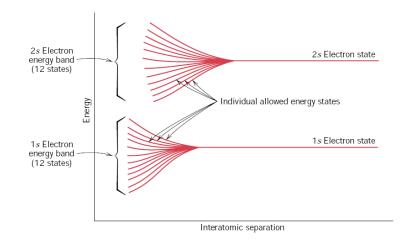
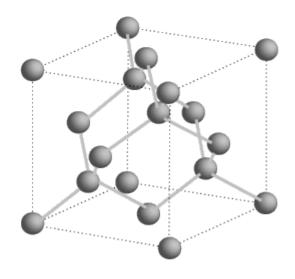
Elétrons em cristais

- Princípio de exclusão de Pauli.
- Átomos multieletrônicos.
- Moléculas.
- Bandas de energia em sólidos.
- Condutores, semicondutores e isolantes.
- Gás de Fermi de elétrons livres.
- Semicondutores:
 - Propriedades.
 - Dopagem.
 - Exemplos.



Propriedades eletrônicas dos materiais

Estrutura cristalina do diamante (C) e do silício (Si):



http://hyperphysics.phy-astr.gsu.edu/hbase/minerals/diamond.html

Diamante: isolante, transparente.

Silício: semicondutor, opaco.

Table 4.3
ELEMENTS WITH THE DIAMOND CRYSTAL
STRUCTURE

ELEMENT	CUBE SIDE a (Å)		
C (diamond)	3.57		
Si	5.43		
Ge	5.66		
α-Sn (grey)	6.49		

Solid State Physics, Ashcroft / Mermin, 1976.

Propriedades eletrônicas dos materiais



http://en.wikipedia.org/wiki/Silicor



http://en.wikipedia.org/wiki/Diamond (gemstone

Silício: semicondutor, opaco.

Diamante: isolante, transparente.

Equação de Schrödinger em 3D:

$$-\frac{\square^2}{2m}\nabla^2\psi(\square)+\psi(\square)\psi(\square)=\mathcal{E}\psi(\square)$$

 $\psi(\stackrel{\square}{}) = \beta \ (f) / \ (\theta, \phi)$ $/ \ (\stackrel{\square}{}) = / \ (f)$

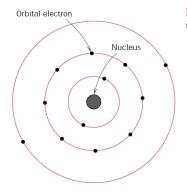


FIGURE 2.1 Schematic representation of the Bohr atom.

Fundamentals of Materials Science and Engineering, Callister.

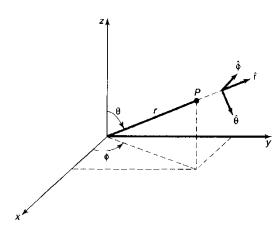


Figure 4.1: Spherical coordinates: radius r, polar angle θ , and azimuthal angle ϕ .

Introduction to Quantum Mechanics, Griffiths, 1995.

O Princípio de Exclusão de Pauli

Enunciado para elétrons em átomos (problema original):

Em um átomo multieletrônico nunca pode haver mais de um elétron ocupando o mesmo estado quântico.

Os números quânticos n, l, m_l e m_s não podem jamais ser todos iguais para dois elétrons em um átomo multieletrônico.



Wolfgang Pauli (1900-1958) Nobel de Física 1945

Enunciado geral:

Dois férmions (partículas com spin semi-inteiro) não podem jamais ocupar o mesmo estado quântico.

Um sistema constituído de vários elétrons (ou férmions idênticos em geral) deve ser descrito por uma função de onda total anti-simétrica.

Preenchimento dos níveis - Princípio de Exclusão:

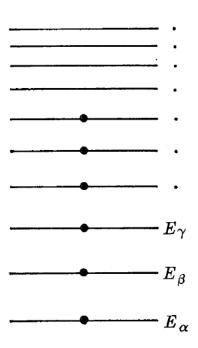


Figure 9-9 A schematic energy-level diagram illustrating the effect of the exclusion principle in limiting the population of each quantum state of an atom with six electrons. Note that the total energy of the atom would be much more negative if the exclusion principle did not operate. The diagram does not indicate that many quantum states are actually degenerate, nor are the spacings between the levels meant to be realistic.

