

Semicondutores Extrínsecos

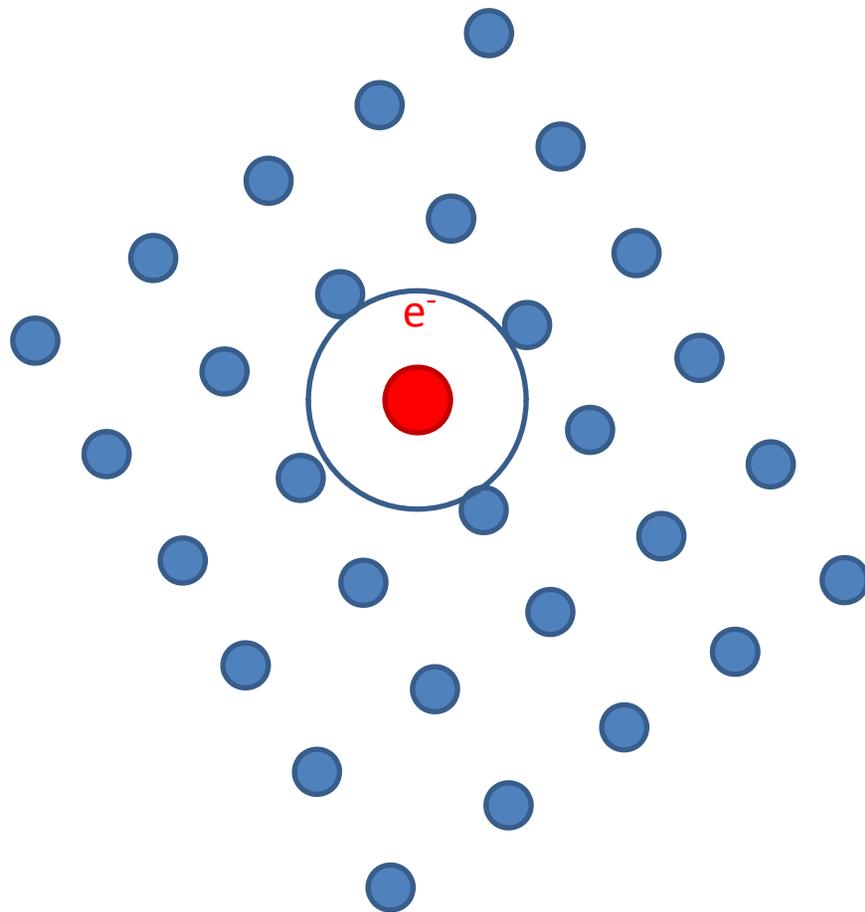
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra																

Tipo p:
 Impurezas com **3**
 electrões de valência

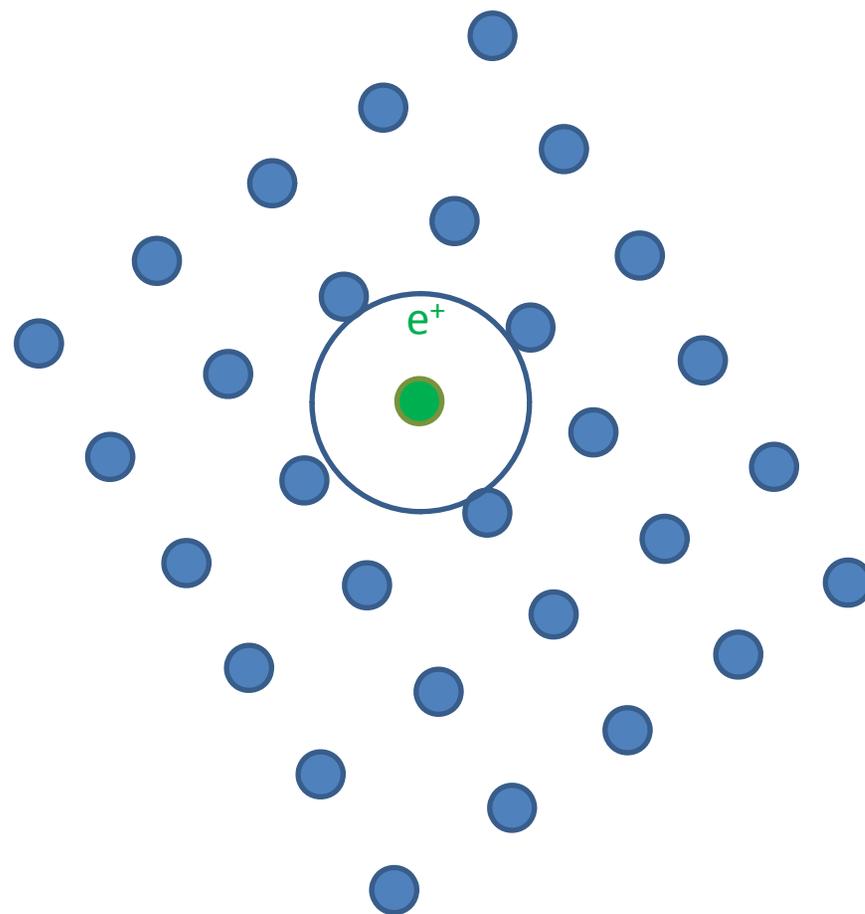
B	C	N	O
Al	Si	P	S
Ga	Ge	As	Se
In	Sn	Sb	Te

Tipo n:
 Impurezas com **5**
 electrões de valência
 +
Li

Si ($[Ne]3s^2 3p^2$) dopado com **As** ($[Ar]3d^{10} 4s^2 4p^3$)



Si ($[Ne]3s^2 3p^2$) dopado com **B** ($1s^2 2s^2 2p^1$)



Impurezas do Grupo 15

Diagrama de Bandas de Energia

[As(Si₄)]

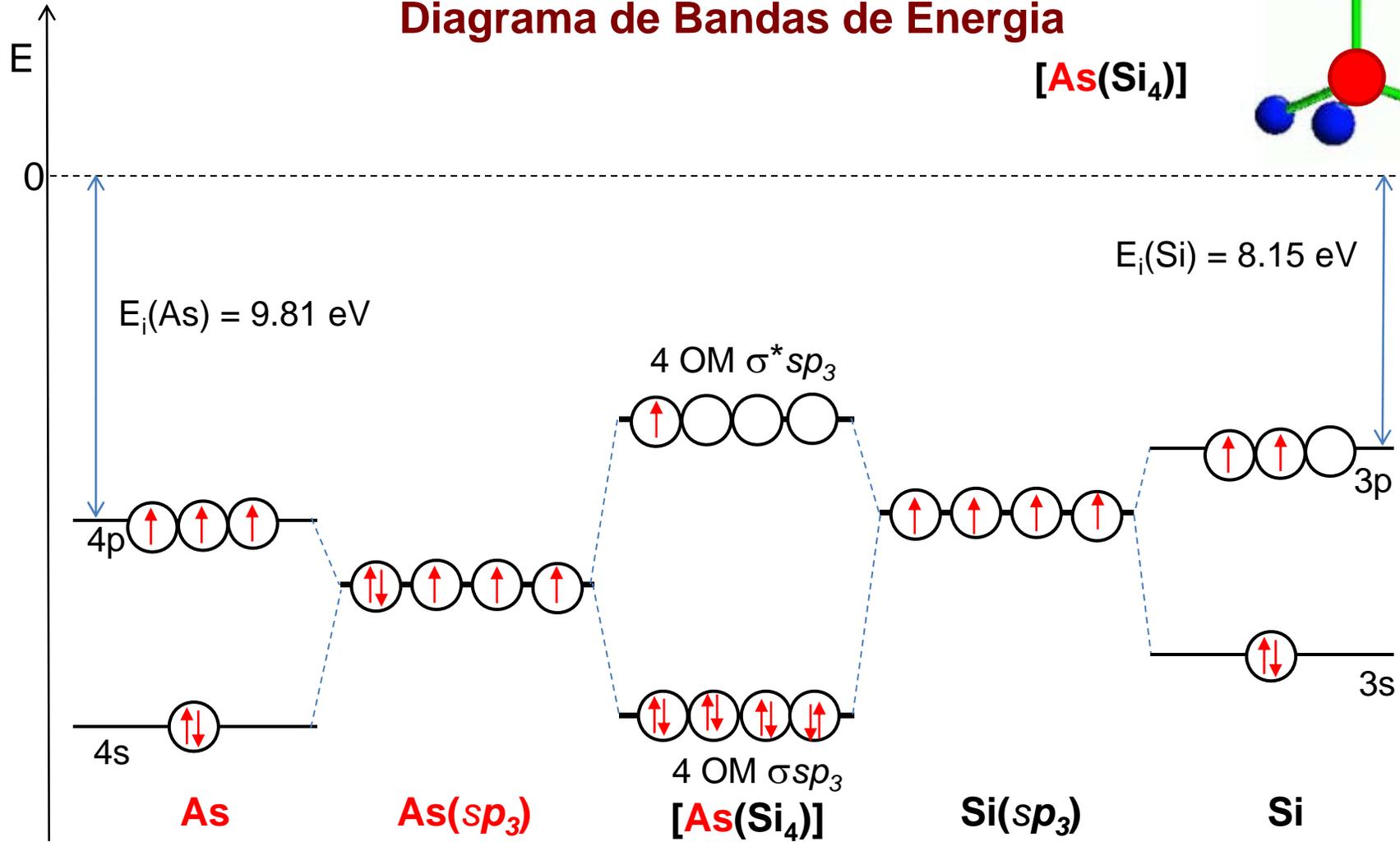
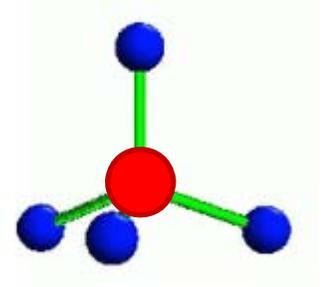


