

Linear Combination of Atomic Orbitals

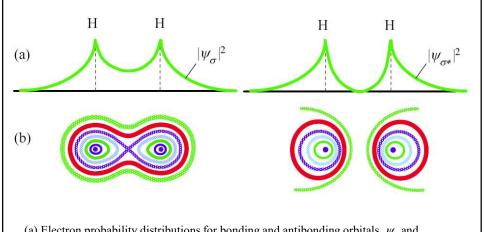
Two identical atomic orbitals ψ_{1s} on atoms A and B can be combined linearly in two different ways to generate two separate molecular orbitals ψ_{σ} and ψ_{σ^*}

 ψ_σ and ψ_{σ^*} generated from a linear combination of atomic orbitals (LCAO)

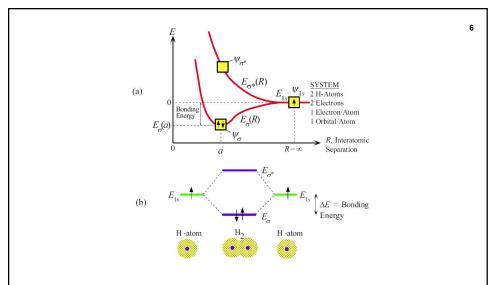
Wavefunction around A Wavefunction around B
$$\psi_{\sigma} = \psi_{ls}(r_A) + \psi_{ls}(r_B)$$

$$\psi_{\sigma}^* = \psi_{ls}(r_A) - \psi_{ls}(r_B)$$

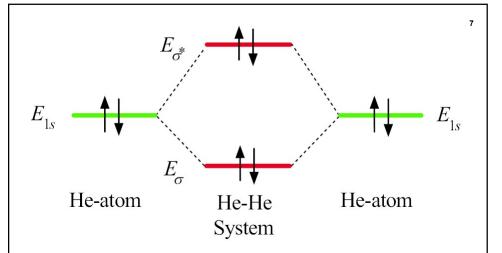
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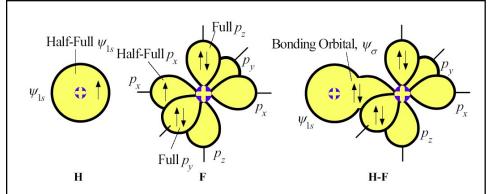
- (a) Electron probability distributions for bonding and antibonding orbitals, ψ_{σ} and ψ_{σ^*} . (b) Lines representing contours of constant probability (darker lines represent greater
- relative probability).



- (a) Energy of ψ_σ and ψ_{σ*} vs. the interatomic separation R.
 (b) Schematic diagram showing the changes in the electron energy as two isolated H atoms, far left and far right, come together to form a hydrogen molecule.

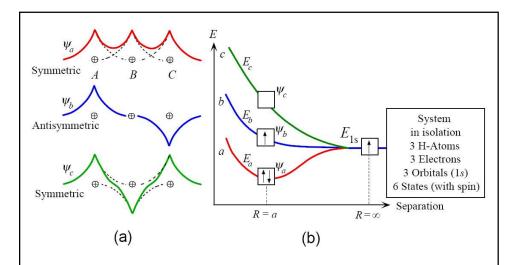


Two He atoms have four electrons. When He atoms come together, two of the electrons enter the $E_{\mathbb{B}}$ level and two the $E_{\mathbb{B}^*}$ level, so the overall energy is greater than two isolated He atoms.

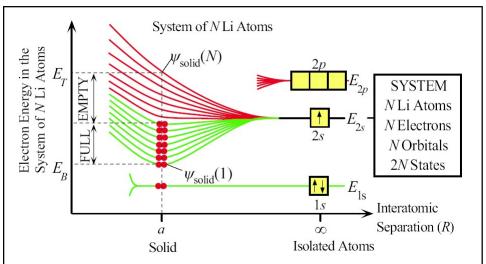


H has one half-empty ψ_{1s} orbital.

F has one half-empty p_x orbital but full p_y and p_z orbitals. The overlap between ψ_{1s} and p_x produces a bonding orbital and an antibonding orbital. The two electrons fill the bonding orbital and thereby form a covalent bond between H and F.

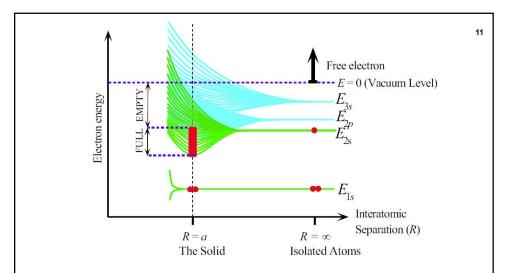


- (a) Three molecular orbitals from three ψ_{1s} atomic orbitals overlapping in three different ways.
- (b) The energies of the three molecular orbitals, labeled a, b, and c, in a system with three H atoms.