Preenchimento dos níveis - Princípio de Exclusão:

Table 9-2 The Energy Ordering of the Outer Filled Subshells

Quantum Numbers n, l	Designation of Subshell	Capacity of Subshell $2(2l+1)$		
		_		
6, 2	6 <i>d</i>	10		
5, 3	5 <i>f</i>	14		
7, 0	7s	2		
6, 1	6 <i>p</i>	6		
5, 2	5d	10		
4, 3	4f	14		
6, 0	6 <i>s</i>	2	Î	
5, 1	5 <i>p</i>	6		
4, 2	4d	10	Increasing energ	
5, 0	5 <i>s</i>	. 2	(less negative)	
4, 1	4p	6		
3, 2	$\dot{3d}$	10		
4, 0	4s	2		
3, 1	3 <i>p</i>	6		
3, 0	3s	2		
2, 1	2p	6		
2, 0	2s	2		
1, 0	1s	2	←Lowest energy (most negative)	

Table 2.1 The Number of Available Electron States in Some of the Electron Shells and Subshells

Principal Quantum	Shell	Subshells	Number of States	Number of Electrons		
Number n	Designation			Per Subshell	Per Shell	
1	K	S	1	2	2	
2	L	s p	1 3	2 6	8	
3	M	s p d	1 3 5	2 6 10	18	
4	N	s p d f	1 3 5 7	2 6 10 14	32	

Quantum Physics, Eisberg & Resnick.

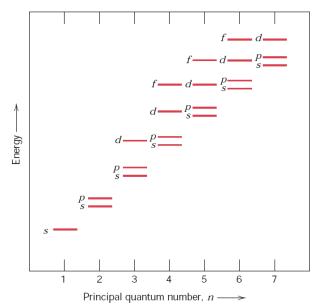


FIGURE 2.4 Schematic representation of the relative energies of the electrons for the various shells and subshells. (From K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*, p. 22. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

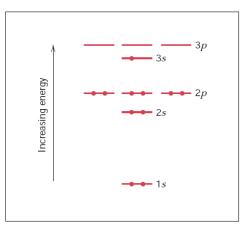
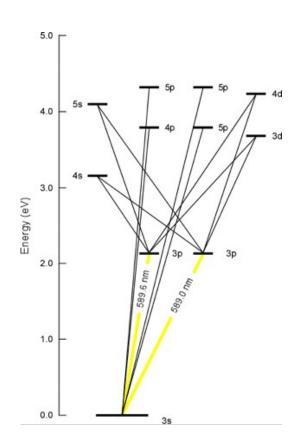


FIGURE 2.5 Schematic representation of the filled energy states for a sodium atom.

Espectros atômicos: Raios X: L series 10⁴ M series Energy (eV) 10³

Figure 9-17 The higher energy x-ray levels for the uranium atom and the transitions between these levels allowed by the selection rules.

Espectros óticos:

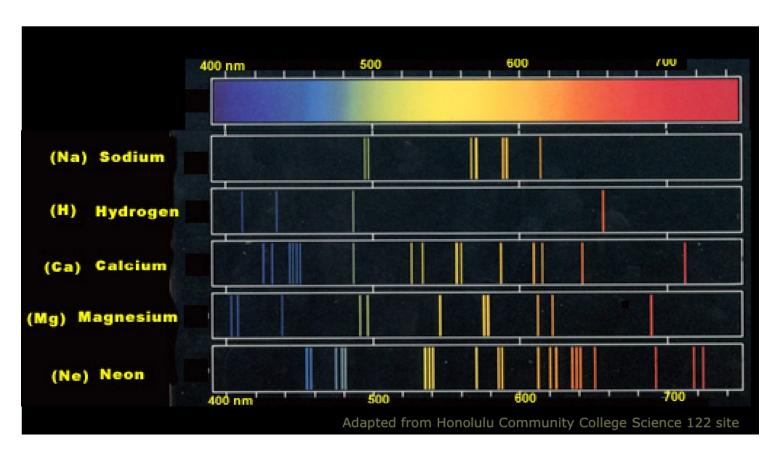


Quantum Physics, Eisberg & Resnick.

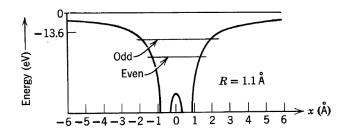
10²

Espectros atômicos

Espectros discretos (raias):



Funções de onda em moléculas



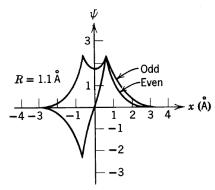


Figure 12-2 Top: The potential function, and the two lowest energy levels, for an electron in a H_2^+ molecule with internuclear separation R=1.1 Å. The potential function is evaluated along the line passing through the two nuclei. Bottom: The even and odd eigenfunctions corresponding to the two energy levels, evaluated along the internuclear line. Near each nucleus, both eigenfunctions have magnitudes that are decreasing exponentials of the distance from the nucleus, as in the ground state of the hydrogen atom.