Diagrama de Bandas de Energia

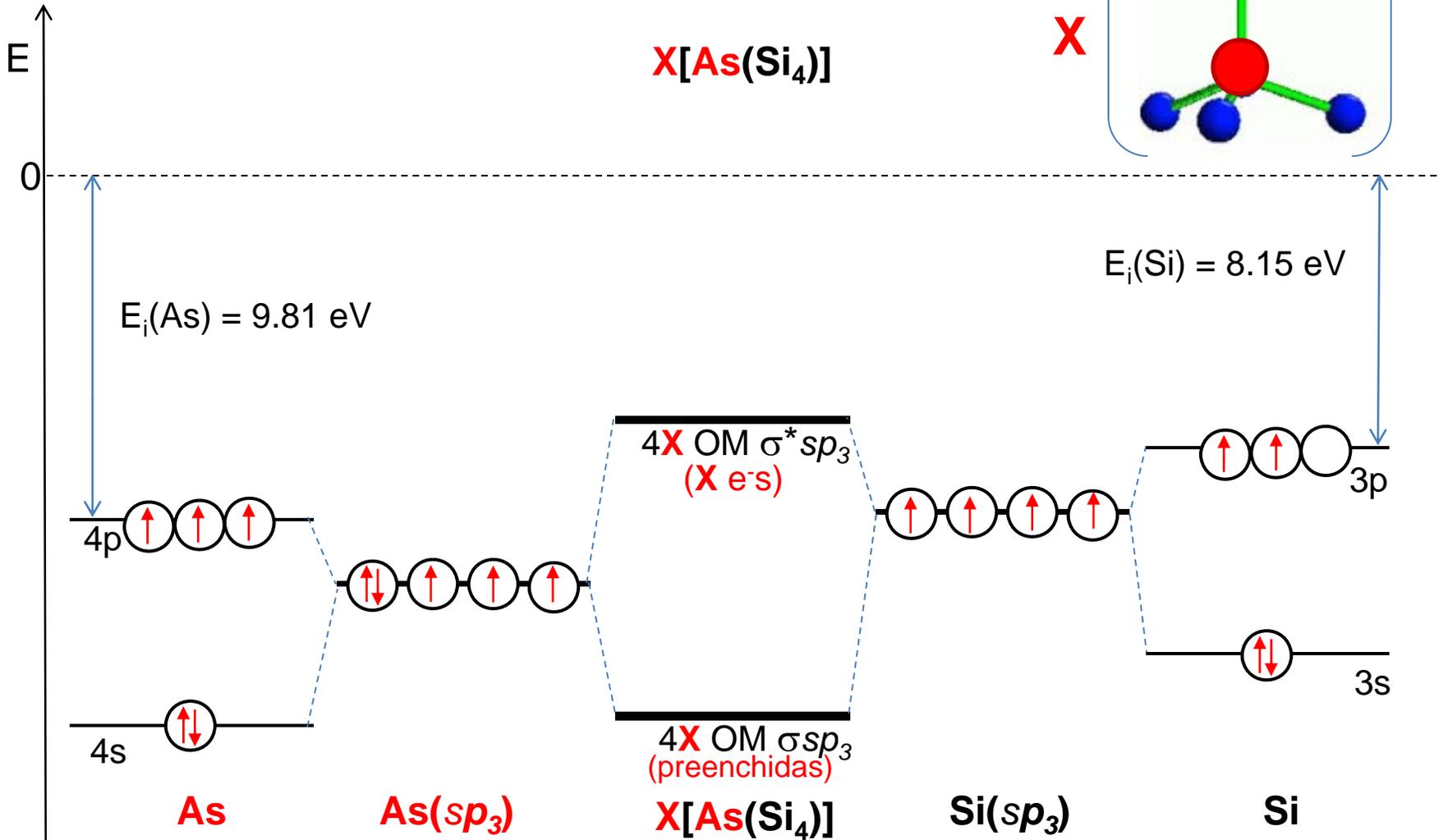
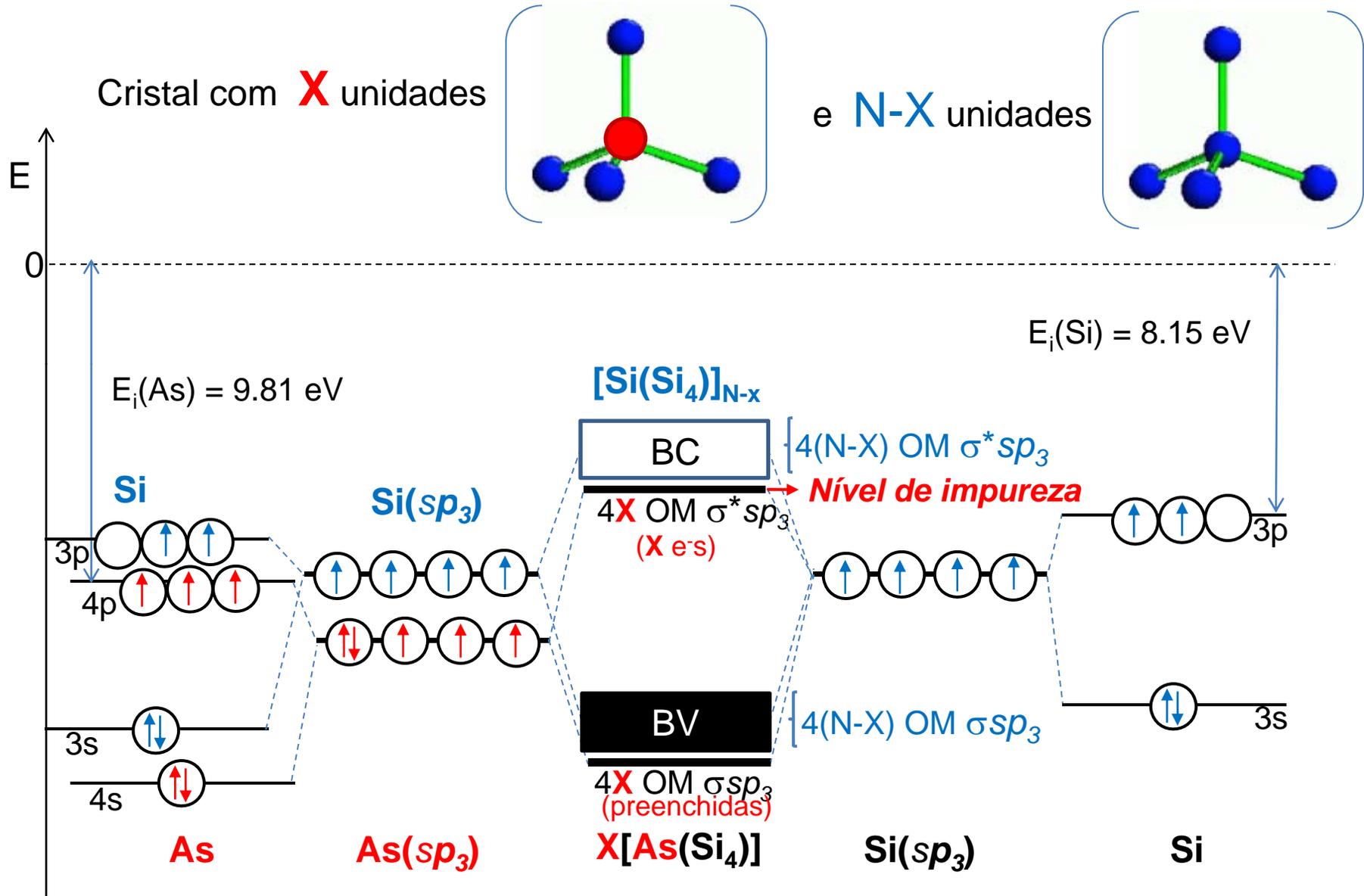