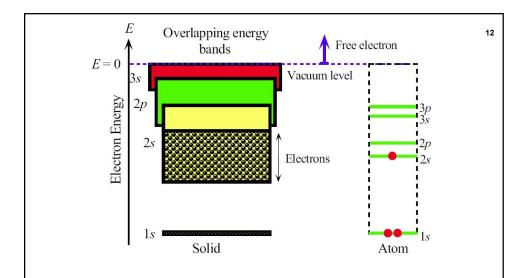


The formation of 2s energy band from the 2s orbitals when N Li atoms come together to form the Li solid.

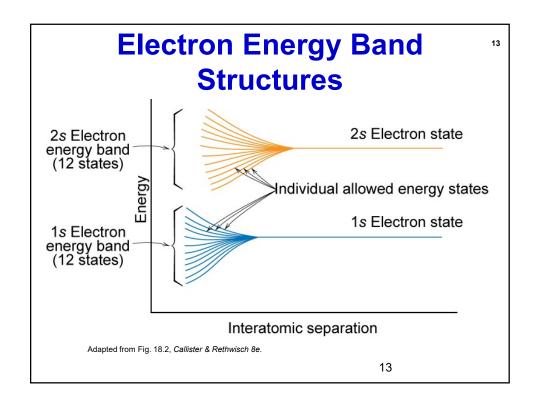
There are N 2s electrons, but 2N states in the band. The 2s band is therefore only half full. The atomic 1s orbital is close to the Li nucleus and remains undisturbed in the solid. Thus, each Li atom has a closed K shell (full 1s orbital).

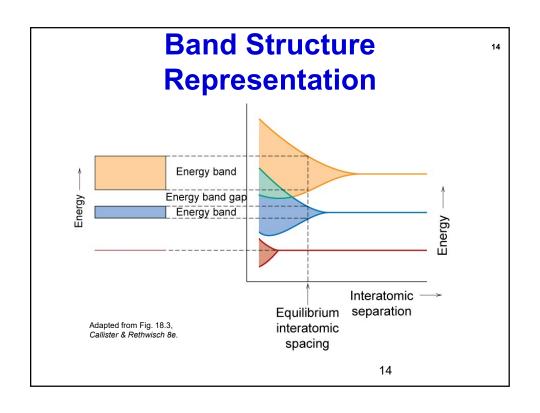


As Li atoms are brought together from infinity, the atomic orbitals overlap and give rise to bands. Outer orbitals overlap first. The 3s orbitals give rise to the 3s band, 2p orbitals to the 2p band, and so on. The various bands overlap to produce a single band in which the energy is nearly continuous.

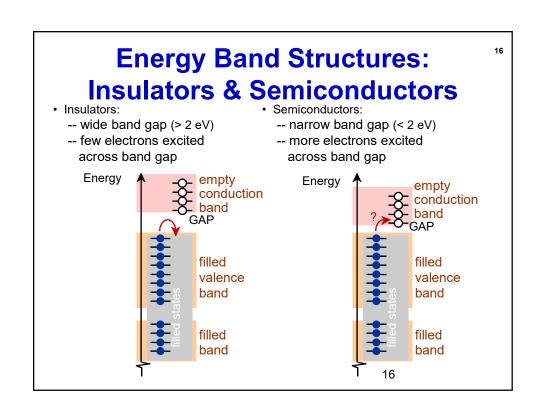


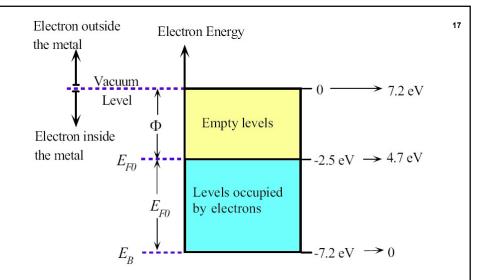
In a metal, the various energy bands overlap to give a single energy band that is only partially full of electrons. There are states with energies up to the vacuum level, where the electron is free.





Conduction & Electron Transport • Metals (Conductors): -- for metals empty energy states are adjacent to filled states. -- thermal energy Partially filled band Overlapping bands excites electrons Energy Energy into empty higher empty energy states. band -- two types of band empty structures for metals - partially filled band partly filled filled - empty band that band band overlaps filled band filled filled band band 15





Typical electron energy band diagram for a metal.

All the valence electrons are in an energy band, which they only partially fill. The top of the band is the vacuum level, where the electron is free from the solid (PE = 0).

Work function Φ

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The energy required to excite an electron from the Fermi level to the vacuum level, that is, to liberate the electron from the metal, is called the **work function** Φ of the metal.

