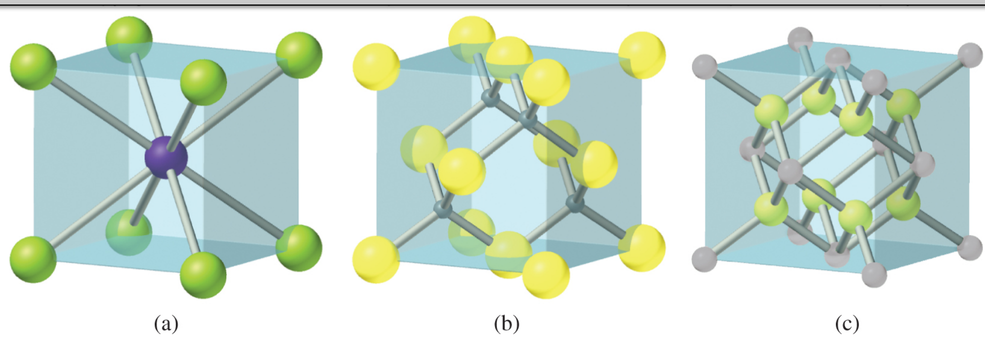
MO Theory of Solids and Properties of Metals

Chapter 12.4, 21.3-4,25.6-7

Supplementary Reading on Metals

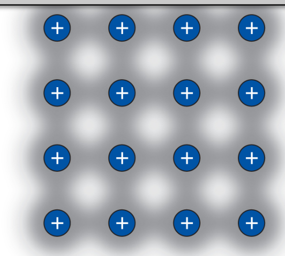
http://courses.chem.psu.edu/chem112/materials/metals.html

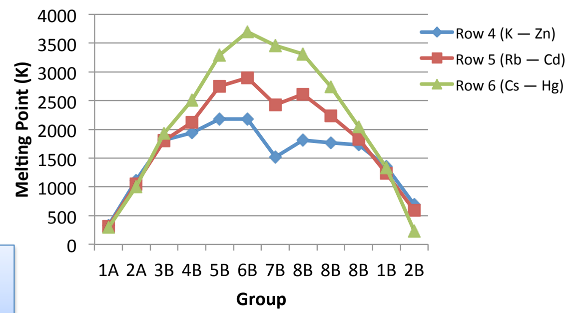
Structures of Metal Solids: Most metals adopt one of a few simple structures.



These pictures show the **unit cells**
(smallest repeating unit of the **crystal lattice**,
which is the 3D array of atoms)

Metallic solids are formed by atoms held together by metallic bonds





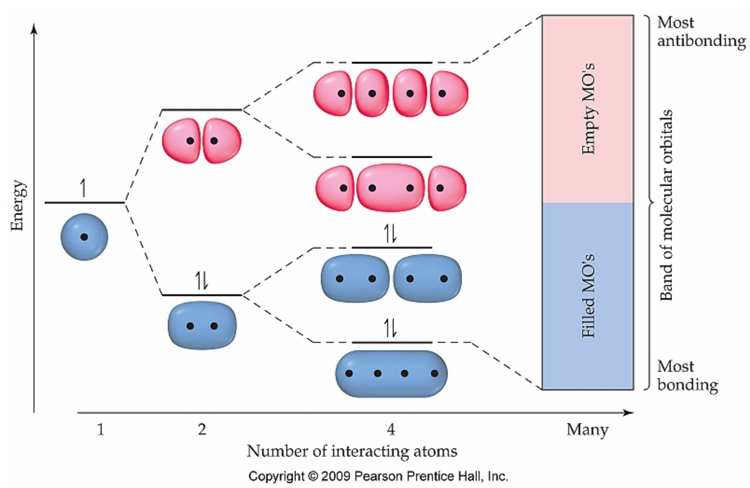
Recall: Electron -sea model of bonding does NOT explain metal properties.

Melting point is related to bond strength: As strength of metallic bond increases, mp of metal increases.

Cannot explain this trend using electron sea model of bonding in metals

How does MO bonding theory help us understand the properties of materials?

Extend molecular orbital theory to 3, 4, and more interacting atoms.