Diagrama de Bandas de Energia



Diagramas de bandas de energia para semicondutores extrínsecos

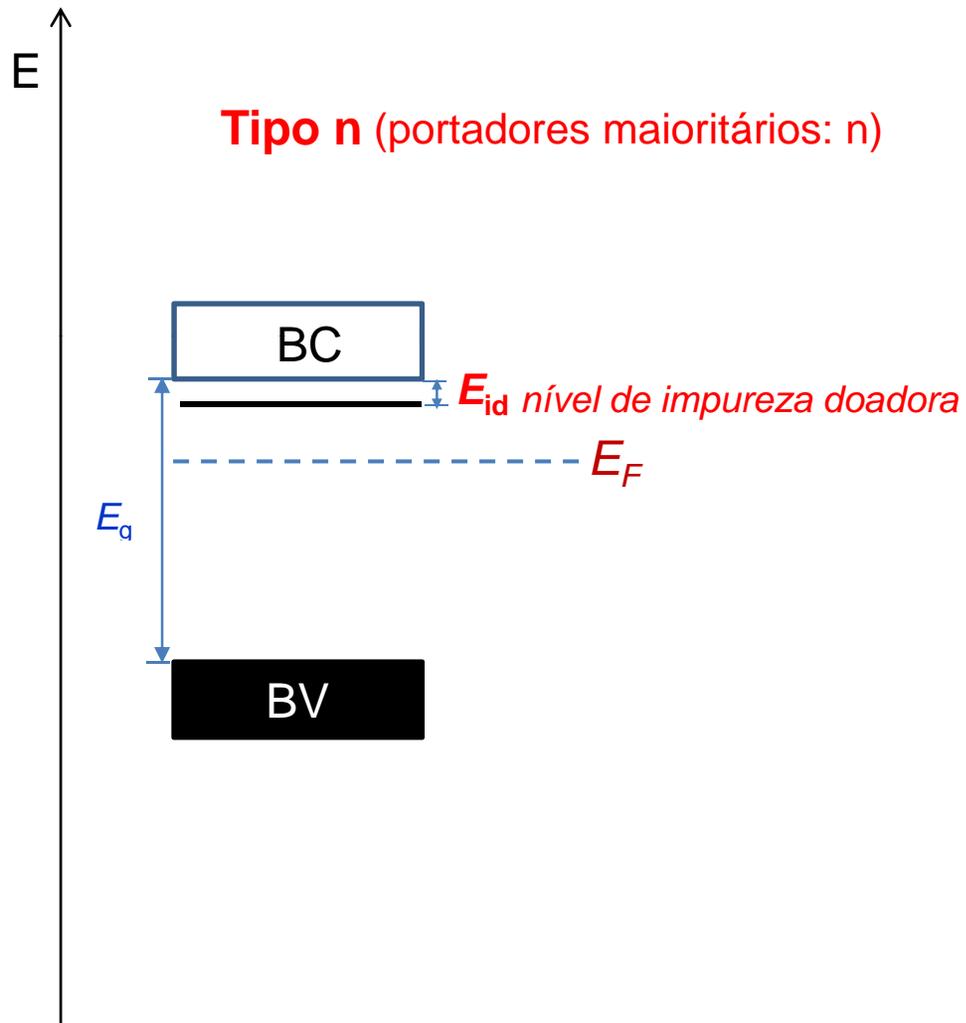
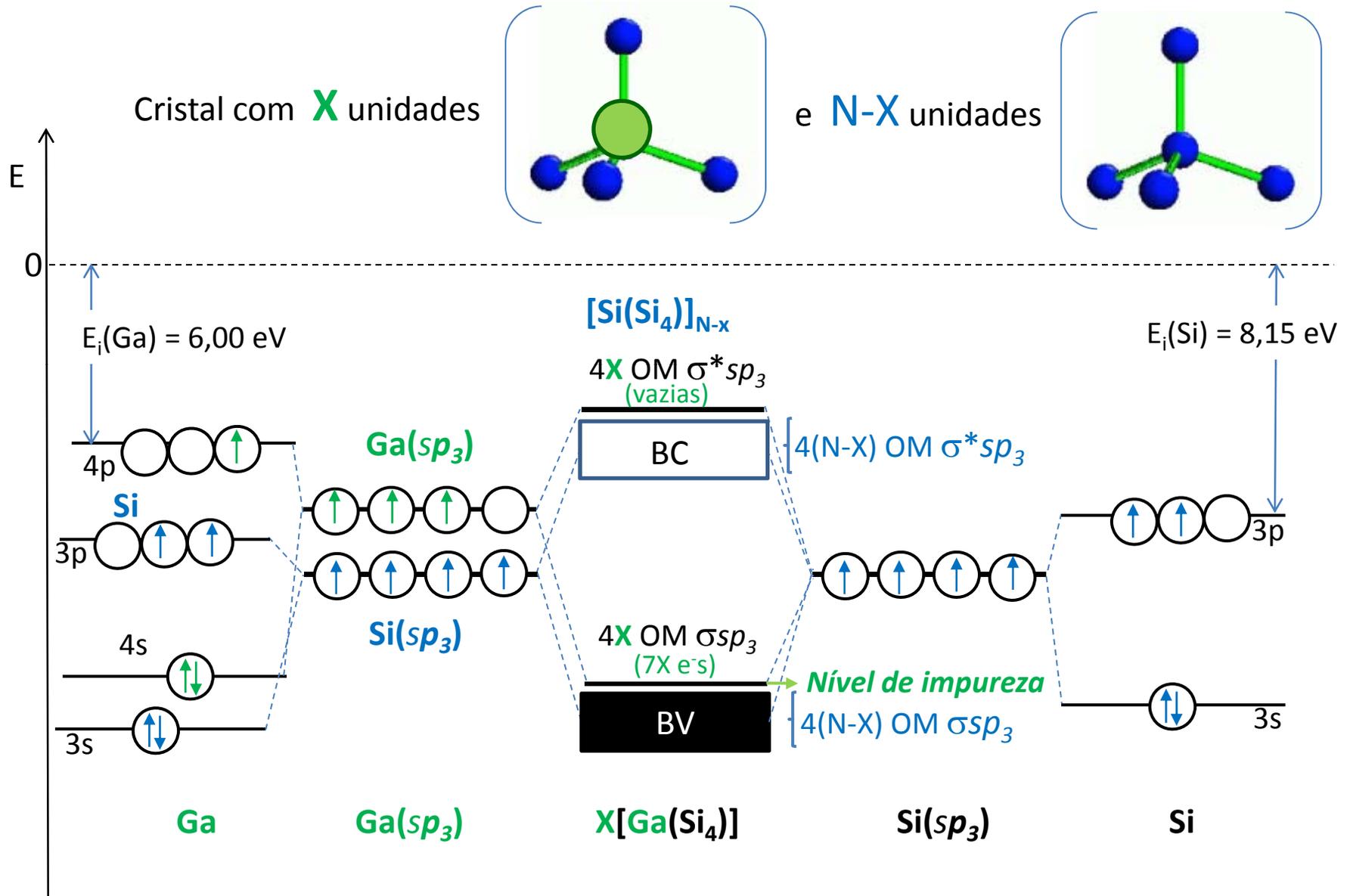
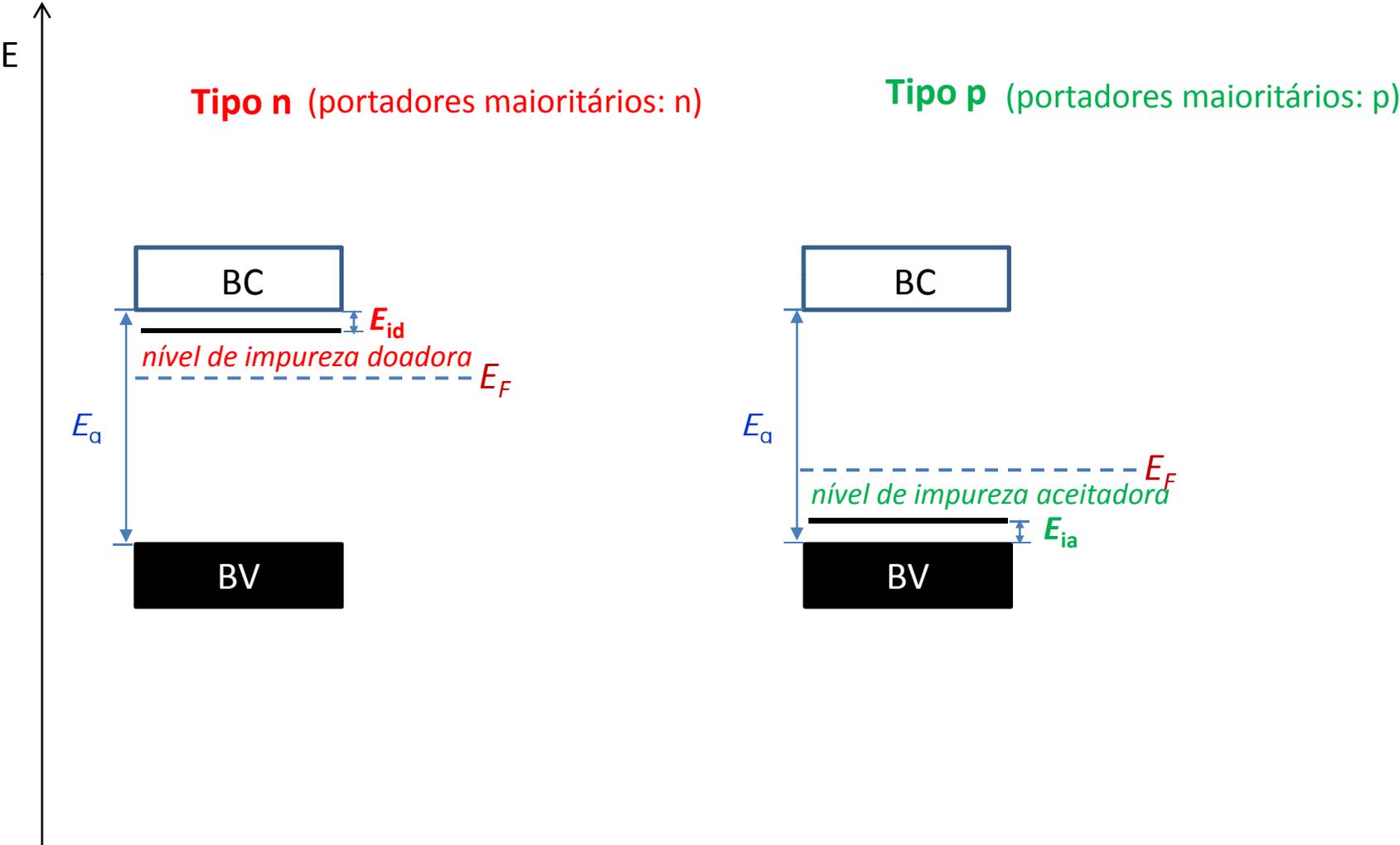