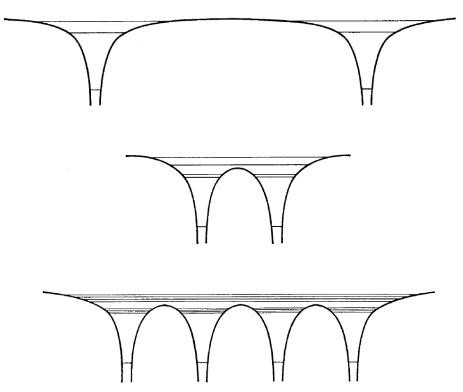
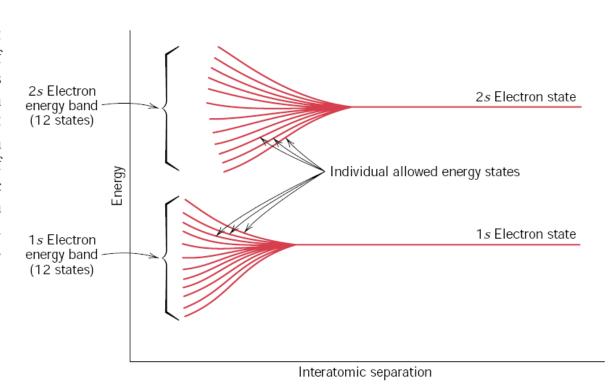


Figure 13-2 *Top:* Energy-level scheme for two isolated atoms. *Middle:* Energy-level scheme for the same two atoms in a diatomic molecule. *Bottom:* Energy-level scheme for four of the same atoms in a rudimentary one-dimensional crystal. Note that the lowest lying levels are not split appreciably because the atomic eigenfunctions for these levels do not overlap significantly.

FIGURE 12.2

Schematic plot of electron energy versus interatomic separation for an aggregate of 12 atoms (N=12). Upon close approach, each of the 1s and 2s atomic states splits to form an electron energy band consisting of 12 states.



Fundamentals of Materials Science and Engineering, Callister.

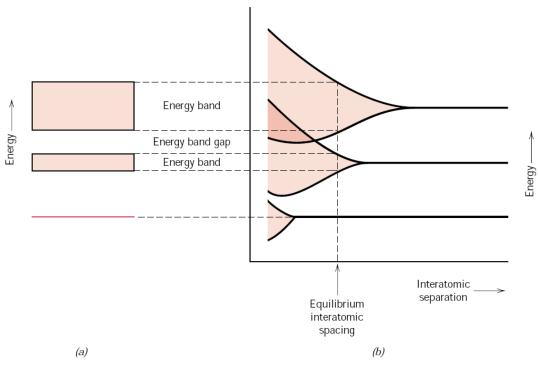
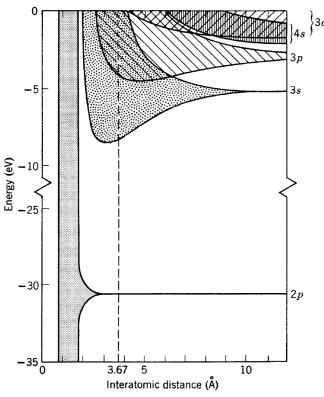


Figure 12.3 (a) The conventional representation of the electron energy band structure for a solid material at the equilibrium interatomic separation.

(b) Electron energy versus interatomic separation for an aggregate of atoms, illustrating how the energy band structure at the equilibrium separation in (a) is generated. (From Z. D. Jastrzebski, *The Nature and Properties of Engineering Materials*, 3rd edition. Copyright © 1987 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)



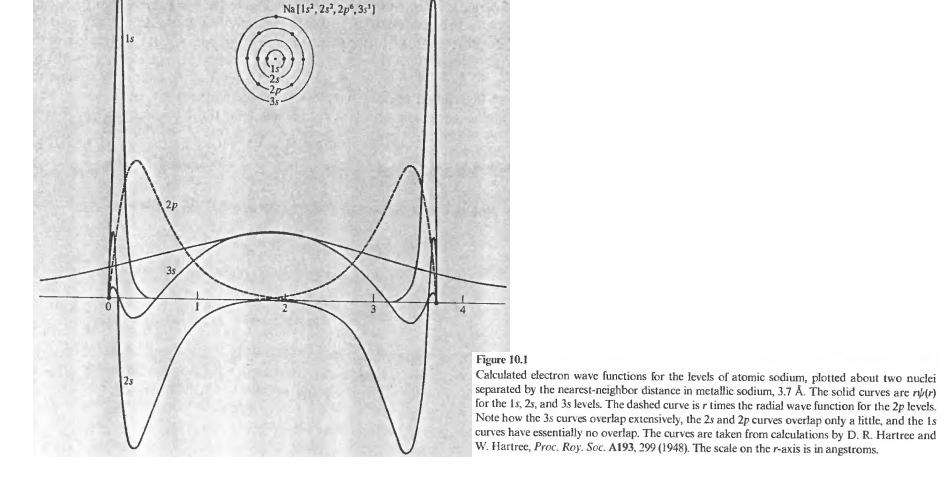
3p 3s 3s 2p 2s 1s

FIGURE 2.5 Schematic representation of the filled energy states for a sodium atom.

