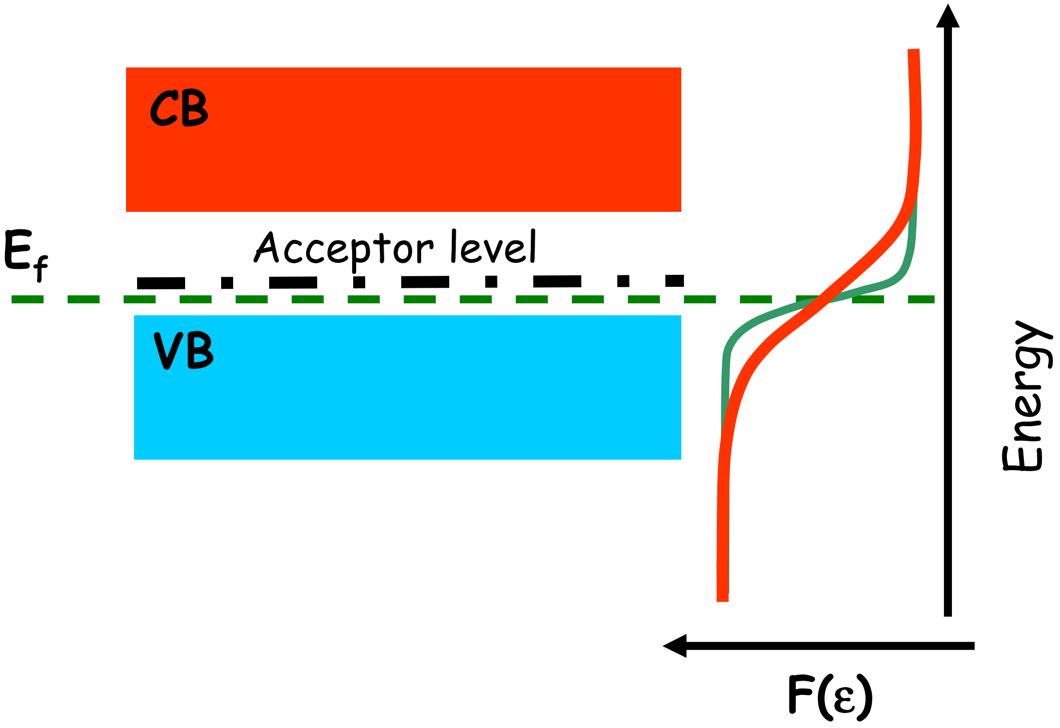
Temperature [°C]	Activation Energy eV		
	1	2	8
100	$3 \cdot 10^{-14}$	$1 \cdot 10^{-27}$	$1 \cdot 10^{-108}$
500	$3 \cdot 10^{-7}$	$1 \cdot 10^{-13}$	$8 \cdot 10^{-53}$
1000	$1 \cdot 10^{-4}$	$1 \cdot 10^{-8}$	$2 \cdot 10^{-32}$
1500	$1 \cdot 10^{-3}$	$2 \cdot 10^{-6}$	$2 \cdot 10^{-23}$
2000	$6 \cdot 10^{-3}$	$4 \cdot 10^{-5}$	$2 \cdot 10^{-18}$

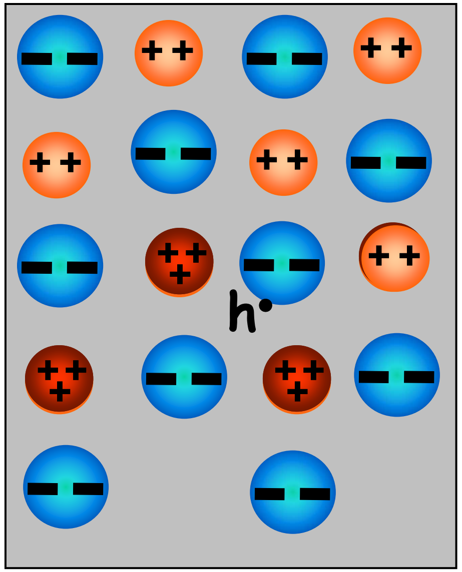
Fe$_{1-x}$O (FeO$_{1+x}$) semiconductor type p

$$4Fe^{x}_{Fe} + O_2 \xrightarrow{FeO} 4Fe^{\bullet}_{Fe} + 2O^{x}_{O} + 2V''_{Fe}$$

$Fe^{\bullet}_{Fe}$ ion can trap an electron from the valence band.
In VB a hole is created.