Diagrama de Bandas de Energia



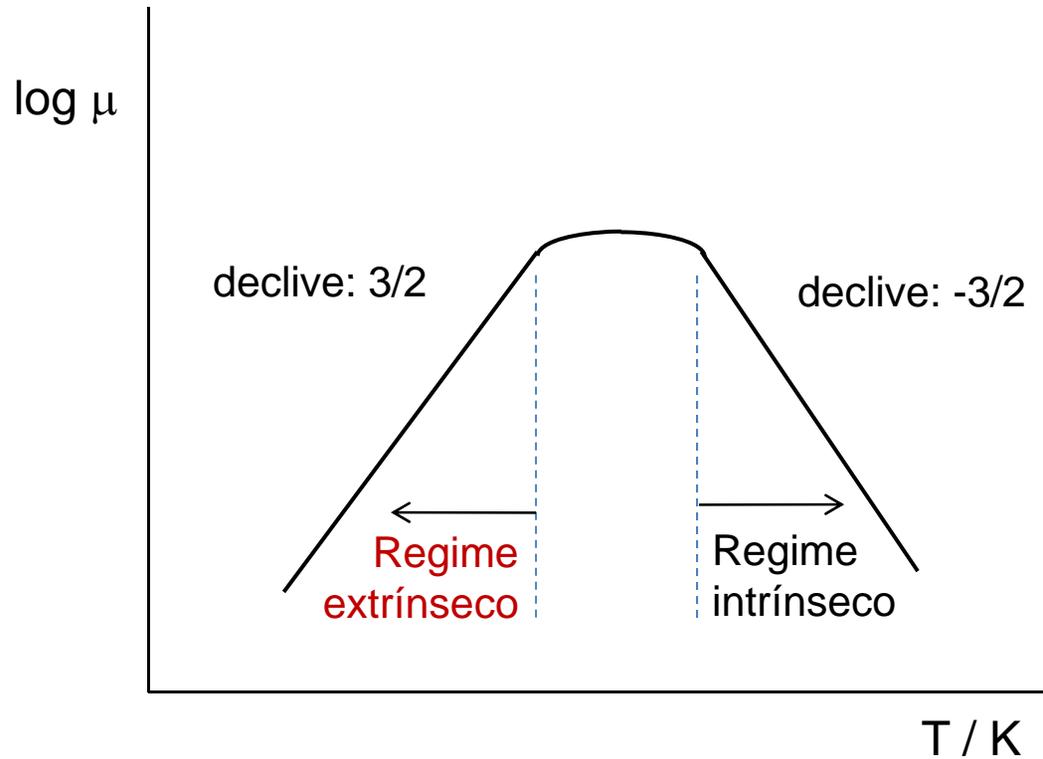
Diagramas de bandas de energia para semicondutores extrínsecos



Varição da mobilidade de portadores com a temperatura

A baixas temperaturas (zona extrínseca): $\mu = b T^{3/2}$

A temperaturas elevadas (zona intrínseca): $\mu = a T^{-3/2}$



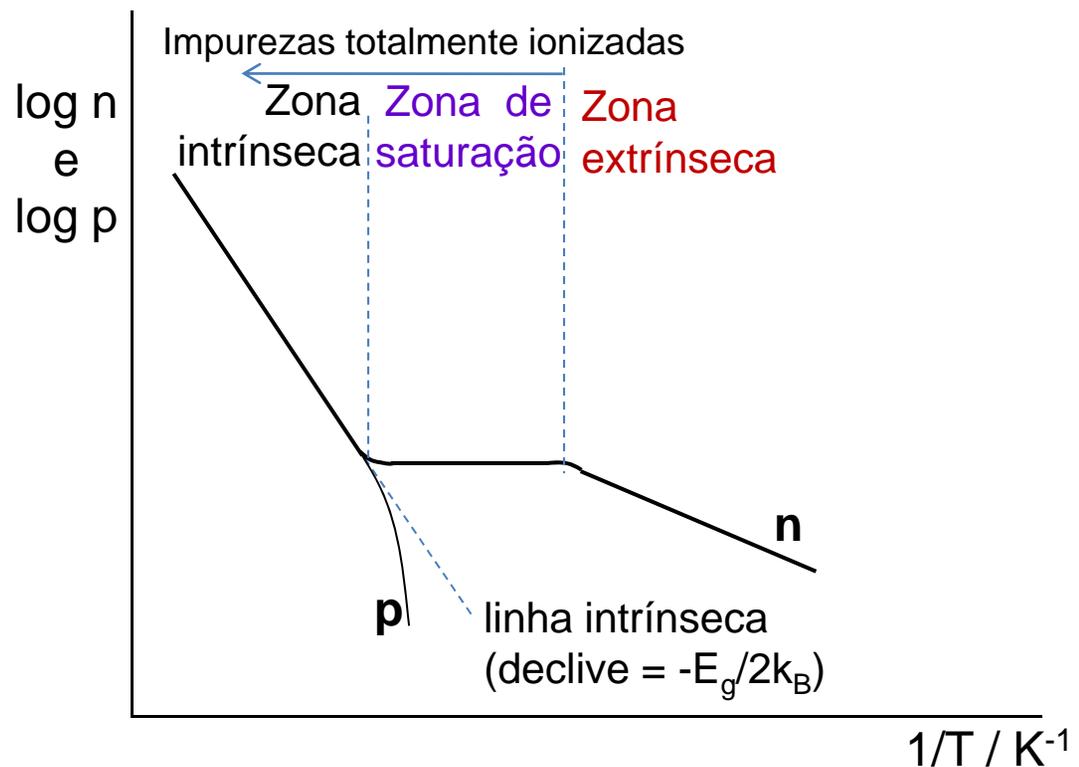
Variação da densidade de portadores com a temperatura

Zona extrínseca ou de impureza: $n = n_0 T^{3/4} \sqrt{N_d} e^{-E_{id}/2k_B T}$ (tipo n)
 ou
 $p = p_0 T^{3/4} \sqrt{N_a} e^{-E_{ia}/2k_B T}$ (tipo p)

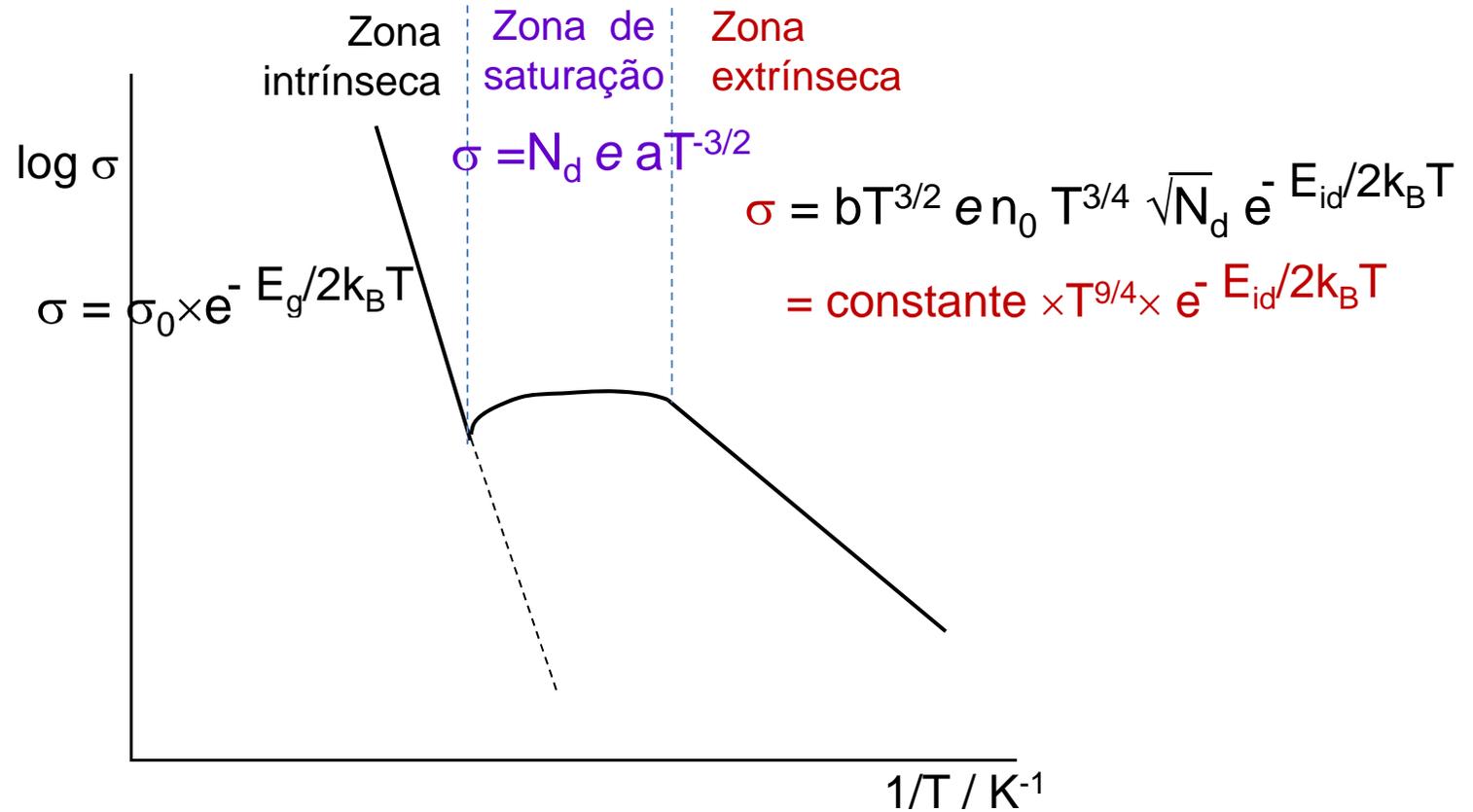
Zona de saturação: **n** constante (tipo n) ou **p** constante (tipo p)