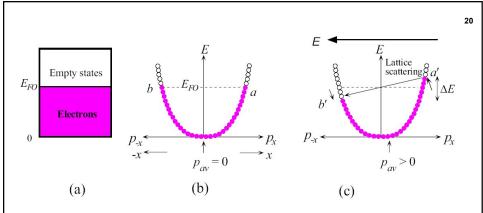
Electron gas in a metal

The electrons in the energy band of a metal are loosely bound valence electrons, which become free in the crystal and thereby form a kind of **electron gas** within the crystal. It is this electron gas that holds the metal ions together in the crystal structure and constitutes the metallic bond.

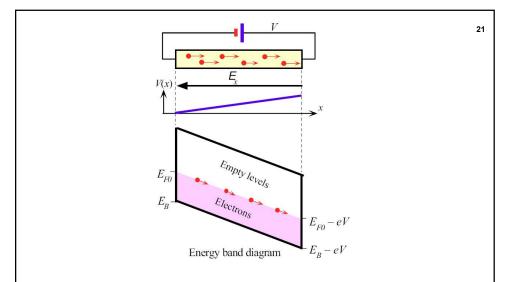
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Table 4.1 Fermi energy and work function of selected metals

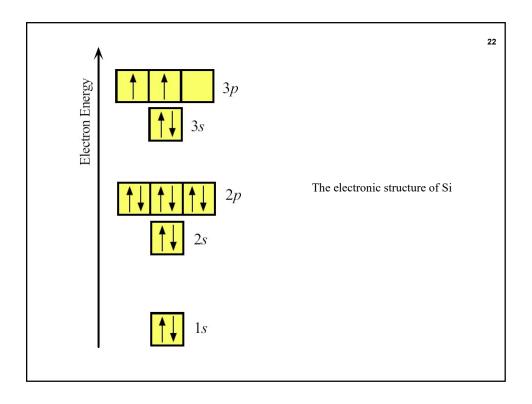
	Metal							
	Ag	Al	Au	Cs	Cu	Li	Mg	Na
Φ (eV)	4.5	4.28	5.0	2.14	4.65	2.3	3.7	2.75
E_{FO} (eV)	5.5	11.7	5.5	1.58	7.0	4.7	7.1	3.2

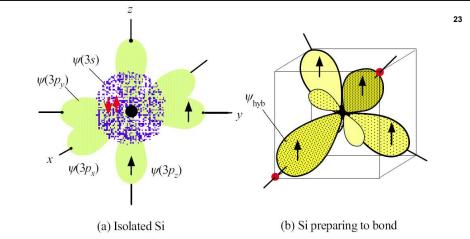


(a) Energy band diagram of a metal. (b) In the absence of a field, there are as many electrons moving right as there are moving left. The motions of two electrons at each energy cancel each other as for a and b. (c) In the presence of a field in the x direction, the electron a accelerates and gains energy to a' where it is scattered to an empty state near E_{FO} but moving in the -x direction. The average of all momenta values is along the +x direction and results in a net electrical current.



Conduction in a metal is due to the drift of electrons around the Fermi level. When a voltage is applied, the energy band is bent to be lower at the positive terminal so that the electron's potential energy decreases as it moves toward the positive terminal.



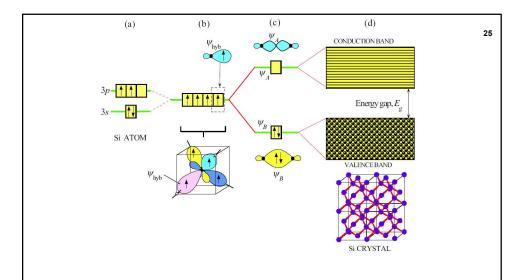


- (a) Si is in Group IV in the Periodic Table. An isolated Si atom has two electrons in the 3s and two electrons in the 3p orbitals.
- (b) When Si is about to bond, the one 3s orbital and the three 3p orbitals become perturbed and mixed to form four hybridized orbitals, ψ_{hyb} , called sp^3 orbitals, which are directed toward the corners of a tetrahedron. The ψ_{hyb} orbital has a large major lobe and a small back lobe. Each ψ_{hyb} orbital takes one of the four valence electrons.

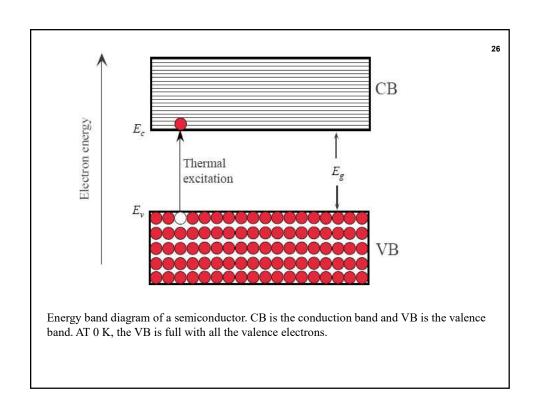
Hybridization

sp³ hybridization

The 3s and 3p energy levels are quite close, and when five Si atoms approach each other, the interaction results in the four orbitals $\psi(3s)$, $\psi(3p_x)$, $\psi(3p_y)$ and $\psi(3p_z)$ mixing together to form four new hybrid orbitals, which are directed in tetrahedral directions; that is, each one is aimed as far away from the others as possible.