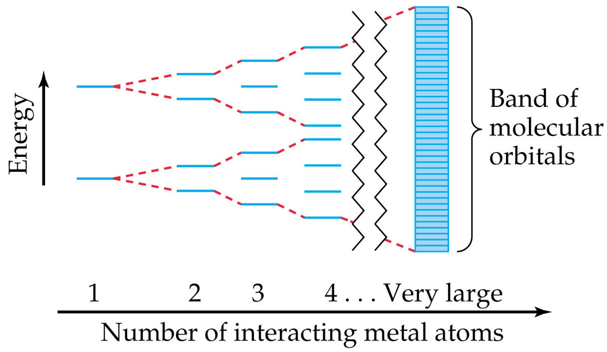


Molecular Orbital picture of bands

Note: bonding and antibonding character

The application of MO theory to solids is called BAND THEORY

- Atomic orbitals (AO) mix to form molecular orbitals (MO)
- Start with 2 AO's, end with 2 MO's
- Start with n AO's, end with n MO's

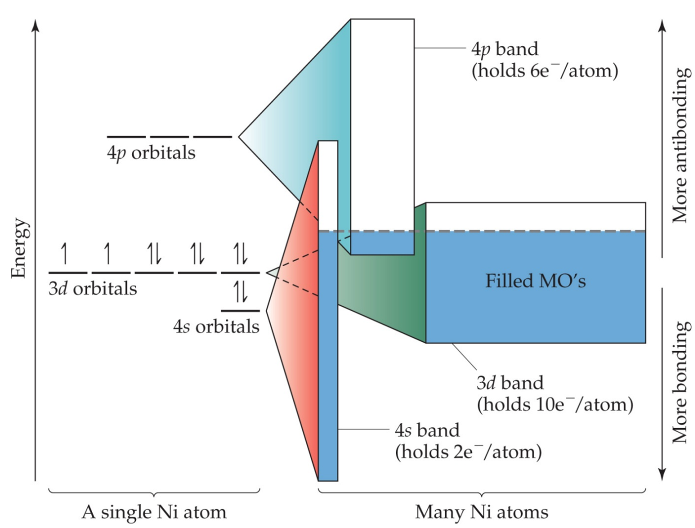


In metals, the energy difference between individual orbitals is very small, so they "blend together"

Orbitals form a continuous bands of allowed energy states where electrons can be located.

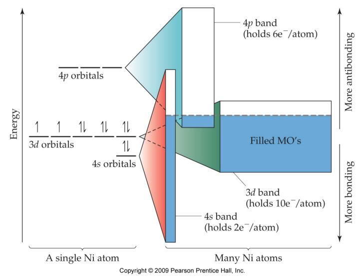
In a real metal, different types of AO (s, p, d) create different bands

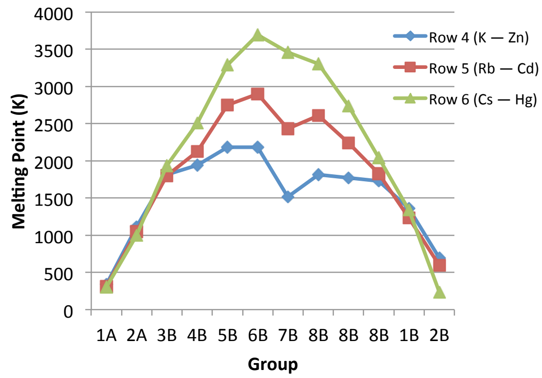
Schematic diagram of the band structure of a metal



Melting point of the metal is related to the strength of metallic bond

As strength of metallic bond increases, mp of metal increases.





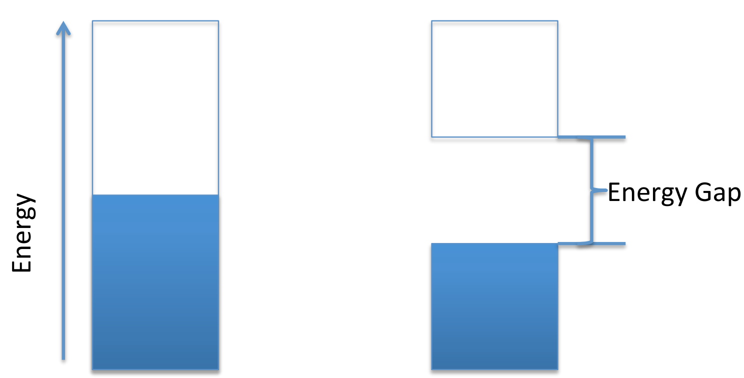
For first 5 transition metals, valence band is ½ filled (filling the Bonding region of the band).