$$Fe^{\bullet}_{Fe} \xrightarrow{FeO} Fe^{x}_{Fe} + h^{\bullet}$$



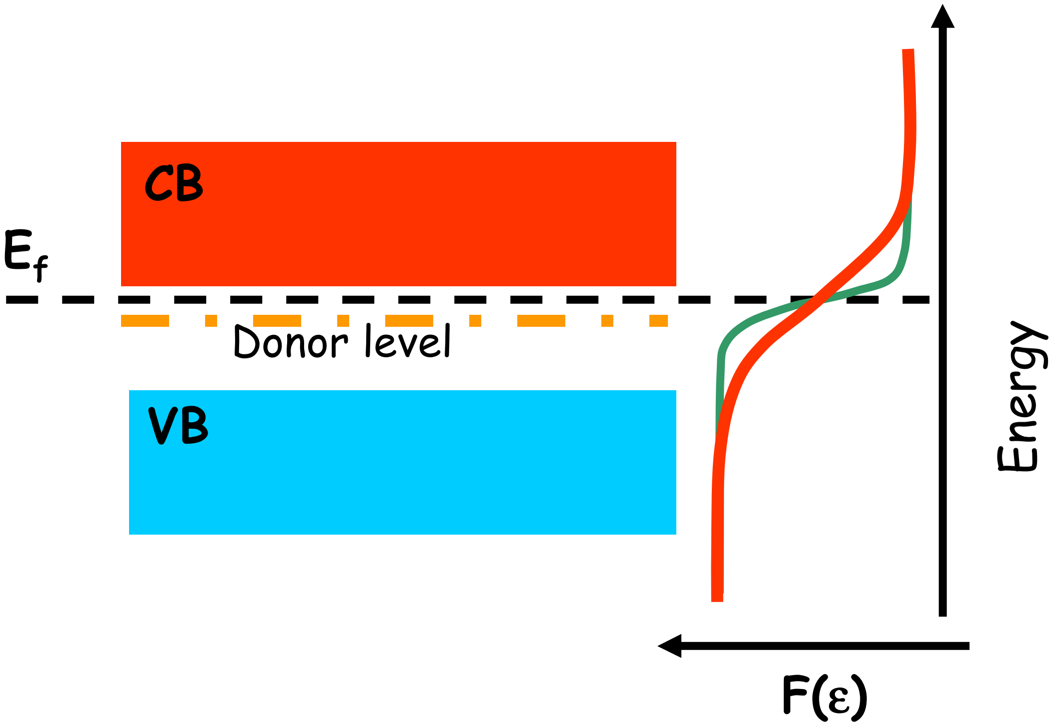


TiO_{2-x} semiconductor type n

$$2Ti^{x}_{Ti} + O^{x}_{O} \xrightarrow{TiO_2} 2Ti'_{Ti} + V^{\bullet\bullet}_{O} + 0.5\ O_2$$

Ti^4

$$Ti'_{Ti} \xrightarrow{TiO_2} Ti^{x}_{Ti} + e'$$



Donor level is situated close to the conductive band.

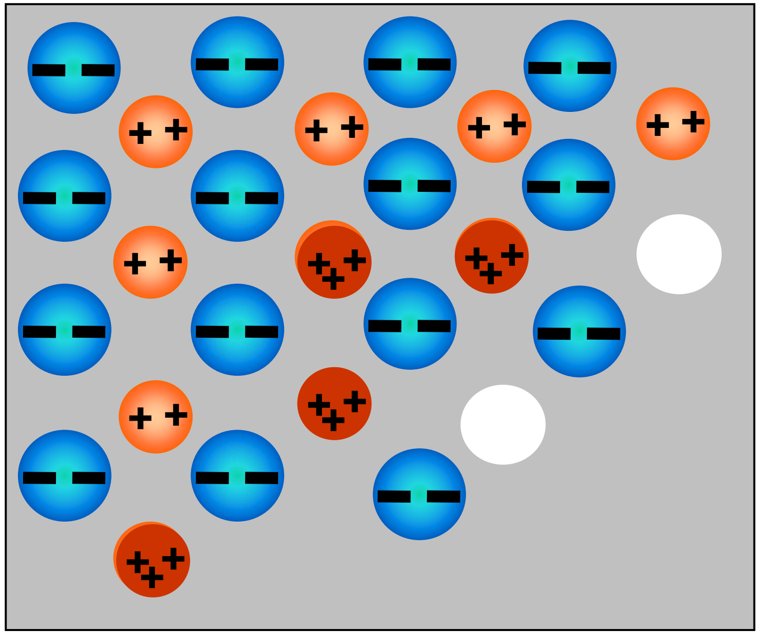
The donor cation Ti'_{Ti} (Ti^{3+}) can inject an electron into conducting band.

Defect semiconductor. $Ni_{1-\delta}O$

p

In NiO nickel vacancies are created when oxidized with oxygen. The charge of the additional oxygen sites is compensated by oxidation of some nickel sites to Ni^{3+}. Through the oxidation the volume of the material increases.

$$0.5O_2 + 2Ni_{Ni}^{\times} \xrightarrow{NiO} V_{Ni}^{//} + 2Ni_{Ni}^{\bullet} + O_O^{\times}$$

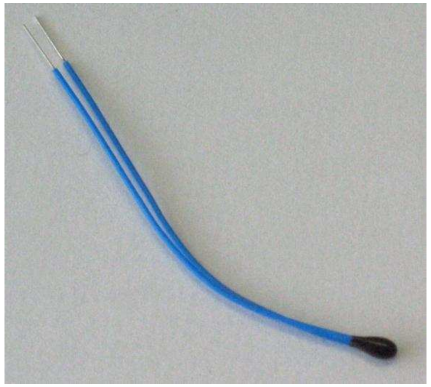


$$Ni_{Ni}^{\bullet} \xrightarrow{NiO} Ni_{Ni}^{\times} + h^{\bullet}$$

Ni^{3+} sites are electron acceptors:

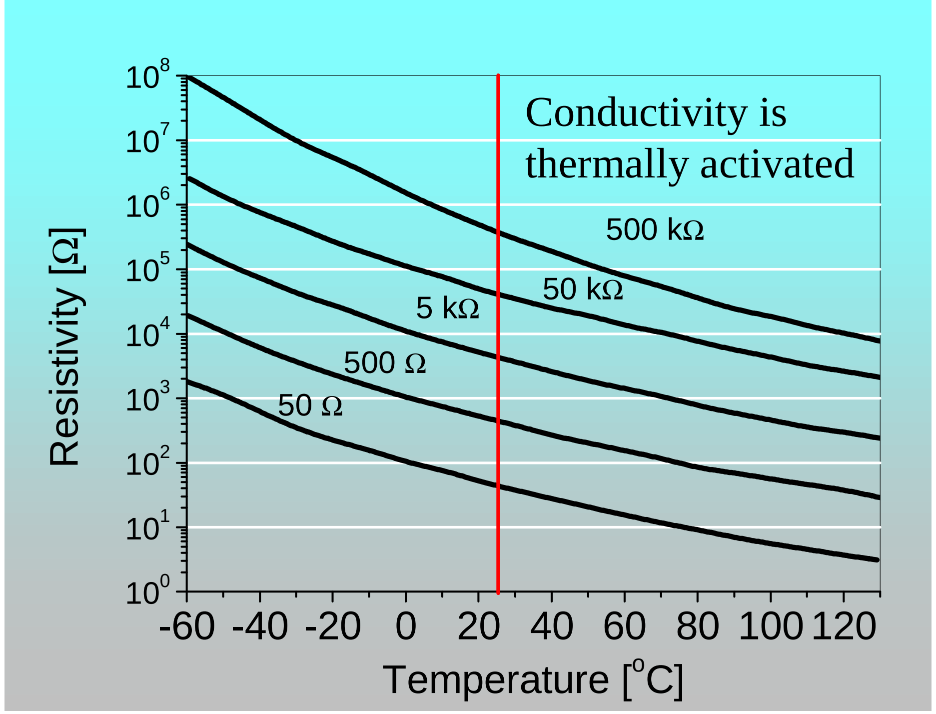
$$Ni_{Ni}^{\bullet} + e^{/} + h^{\bullet} \xrightarrow{NiO} Ni_{Ni}^{\times} + h^{\bullet}$$

Application ceramic semiconductors



NTC- ***thermistors*** (**N**egative **T**emperature **C**oefficient- thermal resistor)

$$\rho(T) = \rho_0 \exp\left(\frac{B}{T}\right) \qquad B = -E_A / k$$



Till 300°C spinels:

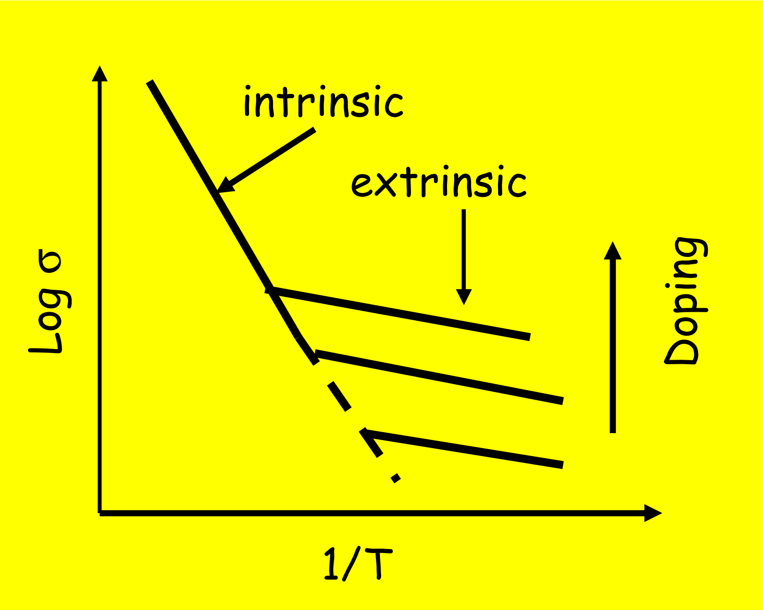
Mn_3O_4

$NiMn_2O_4$

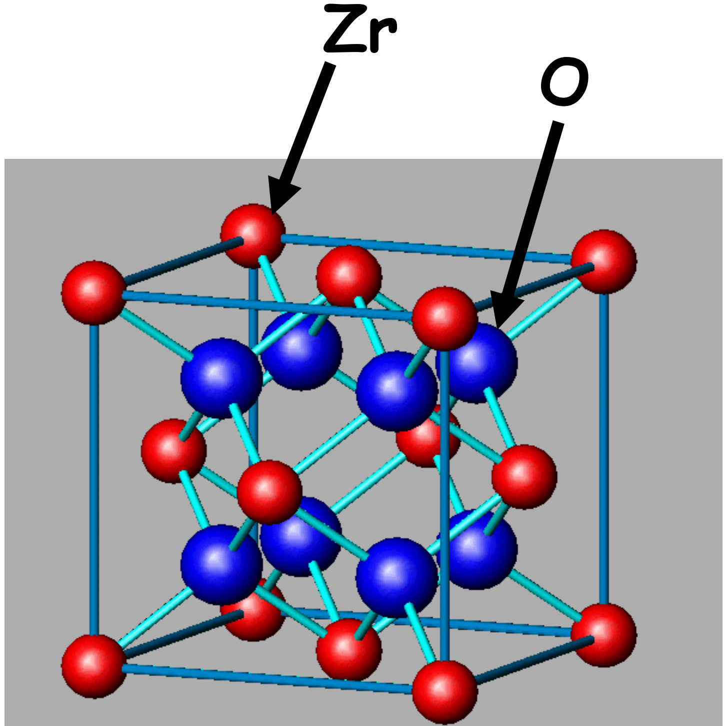
$CoFe_2O_4$

Till ca. 1000°C rare earth oxides eg.:70%Sm_2O_3 30%Tb_2O_3

Extrinsic ionic conductors



Conductivity increase by a doping.