(a) Formation of energy bands in the Si crystal first involves hybridization of 3s and 3p orbitals to four identical ψ_{hyb} orbitals which make 109.5° with each other as shown in (b). (c) ψ_{hyb} orbitals on two neighboring Si atoms can overlap to form ψ_B or ψ_A . The first is a bonding orbital (full) and the second is an antibonding orbital (empty). In the crystal ψ_B overlap to give the valence band (full) and ψ_A overlap to give the conduction band (empty).



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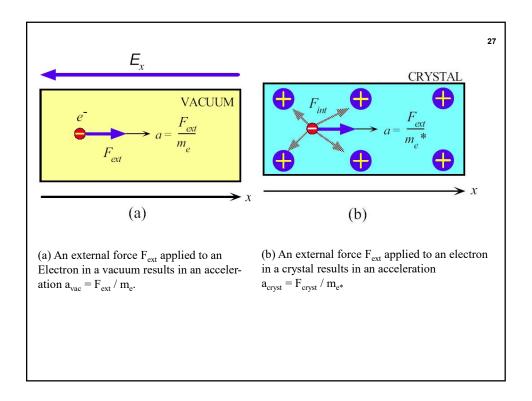
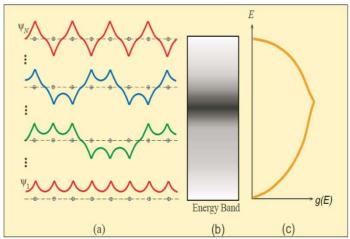


Table 4.2 Effective mass m_e^* of electrons in some metals Metal Bi K Zn Ag Au Cu Li Na Ni Pt m_e^* 0.99 1.10 0.047 1.12 1.28 13 0.85 1.01 1.2 28 $\overline{m_e}$



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- (a) In the solid there are N atoms and N extended electron wavefunctions from ψ_1 all the way to ψ_N . There are many wavefunctions, states, that have energies that fall in the central regions of the energy band.
- (b) The distribution of states in the energy band; darker regions have a higher number of states.
- (c) Schematic representation of the density of states g(E) versus energy E.

Density of States

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- g(E) = Density of states
- g(E) dE is the number of states (*i.e.*, wavefunctions) in the energy interval E to (E + dE) per unit volume of the sample.

$$g(E) = \left(8\pi 2^{1/2}\right) \left(\frac{m_e}{h^2}\right)^{3/2} E^{1/2}$$

Number of Electrons/ Volume

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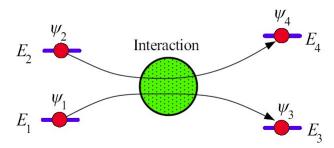
f(E) = Probability that a state with energy E is occupied

g(E) = Density of states

$$n = \int_{Band} f(E)g(E)dE$$

Boltzmann Classical Statistics

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Two electrons with initial wavefunctions ψ_1 and ψ_2 at E_1 and E_2 interact and end up different energies E_3 and E_4 . Their corresponding wavefunctions are ψ_3 and ψ_4 .

Boltzmann Classical Statistics

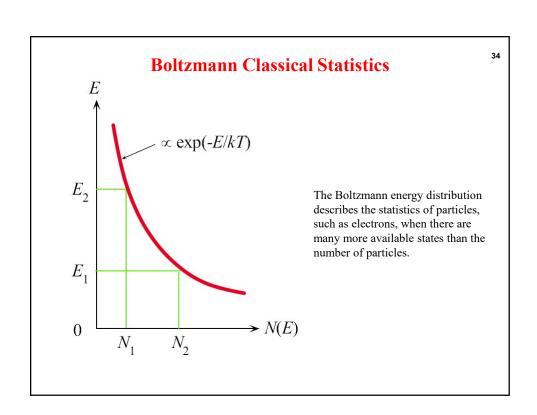
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Boltzmann probability function

$$P(E) = A \exp\left(-\frac{E}{kT}\right)$$

Boltzmann Statistics for two energy levels

$$\frac{N_2}{N_1} = \exp\left(-\frac{E_2 - E_1}{kT}\right)$$



Fermi-Dirac Statistics

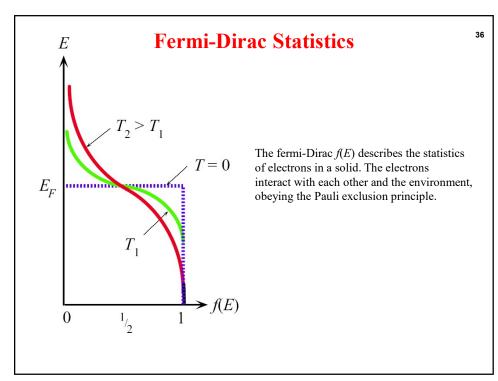
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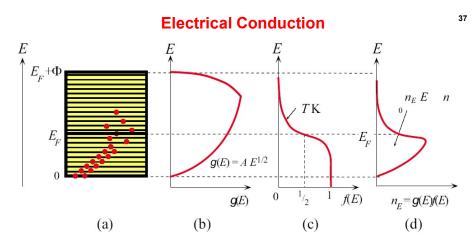
The Fermi-Dirac function