As electrons are added, bond strengthens.

As the the second half of the band fills, antibonding character increases and bond strength decreases.

MO Theory can be used to describe electronic structure in solids.

METAL: Conductor
Valence electrons do not fill available orbitals (not enough electrons)



Partially filled band

Insulator or semiconductor

Valence band is full (or completely empty).

Energy gap (E_g) separates valence band from empty orbitals.

The conductivity of a solid depends on the number of valence electrons and the energy difference between bands of energy levels.

Metals

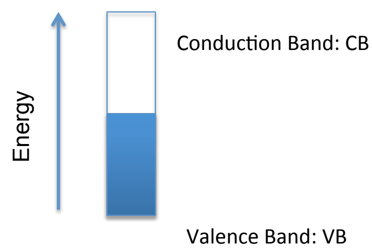
Good electrical conductors – valence electrons do not fill all available orbitals in a band (not enough electrons)

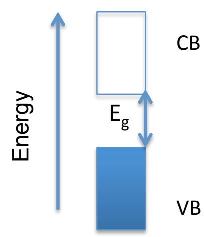
Semiconductors

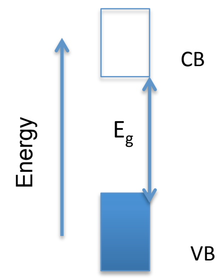
Energy gap exists, but is small – can increase conductivity by chemical modification (doping) or increasing temperature

Insulators

Energy gap is very large and valence band is completely full (or empty) – large energy gap separates valence band from available empty orbitals, making it a **poor conductor**

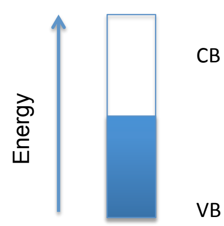




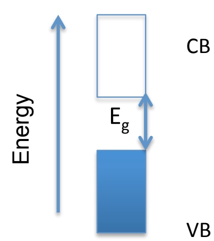


Conductivity is inversely related to the energy of the band gap.

Metals:



Semiconductors:



Insulators:

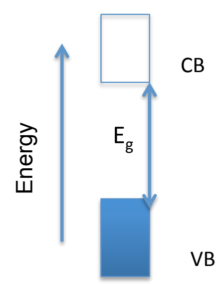


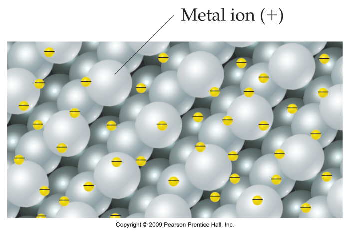
TABLE 12.1 ■ Electronic Properties of Common Materials*

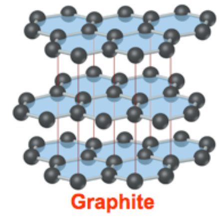
Material	Type	Band Gap Energy, kJ/mol	Band Gap Energy, eV	Conductivity, $ohm^{-1}\ cm^{-1}$
SiO_2	Insulator	~870	~9	$<10^{-18}$
Al_2O_3	Insulator	~850	~8.8	$<10^{-14}$
C (diamond)	Insulator	~530	5.5	$<10^{-18}$
Si	Semiconductor	110	1.1	5×10^{-6}
Ge	Semiconductor	65	0.67	0.02
Al	Metal	—	—	3.8×10^5
Cu	Metal	—	—	5.9×10^5
Ag	Metal	—	—	6.3×10^5
Au	Metal	—	—	4.3×10^5

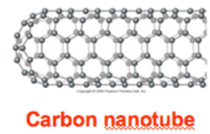
*Band gap energies and conductivities are room temperature values. Electron volts (eV) are a commonly used energy unit in the semiconductor industry; 1 eV = 1.602×10^{-19} J.

What kinds of materials are conductors?