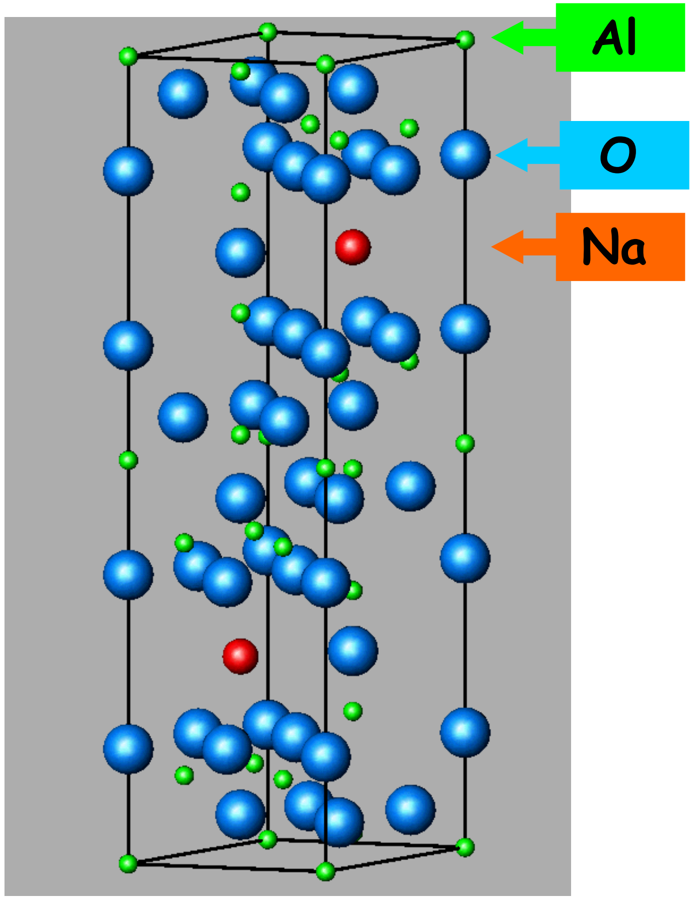


Fluorite structure (CaF_2-type)

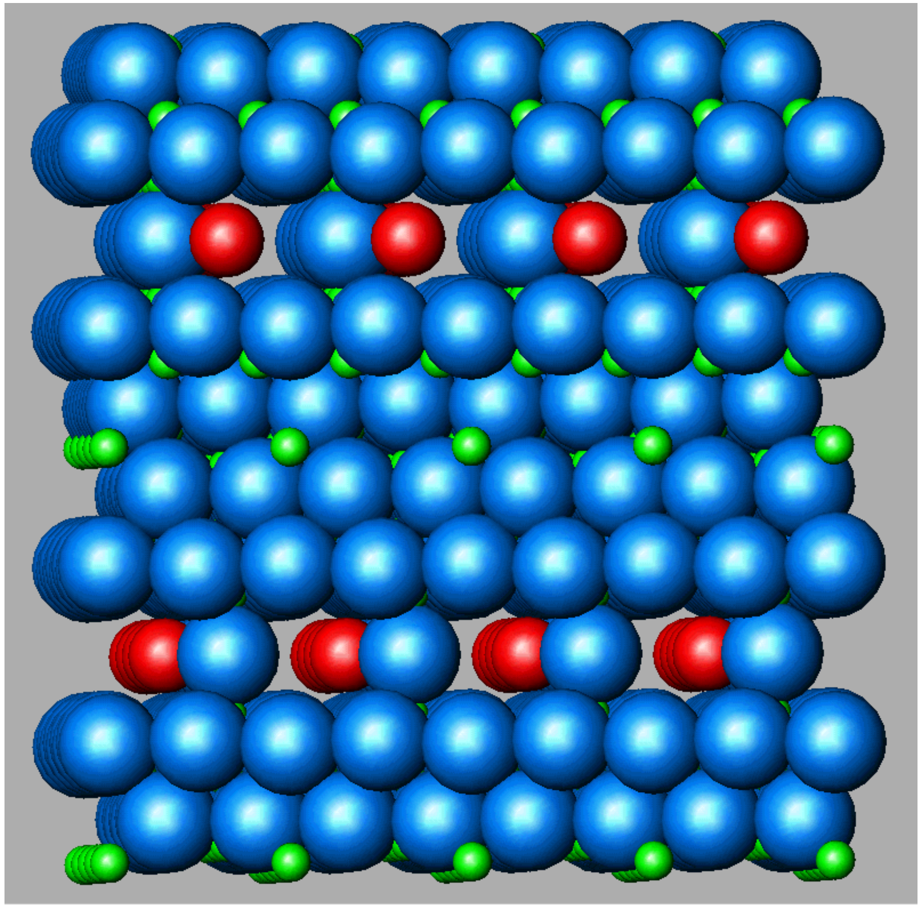
Oxides with fluorite structure (ZrO_2, ThO_2, CeO_2) doped with CaO, MgO, Y_2O_3, Sc_2O_3 and La_2O_3