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

where E_F is a constant called the **Fermi energy**.

f(E) = the probability of finding an electron in a state with energy E is given





- (a) Above 0K, due to thermal excitation, some of the electrons are at energies above E_E.
- (b) The density of states, g(E) versus E in the band.
- (c) The probability of occupancy of a state at an energy E is f(E).
- (d) The product of $g(E) f(\bar{E})$ is the number of electrons per unit energy per unit volume, or the electron concentration per unit energy. The area under the curve on the energy axis is the concentration of electrons in the band.

Fermi Energy

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Fermi energy at T = 0 K

$$E_{FO} = \left(\frac{h^2}{8m_e}\right) \left(\frac{3n}{\pi}\right)^{2/3}$$

n is the concentration of conduction electrons (free carrier concentration)

Fermi energy at T(K)

$$E_F(T) = E_{FO} \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{E_{FO}} \right)^2 \right]$$

Average energy per electron

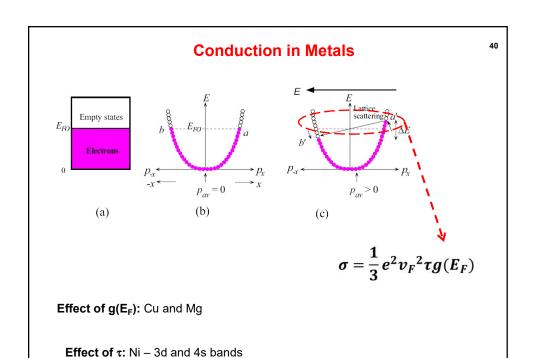
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Average energy per electron at 0 K

$$E_{\rm av}(0) = \frac{3}{5}E_{FO}$$

Average energy per electron at T(K)

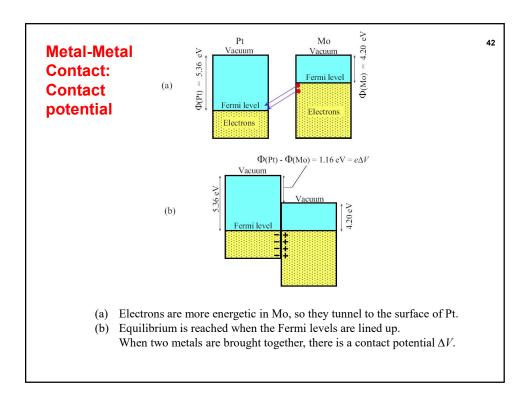
$$E_{\text{av}}(T) = \frac{3}{5} E_{FO} \left[1 + \frac{5\pi^2}{12} \left(\frac{kT}{E_{FO}} \right)^2 \right]$$

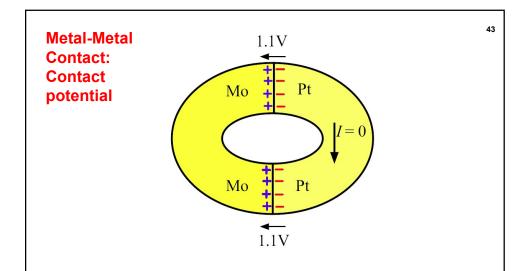


Fermi Energy Significance

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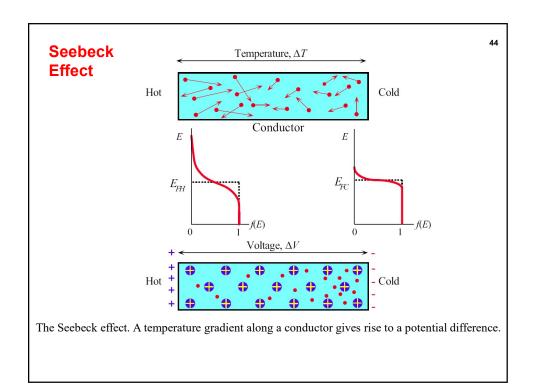
For a given metal the Fermi energy represents the free energy per electron called the **electrochemical potential**. The Fermi energy is a measure of the potential of an electron to do electrical work $(e \times V)$ or nonmechanical work, through chemical or physical processes.





There is no current when a closed circuit is formed by two different metals, even though there is a contact potential at each contact.