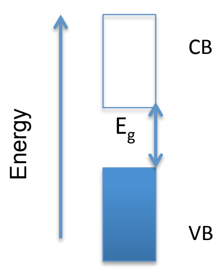
- Most metals (most elements)
- Some network covalent solids (graphite)







- Some polymers (those with conjugated double bonds)
- Some ceramics (transition metal oxides with unusually low or high positive oxidation states, e.g. V^{2+} or Cu^{3+})



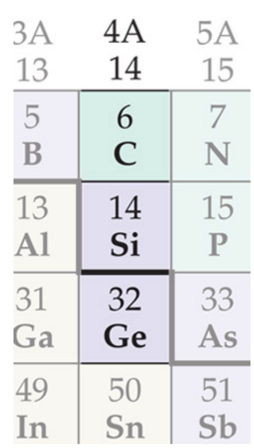
semiconductor

Semiconductors have a gap between the valence band and conduction band of ~50 to 300 J/mol

The conductivity of semi-conductors can be increased with T, or applied fields.

Among elements, only silicon, germanium, and graphite (carbon) are semiconductors. They all have 4 valence electrons.

Inorganic semiconductors (like GaAs) tend to have an average of 4 valence electrons (3 for Ga, 5 for As).



One of the most common uses of semiconductors is in electronic devices (e.g. "silicon chip").

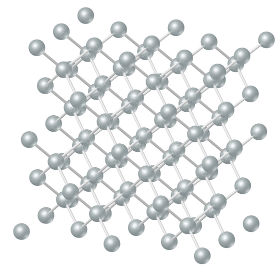
How exactly does a silicon chip work?

Copyright © 2009 Pearson Prentice Hall, Inc.

It has to exhibit electrical conductivity to process information, but it is a semiconductor with a bandgap.

How can this be?

Need to develop strategies for increasing the electrical conductivity of a semiconductor



Copyright © 2009 Pearson Prentice Hall, Inc.

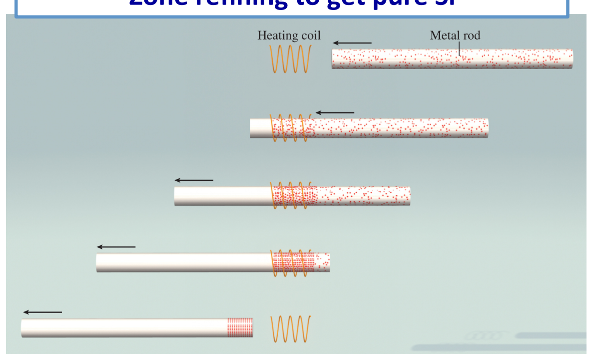
Need to start with very pure Silicon.

Properties:
- shiny, silvery gray
- brittle
- Poor thermal conductor
- SEMI-METAL

Uses:
- alloy (with Al, Mg)
- Silicone polymers

Electronic applications
- for these applications very pure silicon (<1ppb) is required.

Zone refining to get pure Si

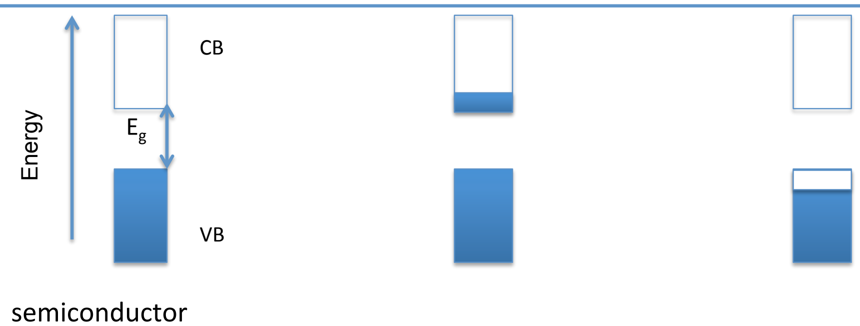


The properties of the Si are modified by adding small amounts of impurities.

What happens when we intentionally add impurities (dopants) to a semiconductor?

Add impurities that donate extra electrons: n-type.
Which represents an **n-type** semiconductor?

Add impurities that accept electrons: p-type.
Which represents an **p-type** semiconductor?



What elements would you use to dope Si to make it an **n-type** semiconductor?

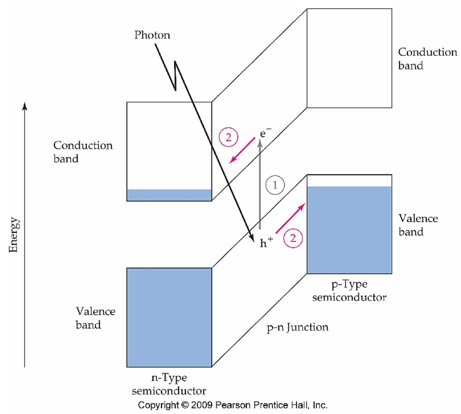
What elements would you use to dope Si to make it a **p-type** semiconductor?