Zona intrínseca : $n \cong p = \text{constante} \times T^{3/2} e^{-E_g/2k_B T}$

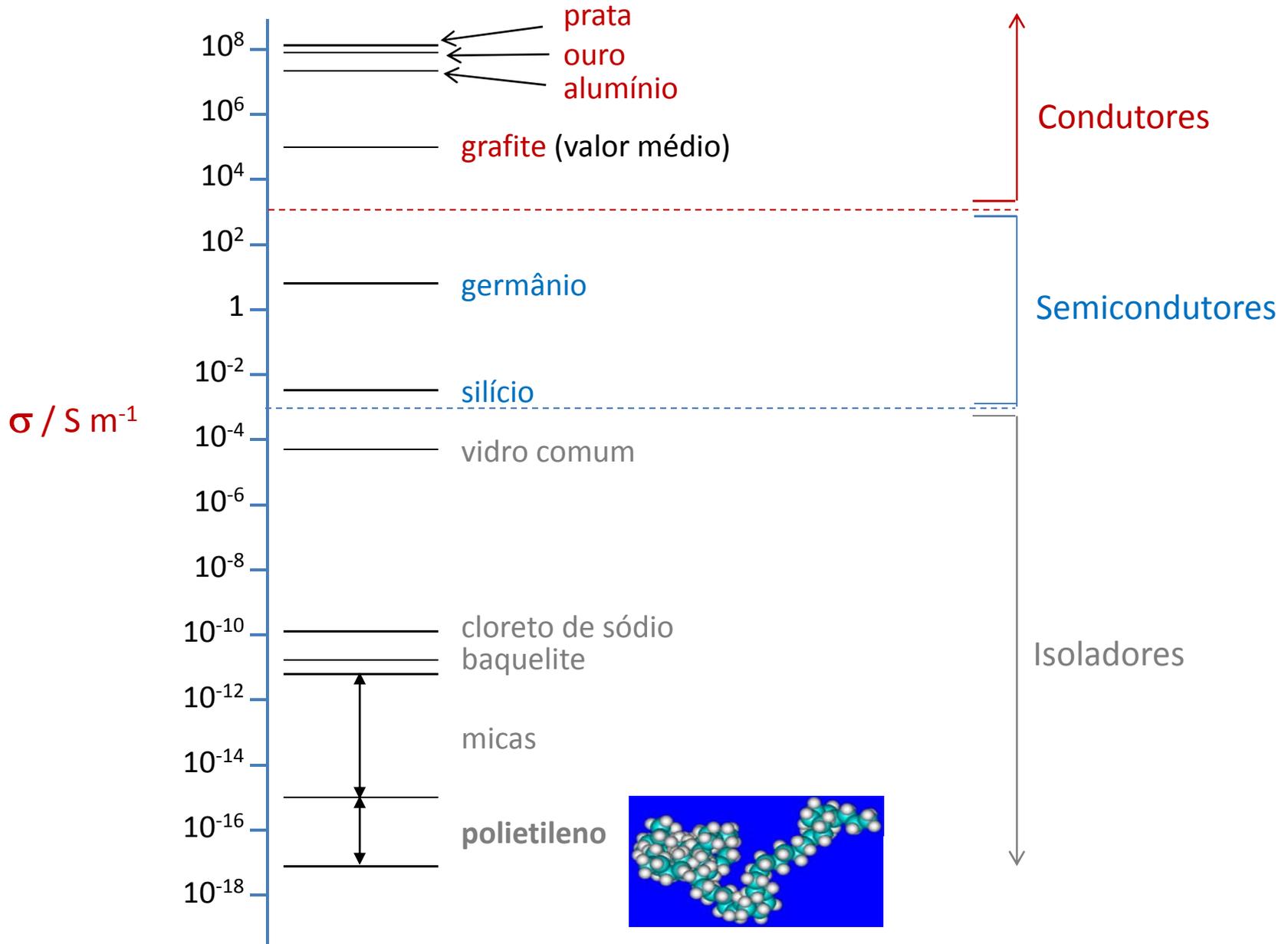
Semicondutor extrínseco
tipo n:



Variação da condutividade de portadores com a temperatura

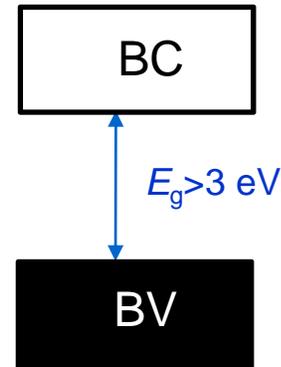


Condutividades de Alguns Materiais à Temperatura Ambiente

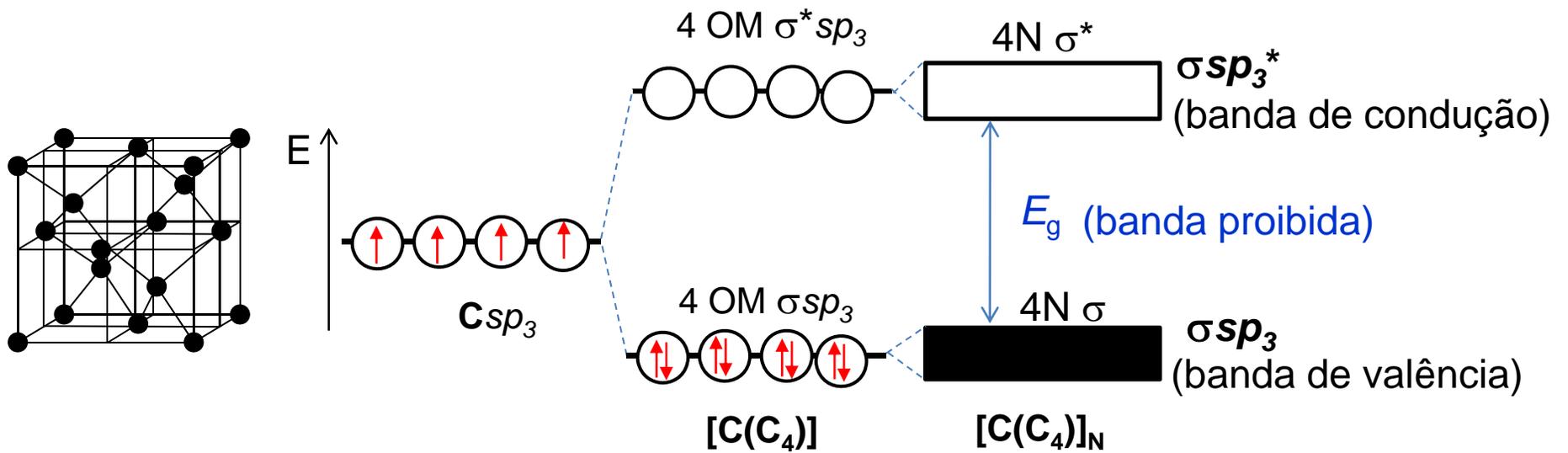


Isolantes

Diagrama de Bandas de Energia

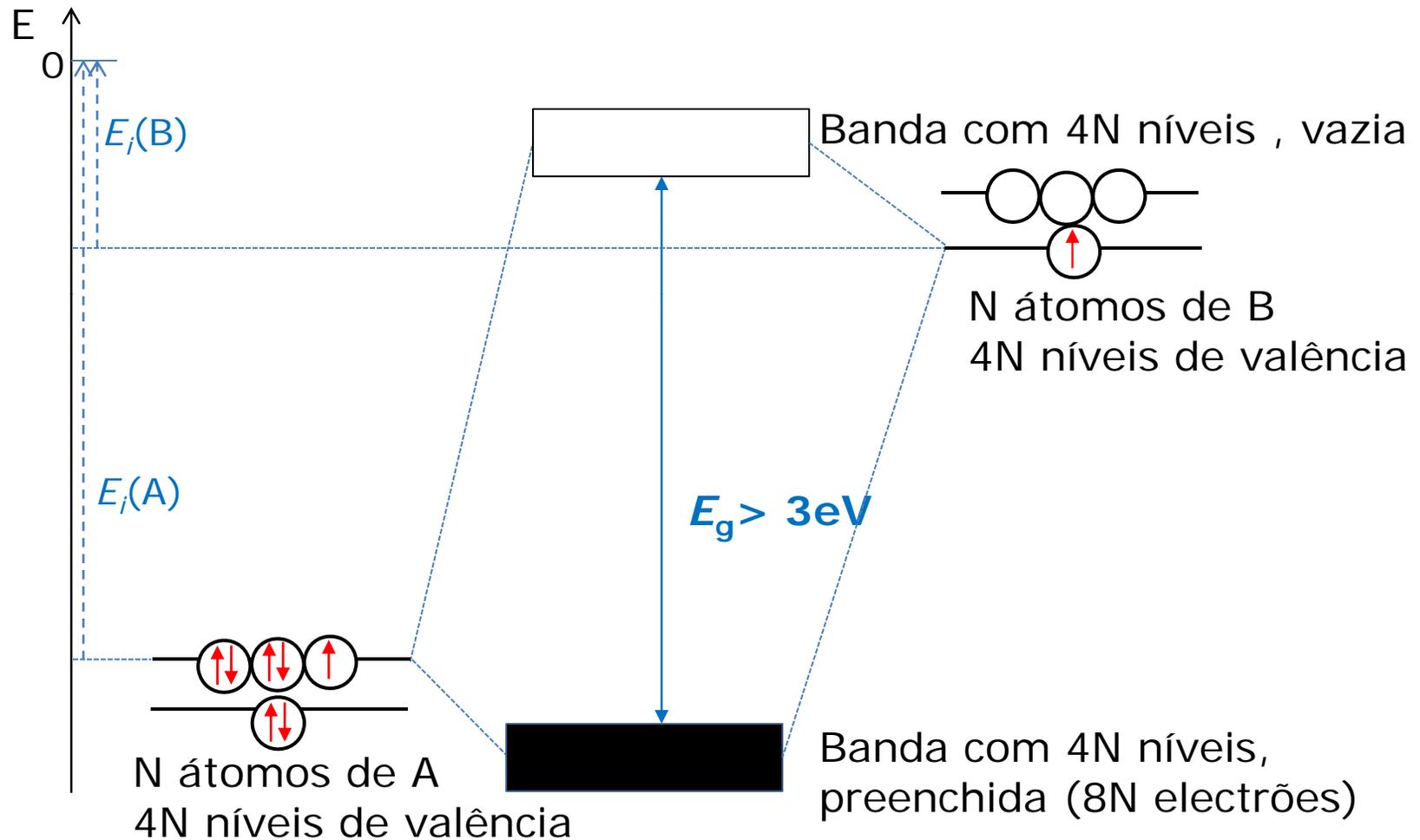


Carbono diamante



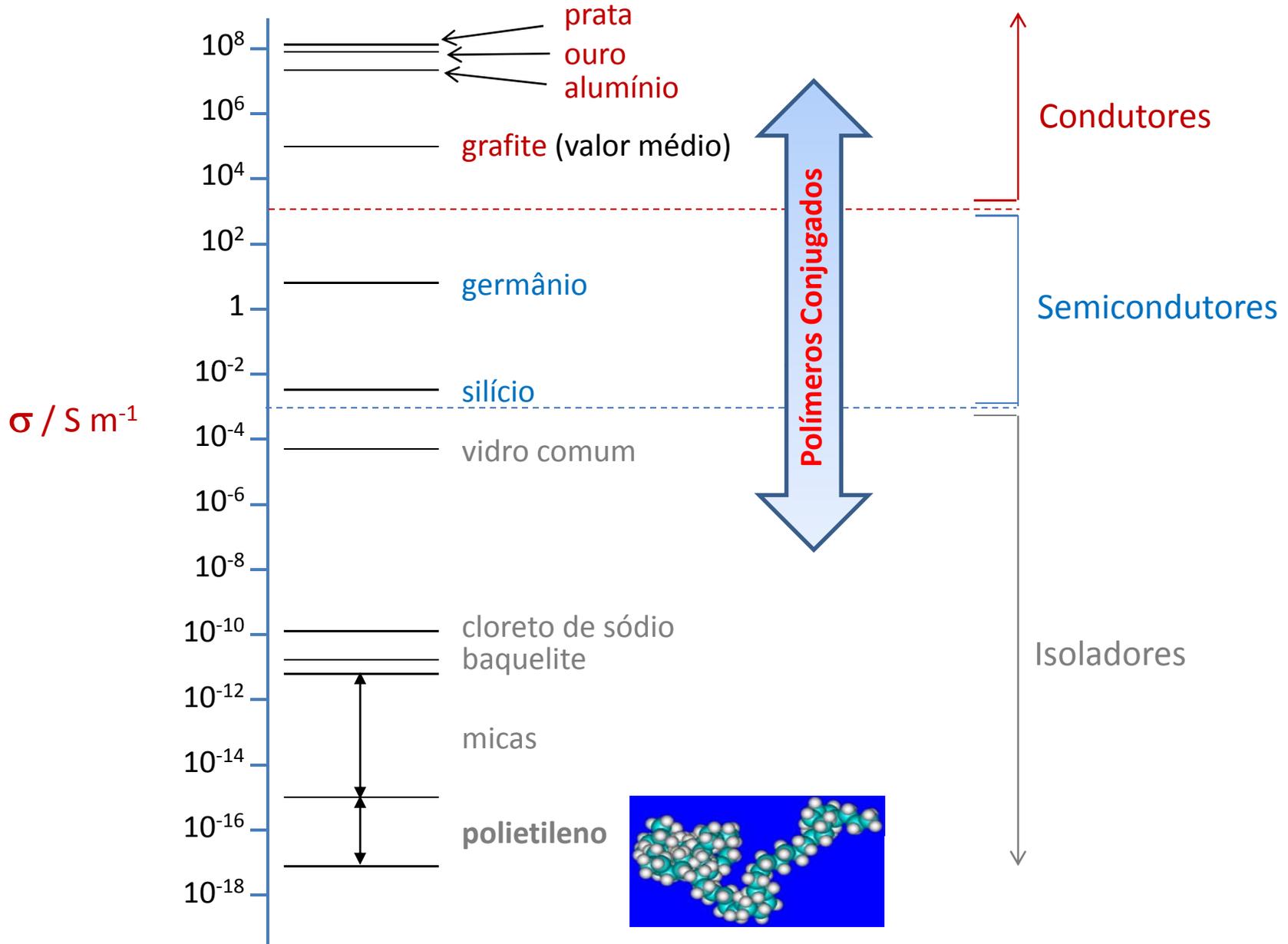
Compostos Iônicos AB

A do grupo 17 (np^5) e **B** do grupo 1 (ns^1)



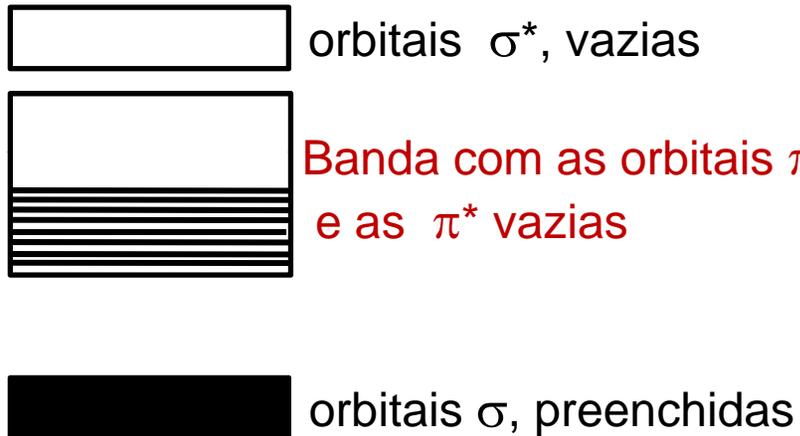
Conduzem a corrente eléctrica quando fundidos, por movimento orientado dos **iões**

Condutividades de Alguns Materiais à Temperatura Ambiente

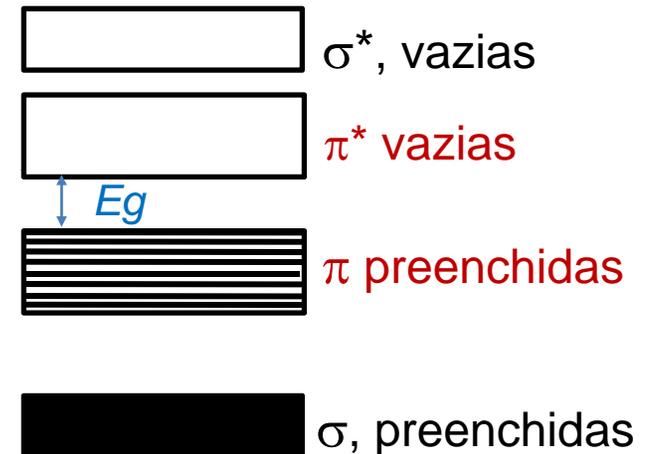


Polímeros Condutores e Semicondutores

condutores



semicondutores



Polímeros Condutores

Alan G. MacDiarmid (EUA, NZ) Hideki Shirakawa (Japão) Alan Meeger (EUA)

The Nobel Prize in Chemistry 2000

The Royal Swedish Academy of Sciences has awarded the Nobel Prize in Chemistry for 2000 jointly to Alan J. Meeger, Alan G. MacDiarmid and Hideki Shirakawa "for the discovery and development of conductive polymers".

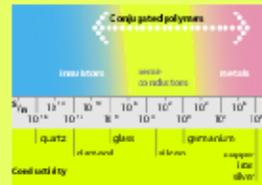
Electrically conductive plastic

Alan Meeger, Alan MacDiarmid and Hideki Shirakawa have been awarded the Nobel Prize in Chemistry for showing how plastic can be made to conduct electric current. The surprising discovery has revolutionized our view of plastics as a material.

Conductive polymers, led by conductive polymer research field of great significance to chemistry and physics.

Brilliant applications

The exciting idea of combining the moldability and low weight of plastic with the conductivity of metals, has prompted intensive development. Since the conductivity can be varied over a very broad area, from poor semiconductor to metal-level conductivity, many commercial uses present themselves. Batteries, condensers, anti-static materials and anti-oxidation substances are some examples.



Plastics that imitate metals

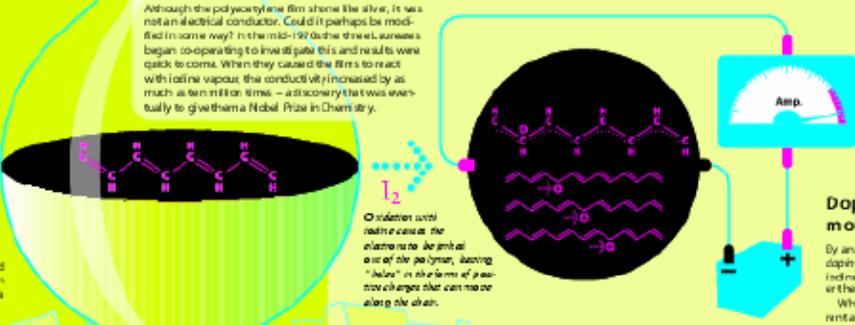
Plastics are polymers, in discrete forms of many identical units bound to each other like pearls in a necklace. For a polymer to be electrically conductive it must "imitate" metals – the electrons in the backbone have to be mobile and free to move bound to the atoms. One condition for this is that the polymer consists of alternate single and double bonds, termed conjugated double bonds. Acetylene gives the simplest possible conjugated polymer. It is obtained by polymerization of acetylene, shown above.

A surprise with a silver lining ...

At the beginning of the 1970s Shirakawa was studying the polymerisation of acetylene. In his reaction vessel, polyacetylene appeared in the form of a metallic black powder. On one occasion a silvery sheen appeared on the surface of the liquid in the vessel. The obvious question was: "If few plastic film shines like a metal, can it conduct electricity, too?"