The contact potentials oppose each other.



Seebeck Effect

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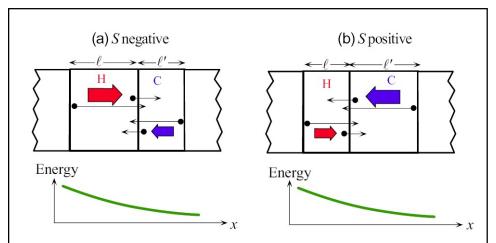
Seebeck effect (thermoelectric power)

is the built-in potential difference ΔV across a material due to a temperature difference ΔT across it.

$$S = \frac{\Delta V}{\Delta T}$$

Sign of S

is the potential of the cold side with respect to the hot side; negative if electrons have accumulated in the cold side.



Consider two neighboring regions H (hot) and C (cold) with widths corresponding to the mean Free paths 1 and 1' in H and C.

Half the electrons in H would be moving in the +x direction and the other half in the -x direction. Half of the electrons in H therefore cross into C, and half in C cross into H.

Seebeck coefficient for metals

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$$S \approx -\frac{\pi^2 k^2 T}{3eE_{FO}} x$$

Mott and Jones thermoelectric power equation

x= a numerical constant that takes into account how various charge transport parameters, such as the mean free path ℓ , depend on the electron energy.

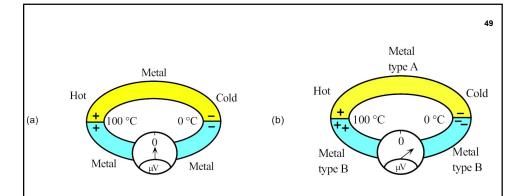
x values are tabulated in Table 4.3

DOES NOT APPLY TO MATERIALS HAVING OVERLAPPING BANDS – e.g. Ni

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 Table 4.3
 Seebeck coefficients of selected metals (from various sources)

Metal	S at 0 °C (μV K ⁻¹)	S at 27 °C $(\mu V K^{-1})$	$E_F(eV)$	x
A1	-1.6	-1.8	11.6	2.78
Au	+1.79	+1.94	5.5	-1.48
Cu	+1.70	+1.84	7.0	-1.79
K		-12.5	2.0	3.8
Li	+14		4.7	-9.7
Mg	-1.3		7.1	1.38
Na		-5	3.1	2.2
Pd	-9.00	-9.99		
Pt	-4.45	-5.28		



(a) If Al wires are used to measure the Seebeck voltage across the Al rod, then the net emf is zero.(b) The Al and Ni have different Seebeck coefficients. There is therefore a net emf in the Al-Ni Circuit between the hot and cold ends that can be measured.

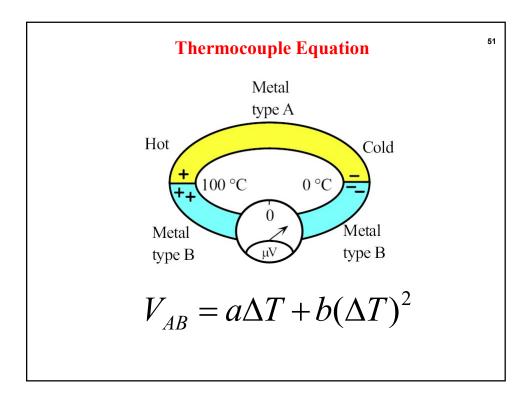
Thermocouple

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We can only measure differences between thermoelectric powers of materials.

When two different metals *A* and *B* are connected to make a **thermocouple**, then the net EMF is the voltage difference between the two elements.

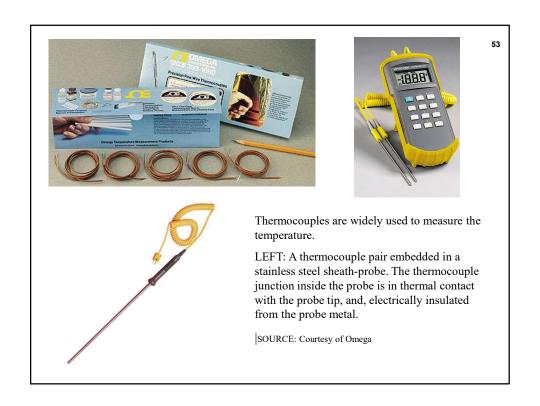
$$V_{AB} = \int_{T_o}^{T} (S_A - S_B) dT = \int_{T_o}^{T} S_{AB} dT$$