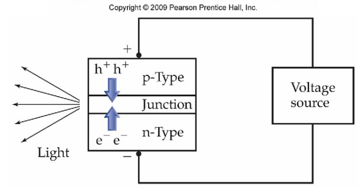
Classify each of the following as **n-type**, **p-type**, or **not doped**

B-doped Si	P-doped Si	As-doped Ge
GaAs	Te-doped GaAs	Si-doped GaAs

Semiconductors are used in everyday applications

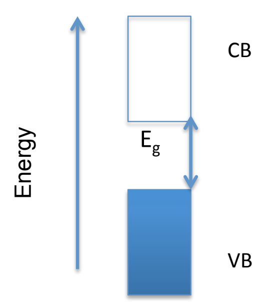
- Silicon Chips
- Solar Energy Conversion
- LED (Light Emitting Diodes)



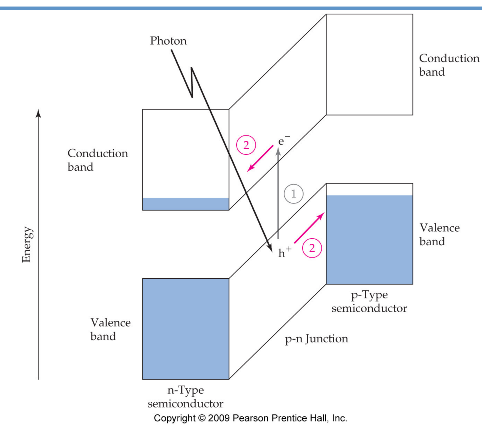


Solar Cells are semiconductor devices that converting light into electricity

Photoconductivity: absorption of electron increases conductivity

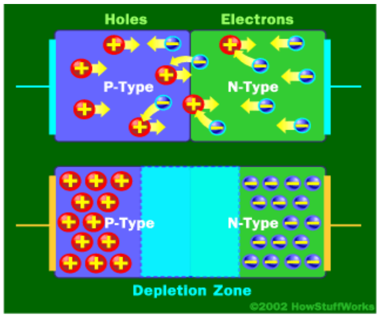


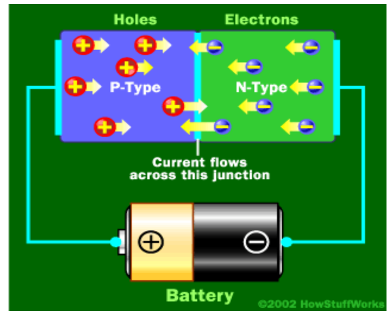
semiconductor



A diode is made using a semiconductor with a p-type material bonded to an n-type material.

A diode allows current to flow in only one direction.





Charge build-up at junction creates Depletion Zone

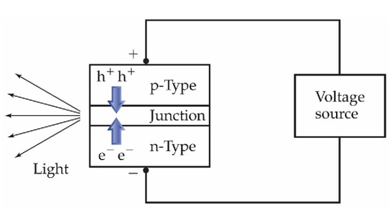
No current flows

- **Apply an external field (battery) to get current to flow**
- **Electrons can flow from n-type to p-type under forward bias**

Light Emitting Diodes (LEDs)
When electrons combine with holes, light is emitted.

The energy of light ($E = h\nu$) is the same as the band gap energy E_g

The band gap energy depends on the material used to make the diode.



Wavelength nm	Color	Material and structure of LEDs
700	red	GaP: Zn-O/GaP
660	red	GaAl0.35 As/GaAs
630	red	GaAs0.35PO.65: N/GaP
610	orange	GaAs0.25Po.75: N/GaP
590	yellow	GaAs0.15PO.85: N/GaP
565	green	Gap: N/GaP
555	green	GaP/GaP

LEDs is a small light bulb that produces useful light from the flow of electrons through a semiconductor diode

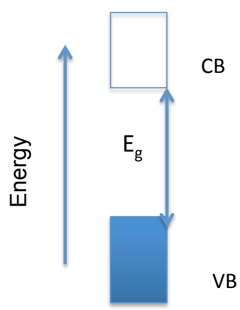
LEDs are more energy efficient than incandescent lighting

LEDs producing visible light are typically made from doped Aluminum-Gallium-Arsenide (AlGaAs)

Changing the dopants changes the size of the depletion zone and the color the visible light produced

EXAMPLE

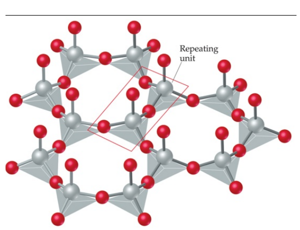
The energy band gap in an insulator is > 300kJ



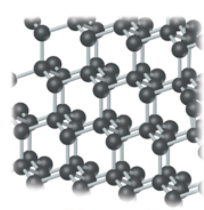
insulator

They are not electrical conductors.