... and a Nobel medal in gold

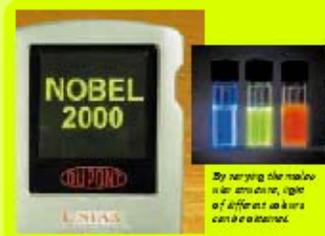
Although the polyacetylene film shone like silver, it was not an electrical conductor. Could it perhaps be modified in some way? In the mid-1970s the three scientists began co-operating to investigate this, and results were quick to come. When they caused the films to react with iodine vapour, the conductivity increased by as much as ten million times – a discovery that was eventually to give them a Nobel Prize in Chemistry.



Oxidation with iodine causes the electrons to be pulled away from the polymer, leaving "holes" or absence of a positive charges that can move along the chain.

Light-emitting diodes

Just now the most intensive development is aimed at conjugated polymers in their un-doped semiconductor state. This is because it was discovered some years ago that some conjugated polymers exhibit electroluminescence, the glow when a voltage is applied across them. Many applications are predicted for luminescent plastics. We shall soon be seeing the first practical use in light displays in mobile telephones and on information boards. In a few years flat TV screens in luminescent plastic may have become a reality.



Solar cells

The process giving rise to electroluminescence can also be "run backwards". A absorption of light creates positive and negative charges that are pulled apart by the electrodes, providing an electric current. This is the principle of the solar cell. The advantage of plastic is that large, flexible, conformable modules can be relatively easily and cheaply. Solar cell plastic could be spread out over large areas and give us environmental friendly electricity in the non-too-distant future.



Doping raises molecule performance

By analogy with semiconductor technology one speaks of doping the polymer when it is subjected to oxidation with iodine vapor. The more electrons are removed, the higher the degree of doping and the greater the conductivity. While polyacetylene can be persuaded to conduct currents as well as many metals, this material is unfortunately not good for practical use. Its conductivity drops rapidly in contact with air. This has led to the development of more stable, conjugated polymers, such as polypyrrole, polyaniline and polythiophene.

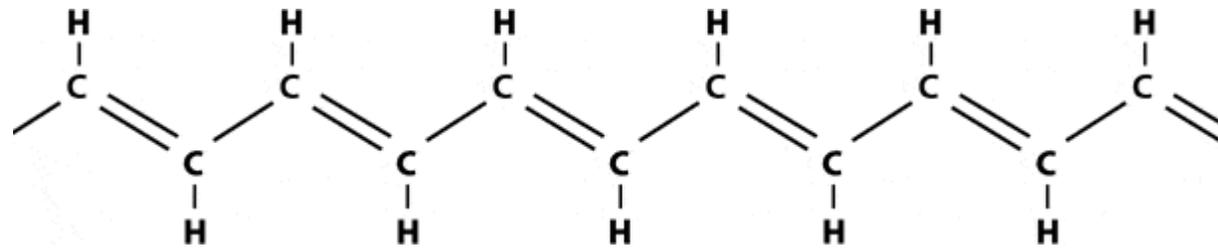
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 • Conductive Polymers – 1st Edition (Polymers) see also the Nobel Prize 2000, The Royal Swedish Academy of Sciences website www.nobel.se/2000
 • Basic Electronics, D. DeLoach, Physics World, p. 71, March 1998. • See for web in catala: www.ri.ccn.cs.cmu.edu/2000
 • Conductive Polymers, J. G. MacDiarmid, P. H. Geiger, S. I. Stupp, Science (1990) 249, 1163-1170



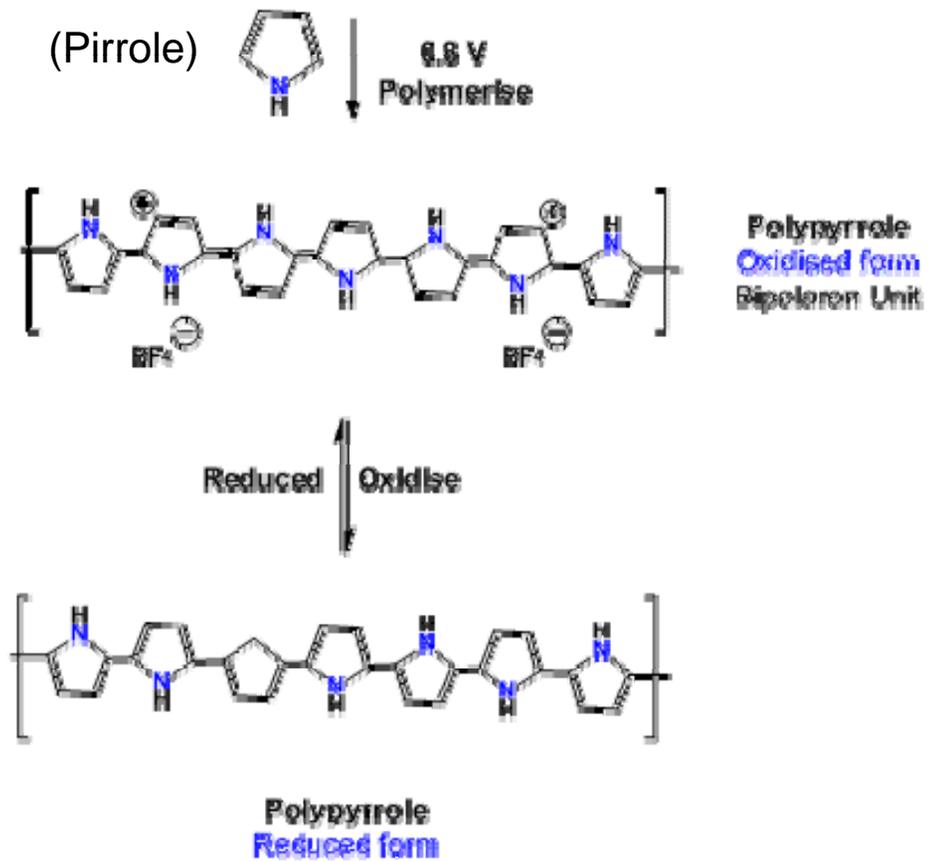
Universitetet i Oslo, Norges Nobelkomitee, P.O. Box 1047, NO-0103 Oslo, Norway
 100 King Street, New York, NY 10038, USA
 100 King Street, New York, NY 10038, USA
 100 King Street, New York, NY 10038, USA

Polímeros Conjugados

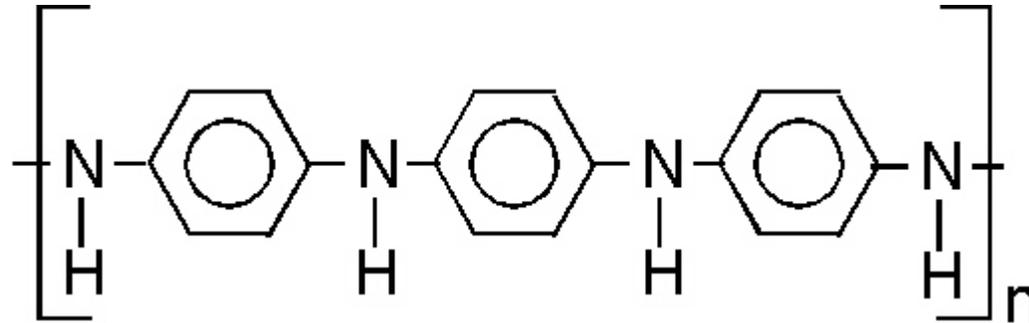
Poliacetileno (PA)



Polipirrole (PPy)



Polianilina



Vantagens dos polímeros condutores:

propriedades mecânicas

Utilizações:

Emissão de luz: polímeros electroluminescentes

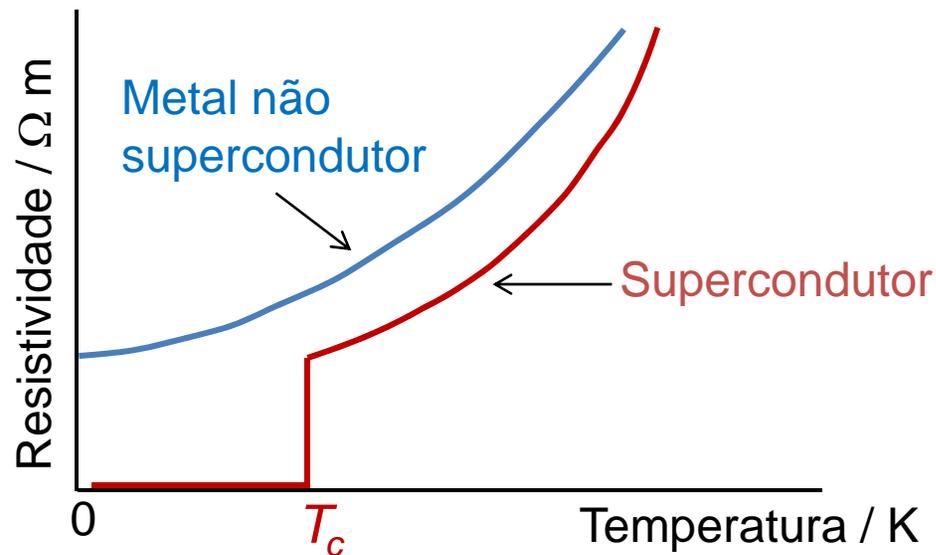
Células solares (voltaicas)

Supercondutores

Abaixo de uma **temperatura crítica** conduzem a corrente eléctrica **sem qualquer resistência**: há uma modificação brusca das propriedades de metal
(Descoberta em 1911 por Heike Onnes)

Tipo 1 : Metais e Metalóides com alguma condutividade à T ambiente.