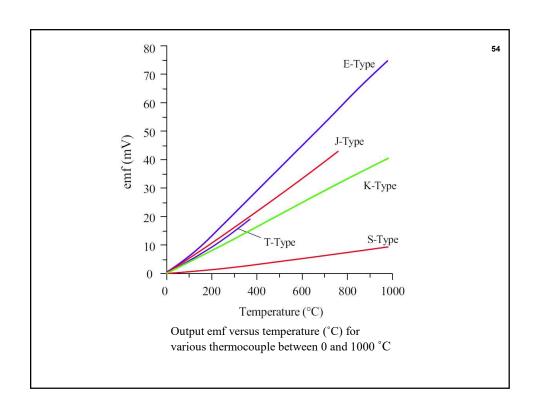


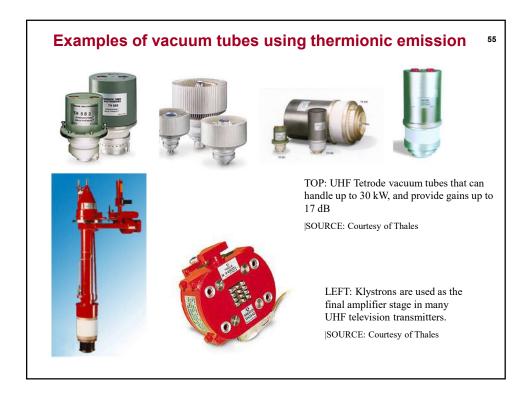
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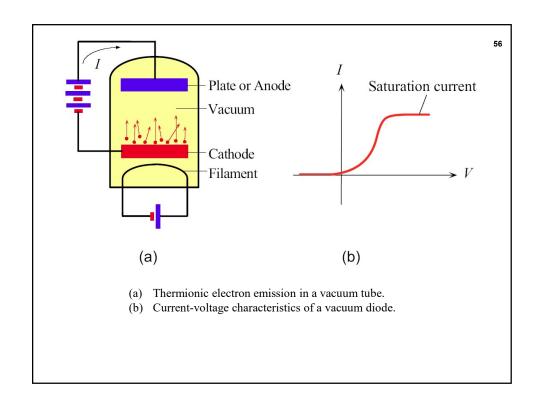
Table 4.4 Thermoelectric emf for metals at 100 and 200 $^{\circ}$ C with respect to Pt and the reference junction at 0 $^{\circ}$ C

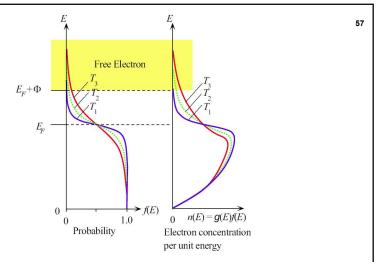
	emf (1	mV)
Material	At 100 °C	At 200 °C
Copper, Cu	0.76	1.83
Aluminum, Al	0.42	1.06
Nickel, Ni	-1.48	-3.10
Palladium, Pd	-0.57	-1.23
Platinum, Pt	0	0
Silver, Ag	0.74	1.77
Alumel	-1.29	-2.17
Chromel	2.81	5.96
Constantan	-3.51	-7.45
Iron, Fe	1.89	3.54
90% Pt-10% Rh	0.643	1.44
(platinum-rhodium)		











Fermi-Dirac function f(E) and the energy density of electrons n(E) (electrons per unit energy and per unit volume) at three different temperatures. The electron concentration extends more and more to higher energies as the temperature increases. Electrons with energies in excess of $E_F+\Phi$ can leave the metal (thermionic emission)

Thermionic Emission

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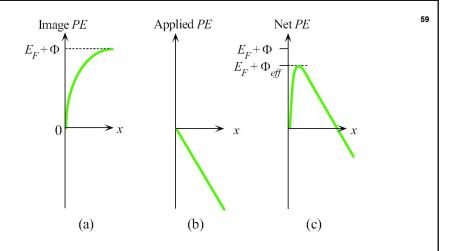
Richardson-Dushman thermionic emission equation

$$J = B_o T^2 \exp\left(-\frac{\Phi}{kT}\right)$$

 B_o =4 π em_e k^2/h^3 = 120×10⁶ A m⁻² K⁻² Richardson-Dushman constant

$$J = B_e T^2 \exp\left(-\frac{\Phi}{kT}\right)$$

where B_e = effective emission constant = (1-R) B_0 R = Reflection coefficient



- (a) PE of the electron near the surface of a conductor.
- (b) Electron PE due to an applied field, that is, between cathode and anode.
- (c) The overall PE is the sum.