What kinds of materials are insulators?



Two-dimensional silicate sheet, $Si_2O_5^{2-}$



Diamond

Ceramics are inorganic non-metallic solids

Crystalline:

- Oxides (Al_2O_3, ZrO_2,BeO)
- Carbides (SiC, Ca_2C)
- Nitrides (BN)
- Silicates (SiO_2 mixed with metal oxides)
- Aluminosilicates (Al_2O_3 + SiO_2 + metal oxides: Mica, Talc, Pottery, Clay)

Amorphous (glasses)

Ceramics are held together by ionic or polar covalent bonds: This influences the properties of Ceramics

- **Typically hard and brittle**
  - Less dense than metals, lighter
  - Do not deform under stress
  - Resist corrosion and wear, don't deform
- **Stable at high temperatures**
  - High melting
- **Can be covalent network and/or ionic**
  - Usually electrical insulators

Piezoelectric effect: ability of a material to generate electricity in response to a mechanical stress; **grill lighter**

or convert an electrical impulse into a mechanical response; **quartz watch**

Superconductors show no resistance to the flow of electricity

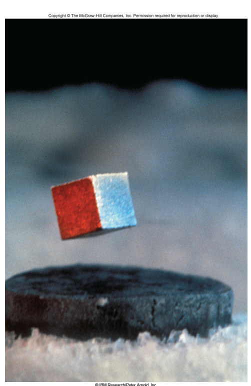
Superconducting behavior starts below the superconducting transition temperature, T_c.

Much research has been done in the search for a high-temperature superconductor.

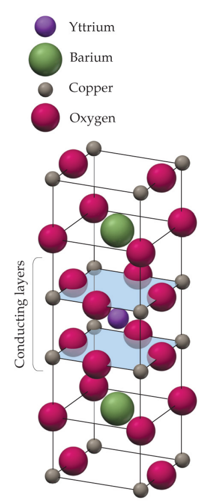
Substance	Discovery Date	T_c (K)
Hg	1911	4.0
NbO	1933	1.5
NbN	1941	16.1
Nb_3Sn	1954	18.0
Nb_3Ge	1973	22.3
$BaPb_{1-x}Bi_xO_3$	1975	13
$La_{2-x}Ba_xCuO_4$	1986	35
$YBa_2Cu_3O_7$	1987	95
$Bi_2Sr_2Ca_2Cu_3O_{10}$	1990	110
$Tl_2Ba_2Ca_2Cu_3O_{10}$	1990	125
$HgBa_2Ca_2Cu_3O_{8+x}$	1993	133
$Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8.33}$	1993	138
Cs_3C_{60}	1995	40
MgB_2	2001	39

A superconductor excludes all magnetic field lines. This is one way to tell that a substance is acting as a super conductor (that it is below T_c).

- Demonstrate the Meissner effect:



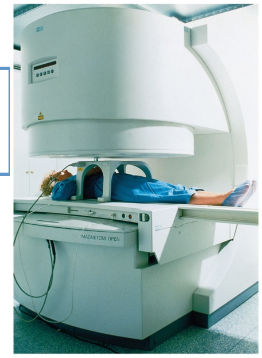
Superconducting Ceramic Oxides

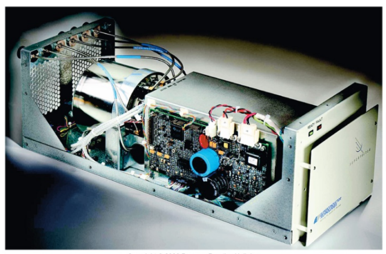


The development of higher and higher temperature superconductors will have a tremendous impact on modern culture.

Levitating trains

MRI , NMR (magnetic resonance imaging)





Cell phone frequency filter