$$Y_2O_3 \xrightarrow{ZrO_2} 2Y'_{Ce} + 3O^{x}_{O} + V^{\bullet\bullet}_{O}$$

Intrinsic superionic conductor.
β-aluminum oxide- Na^+ ionic conductor

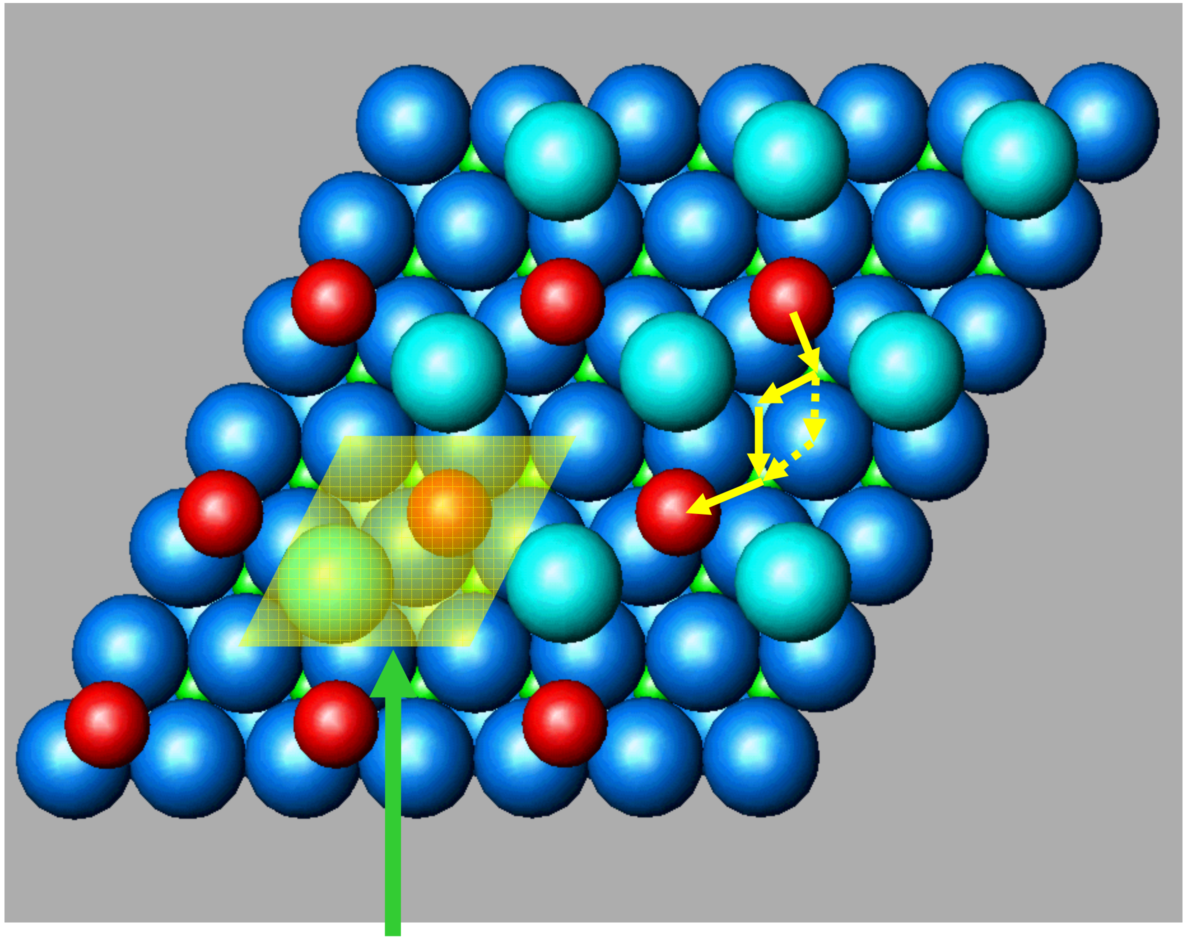


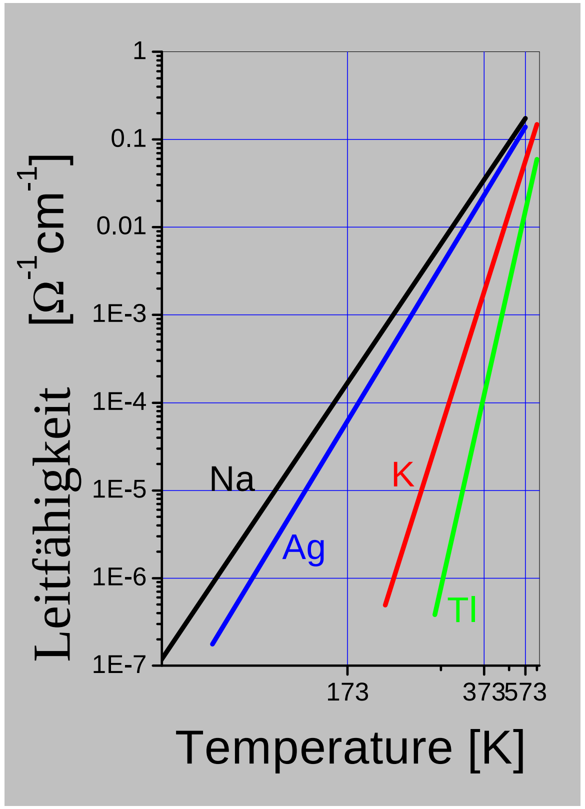
β-aluminum oxide $Na_2O \cdot 11Al_2O_3$



Layered structure of β-aluminum oxide

β-Aluminiumoxid II

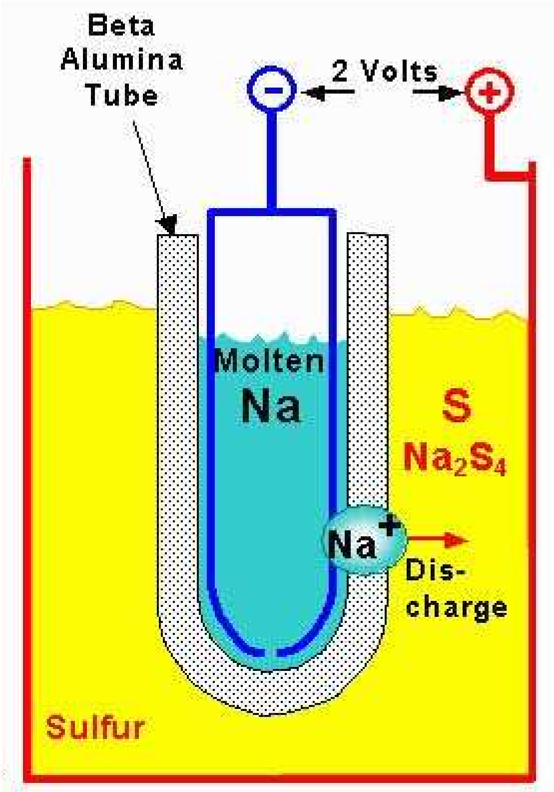




Hexagonal unit cell.

For larger cations (K^+, Tl^+) lower conductivity is observed

Sodium Sulfur Cell



High energy density, high efficiency of charge/discharge (89–92%) and long cycle life, and is fabricated from inexpensive materials.

High operating temperatures of 300 to 350 °C and the highly corrosive sodium polysulfides and sodium.