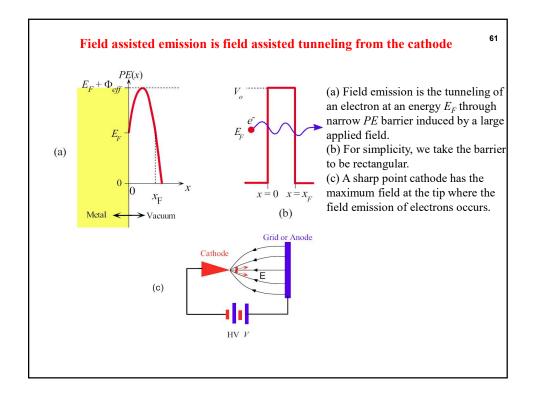
Schottky effect

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When a positive voltage is applied to the anode with respect to the cathode, the electric field at the cathode helps the thermionic emission process by lowering the PE barrier Φ by an amount $\beta_S \mathcal{E}^{1/2}$. The current density in field assisted thermionic emission is

Metal's work function Schottky coefficient

$$J = B_e T^2 \exp\left(-\frac{\Phi - \beta_S \mathcal{E}^{1/2}}{kT}\right)$$



Field-assisted Tunneling

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Field-assisted tunneling probability

Effective work function due to the Schottky effect

$$p \approx \exp \left[-\frac{2(2m_e \Phi_{\text{eff}})^{1/2} \Phi}{e\hbar \mathcal{E}} \right]$$

Field-assisted tunneling: the Fowler-Nordheim equation

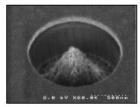
$$J_{\text{field-emission}} \approx C \mathcal{E}^2 \exp \left(-\frac{\mathcal{E}_c}{\mathcal{E}}\right)$$

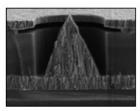
Applied field at the cathode

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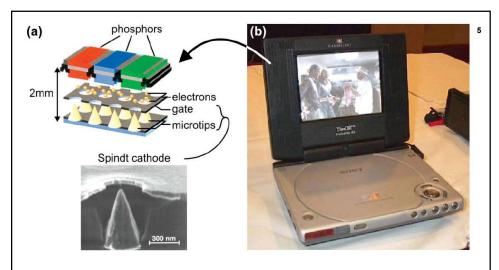
Left: A scanning electron microscope image of an array of electron field emitters (icebergs). Center: One iceberg. Right: A cross section of a field emitter. Each iceberg is a source of electron emission arising from Fowler–Nordheim field emission; for further information see B. Chalamala, et al., IEEE Spectrum, April 1998, pp. 42–51.

| SOURCE: Courtesy of Dr. Babu Chalamala, Flat Panel Display Division, Motorola.



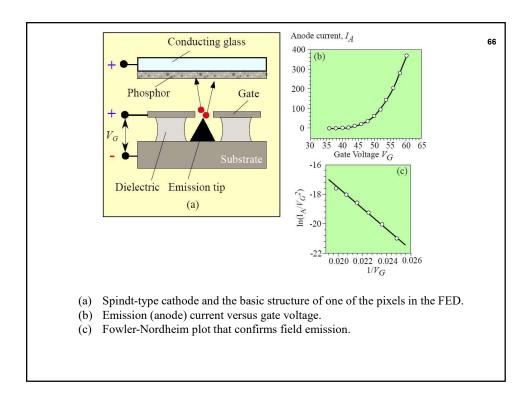
Motorola's prototype flat panel display based on the Fowler-Nordheim field emission principle. The display is 14 cm in diagonal and 3.5 mm thick with a viewing angle 160°. Each pixel (325 μ m thick) uses field emission of electrons from microscopic sharp point sources (icebergs). Emitted electrons impinge on colored phosphors on a screen and cause light emission by cathodoluminescence. There are millions of these microscopic field emitters to constitute the image.

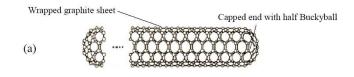
I SOURCE: Courtesy of Dr. Babu Chalamala, Flat Panel Display Division, Motorola.

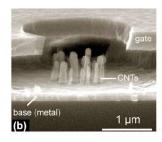


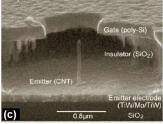
Cross-section of a field emission display showing a Spindt tip cathode, (b) Sony portable DVD player using a field emission display.

SOURCE: Courtesy of Professor W.I. Milne, University of Cambridge, England. Carbon nanotubes as field emission sources, W. I. Milne, K. B. K. Teo, G. A. J. Amaratunga, P. Legagneux, L. Gangloff, J.-P. Schnell, V. Semet, V. Thien Binh and O. Groening, Journal of Materials Chemistry, 14, 933, 2004









(a) A carbon nanotube (CNT) is a whisker-like very thin and long carbon molecule with rounded ends; almost a perfect shape as an electron field-emitter. (b) Multiple CNTs as electron emitters. (c) A single CNT as an emitter.

SOURCE: Courtesy of Professor W.I. Milne, University of Cambridge; G. Pirio *et al*, *Nanotechnology*, **13**, 1, 2002.

CNT (Carbon NanoTube)

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A carbon nanotube (CNT) is a very thin filament-like carbon molecule whose diameter is in the nanometer range but whose length can be quite long, e.g., 10-100 microns, depending on how it is grown or prepared.