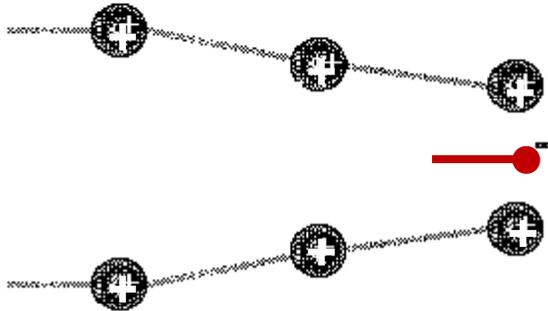
Transição à supercondutividade **muito abrupta** e **diamagnetismo perfeito**.



Explicação teórica em 1957 (Bardeen, Cooper e Schrieffer) – Teoria BCS
- Prémio Nobel da Física em 1972 -

A corrente eléctrica é transportada por pares de electrões (pares de Cooper)

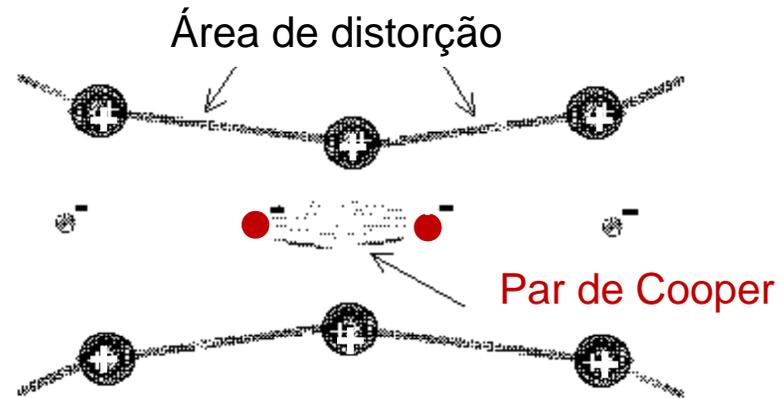
Estado supercondutor



A passagem de um e^- entre os átomos carregados positivamente atrai-os para dentro e causa uma distorção.

A rede distorcida cria uma região de potencial mais positivo que atrai outro electrão – forma-se um **par de Cooper**.

Estado supercondutor



Os dois electrões (pares de Cooper) ficam ligados e movem-se através da rede

Exemplos de supercondutores de Tipo 1

Metal/Metalóide	T_c	Estrutura
Lead (Pb)	7.196 K	FCC
Lanthanum (La)	4.88 K	HEX
Tantalum (Ta)	4.47 K	BCC
Mercury (Hg)	4.15 K	RHL
Indium (In)	3.41 K	TET
Thallium (Tl)	2.38 K	HEX
Rhenium (Re)	1.697 K	HEX
Protactinium (Pa)	1.40 K	TET
Thorium (Th)	1.38 K	FCC
Aluminum (Al)	1.175 K	FCC
Gallium (Ga)	1.083 K	ORC
Molybdenum (Mo)	0.915 K	BCC
Osmium (Os)	0.66 K	HEX
Zirconium (Zr)	0.61 K	HEX
Cadmium (Cd)	0.517 K	HEX
Ruthenium (Ru)	0.49 K	HEX
Titanium (Ti)	0.40 K	HEX
Uranium (U)	0.20 K	ORC
Hafnium (Hf)	0.128 K	HEX
Iridium (Ir)	0.1125 K	FCC
Beryllium (Be)	0.023 K (SRM 768)	HEX
Tungsten (W)	0.0154 K	BCC
Rhodium (Rh)	0.000325 K	FCC

Supercondutores

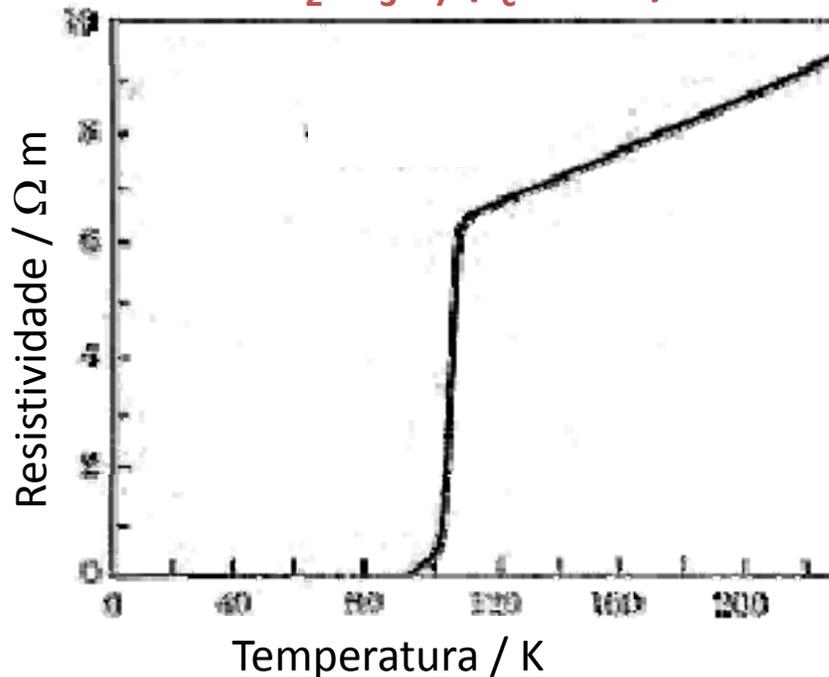
Tipo 2: Compostos metálicos

Ligas

“Perovskites” (cerâmicos de óxidos metálicos)

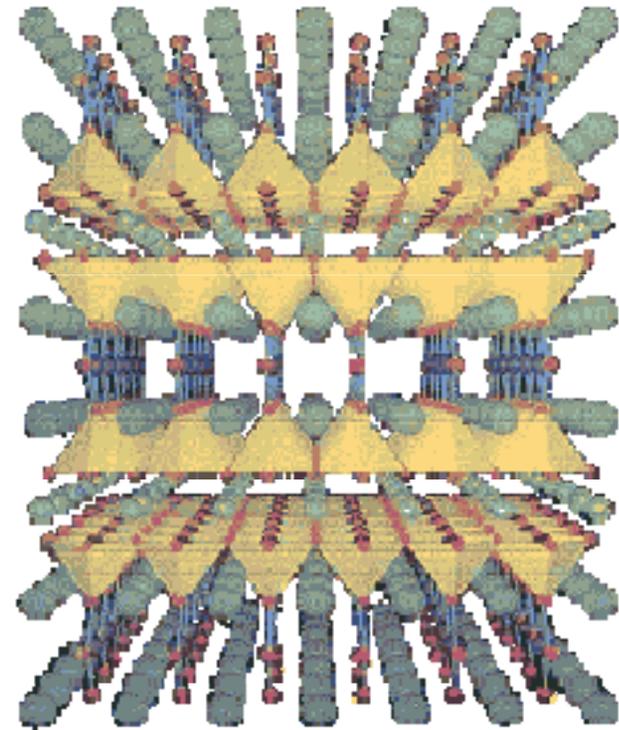
Transição à supercondutividade **muito suave** e **temperaturas críticas mais elevadas** que os de Tipo 1.

$\text{YBa}_2\text{Cu}_3\text{O}_7$ ($T_c = 92 \text{ K}$)



Vários mecanismos propostos

Cuprato (óxido de cobre)



(estrutura em camadas)

Exemplos de supercondutores de Tipo 2

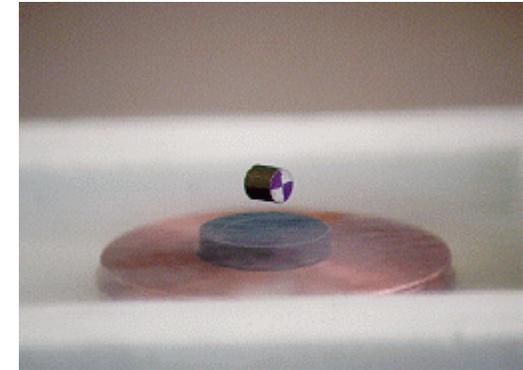
- Compostos metálicos
- Ligas
- "Perovskites" (cerâmicos de óxidos metálicos)

Supercondutor	T_c
$(\text{Tl}_4\text{Ba})\text{Ba}_2\text{Ca}_2\text{Cu}_7\text{O}_{13+}$	254
$\text{InSnBa}_4\text{Tm}_4\text{Cu}_6\text{O}_{18+}$ (*)	~150 K
$(\text{Hg}_{0.8}\text{Tl}_{0.2})\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.33}$	138 K
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$	133-135 K
$\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+}$	125-126 K
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	127-128 K
$(\text{Tl}_{1.6}\text{Hg}_{0.4})\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+}$	126 K
$\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9+}$	123 K
$\text{Sn}_2\text{Ba}_2(\text{Ca}_{0.5}\text{Tm}_{0.5})\text{Cu}_3\text{O}_x$	~115 K
$\text{SnInBa}_4\text{Tm}_3\text{Cu}_5\text{O}_x$	~113 K
$\text{Bi}_{1.6}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_2\text{Sb}_{0.1}\text{Cu}_3\text{O}_y$	115 K (filme espesso em substrato de MgO)

(*) – Patente pendente

Levitação magnética (efeito de Meissner)

Um supercondutor abaixo de T_c tem diamagnetismo perfeito e é repelido por um campo magnético aplicado



Maglev de *Shanghai*

Sumário 22

- **Propriedades Eléctricas dos Materiais**
 - **Semicondutores Extrínsecos**
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 - Variação da mobilidade, densidade de portadores e condutividade com a temperatura
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 - Exemplos
 - **Polímeros Condutores e Semicondutores**
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 - Vantagens e Utilizações
 - **Supercondutores**
 - Tipo 1 e Tipo 2. Exemplos.
 - Efeito de Meissner