- Anode

$$2Na_{(l)} \rightarrow 2Na^+ + 2e^-$$

+ Cathode

$$2Na^+ + 5S_{(l)} + 2e^- \rightarrow Na_2S_{5(l)}$$

Discharging

$$2Na_{(l)} + 5S_{(l)} \rightarrow Na_2S_{5(l)}$$

The sodium is separated by a beta-alumina solid electrolyte (BASE) cylinder from the container of molten sulfur.

Charging

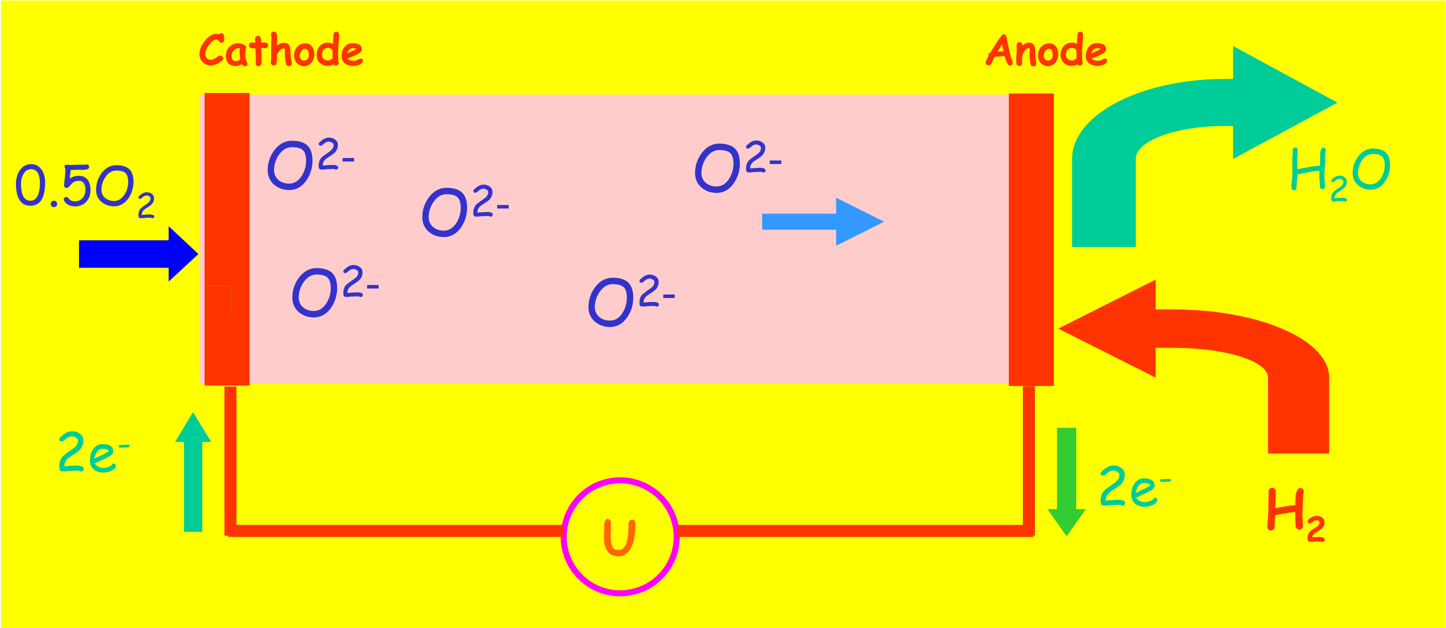
$$Na_2S_{5(l)} \rightarrow 2Na_{(l)} + 5S_{(l)}$$

Solid Oxide Fuel Cells (SOFC)

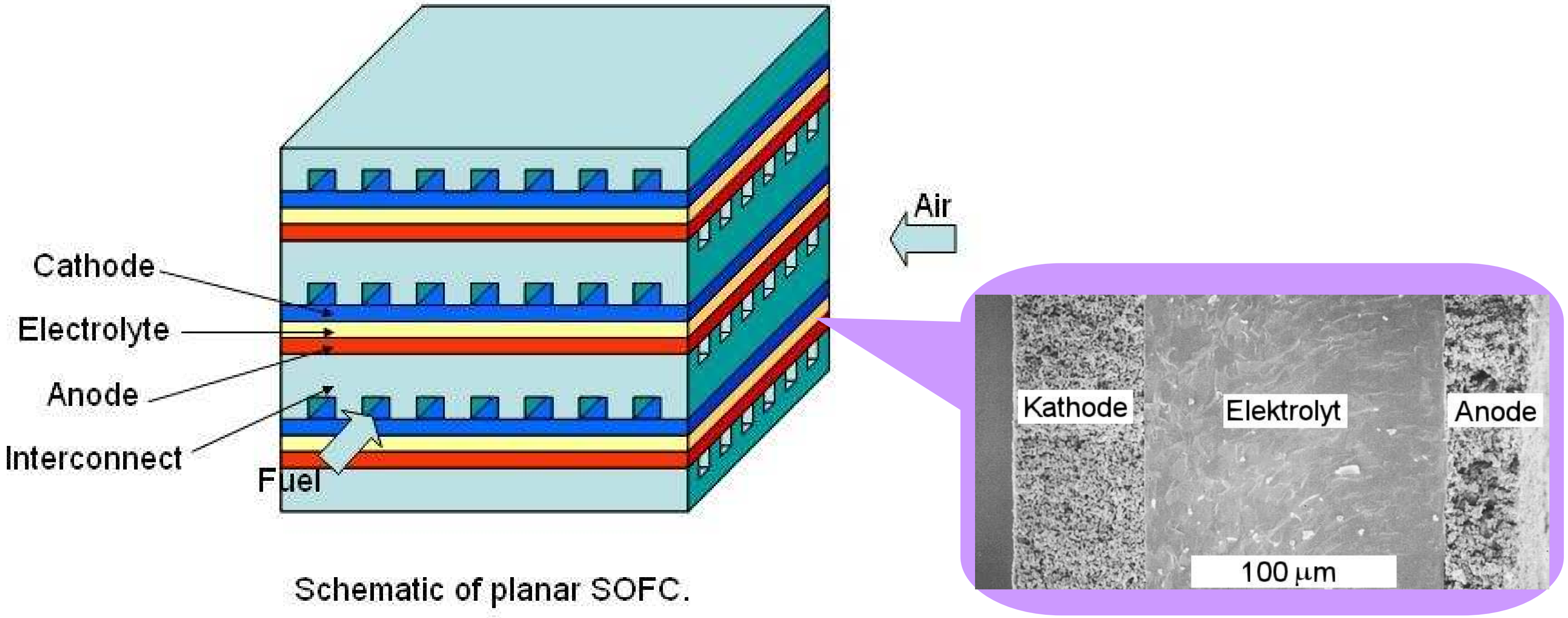
Electrochemical conversion device that produces electricity directly from oxidizing a fuel.

$$\frac{1}{2} O_2 + H_2 \rightarrow H_2O$$

Temperature range: 800-1000°C

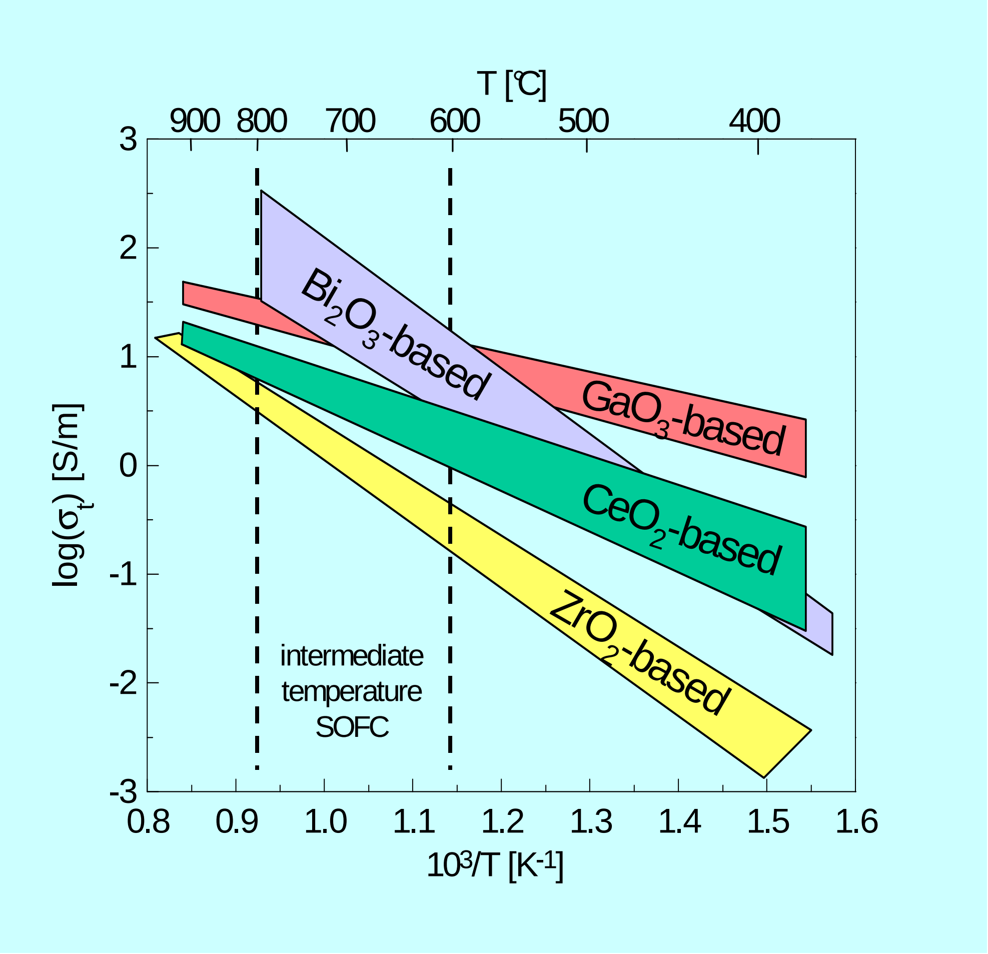


Solid electrolyte- Solid Oxide Fuel Cells



Schematic of planar SOFC.

SOFC. Solid Elektrolyte



- High stability in air and also strongly reduced atmosphere at high temperature

Tetragonal or cubic stabilized ZrO_2 (3, resp. 8 mol% Y_2O_3 in ZrO_2). Thickness ~ 200µm.

Stability other materials (e.g. doped CeO_2) in reduced atmosphere is not sufficient. Partial reduction gives electronic conductivity!

PostAuto
Die gelbe Klasse.

PostAuto Schweiz AG

→zurück

Im Aargau fahren die ersten Postautos mit Brennstoffzellenantrieb

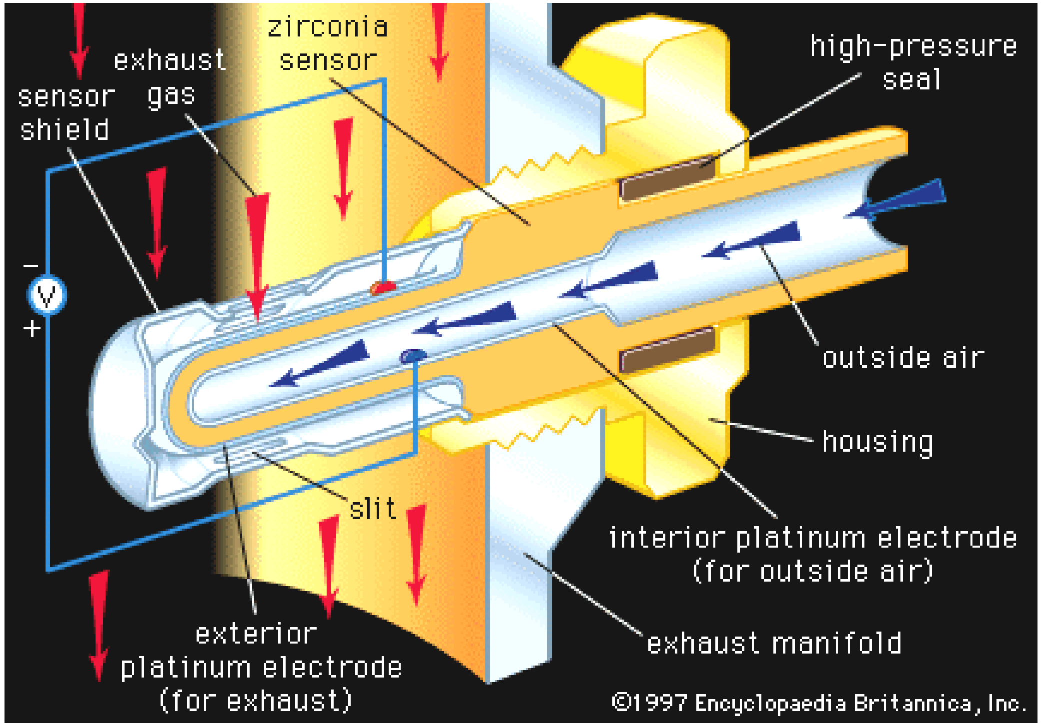
Mitteilung vom 09.11.2011

PostAuto setzt als erstes Schweizer Unternehmen die Brennstoffzellentechnologie im öffentlichen Verkehr ein. Ab Fahrplanwechsel im Dezember 2011 fahren auf PostAuto-Linien in und um Brugg (AG) Brennstoffzellenpostautos. Der Langzeittest wird von verschiedenen Partnern massgeblich unterstützt, wie etwa vom Kanton Aargau, dem Bundesamt für Energie und der Europäischen Union.

In den nächsten fünf Jahren testet PostAuto den Brennstoffzellenantrieb und nutzt als erstes Schweizer ÖV-Unternehmen Wasserstoff als Treibstoff. Ab 11. Dezember 2011 nehmen fünf Brennstoffzellenpostautos in Brugg schrittweise den Linienbetrieb auf.

Oxygen sensor (lambda sensor)

$$C_mH_n + (m+n/4)O_2 \rightarrow mCO_2 + n/2H_2O$$



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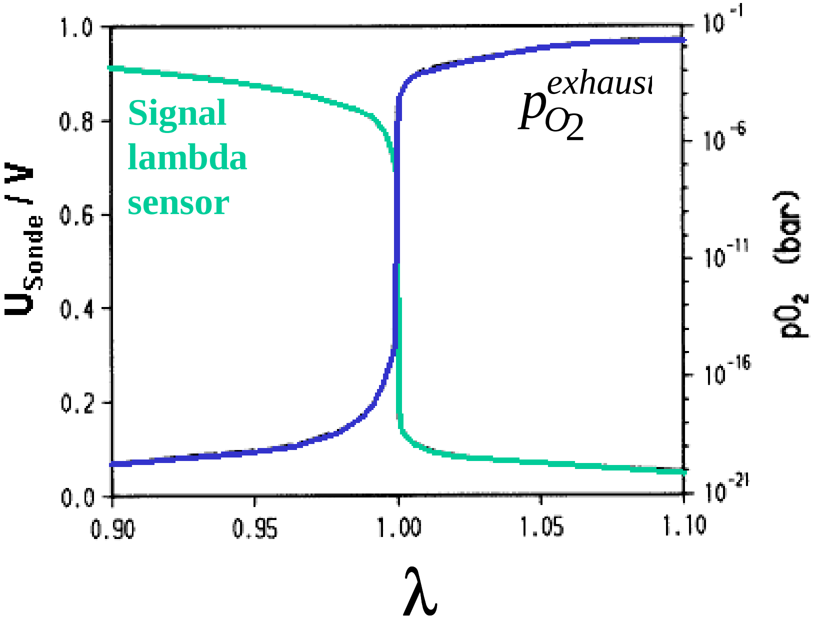
$$\lambda = \frac{\text{Delivered amount of } O_2}{\text{Stoichiometic amount of } O_2}$$

$\lambda<1$	fuel excess
$\lambda=1$	stoichiometric combustion
$\lambda>1$	oxygen excess



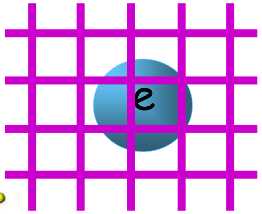
$$E = \frac{RT}{4F} \cdot \ln\left(\frac{p_{O2}^{Air}}{p_{O2}^{exhaust}}\right)$$

Oxygen sensor (lambda sensor)

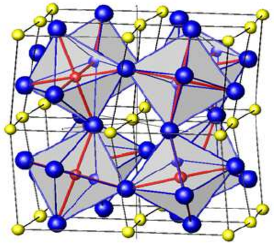
Summary

Itinerant and localized electrons (holes) in solids

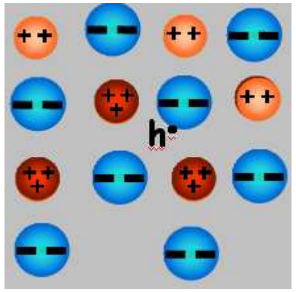
- Mott-Hubbard transition



- Structure influence



- Doping (stoichiometry)



Ions in solids as charge carriers