 $\label{lem:condition} \textit{Fundamentals of Materials Science and Engineering} \ , \textit{Callister}.$

Figure 13-3 Showing the formation of energy bands from the energy levels of isolated sodium atoms as the interatomic separation decreases. The dashed line indicates the observed interatomic separation in solid sodium. The several overlapping bands that constitute each p or d band are not indicated.

Quantum Physics, Eisberg & Resnick.



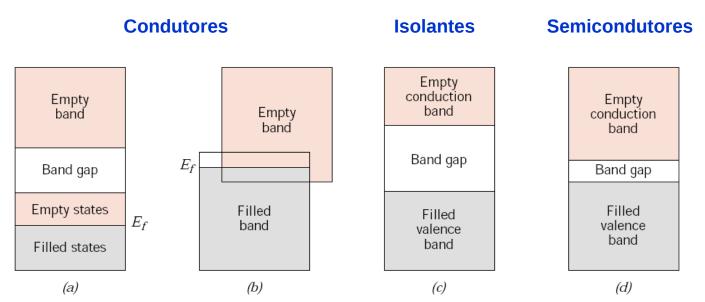
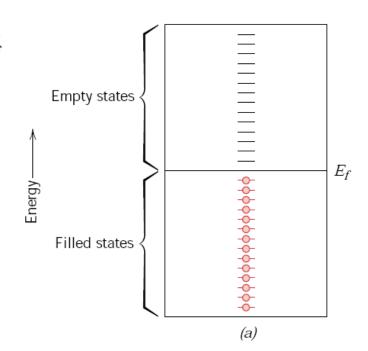


Figure 12.4 The various possible electron band structures in solids at 0 K. (a) The electron band structure found in metals such as copper, in which there are available electron states above and adjacent to filled states, in the same band. (b) The electron band structure of metals such as magnesium, wherein there is an overlap of filled and empty outer bands. (c) The electron band structure characteristic of insulators; the filled valence band is separated from the empty conduction band by a relatively large band gap (>2 eV). (d) The electron band structure found in the semiconductors, which is the same as for insulators except that the band gap is relatively narrow (<2 eV).

FIGURE 12.5 For a metal, occupancy of electron states (a) before and (b) after an electron excitation.



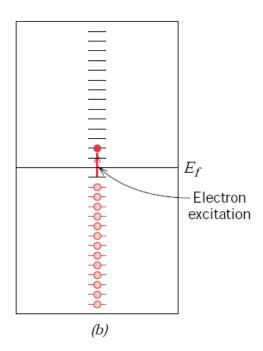
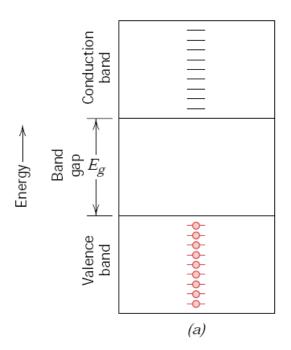
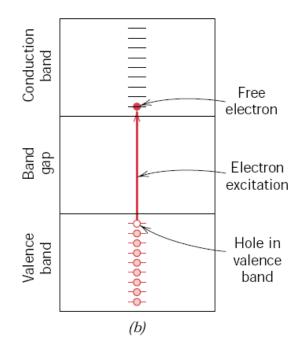


FIGURE 12.6

For an insulator or semiconductor, occupancy of electron states (a) before and (b) after an electron excitation from the valence band into the conduction band, in which both a free electron and a hole are generated.





Silício: $E_q = 1,1$ eV.

Diamante: $E_a = 5.4$ eV.

Propriedades eletrônicas dos materiais



http://en.wikipedia.org/wiki/Silicon



http://en.wikipedia.org/wiki/Diamond_(gemstone)

Silício: semicondutor, opaco.

Diamante: isolante, transparente.

Table 1 Energy gap between the valence and conduction bands (i = indirect gap; d = direct gap)

	Gap	E_{g} , eV				E_g , eV	
Crystal		0 K	300 K	Crystal	Gap	0 K	300 K
Diamond	i	5.4		HgTea	d	-0.30	
Si	i	1.17	1.11	PbS	d	0.286	0.34-0.37
Ge	i	0.744	0.66	PbSe	i	0.165	0.27
α Sn	d	0.00	0.00	PbTe	i	0.190	0.29
InSb	d	0.23	0.17	CdS	d	2.582	2.42
InAs	d	0.43	0.36	CdSe	d	1.840	1.74
InP	d	1.42	1.27	CdTe	d	1.607	1.44
GaP	i	2.32	2.25	ZnO		3.436	3.2
GaAs	d	1.52	1.43	ZnS		3.91	3.6
GaSb	d	0.81	0.68	SnTe	d	0.3	0.18
AlSb	i	1.65	1.6	AgCl		-	3.2
SiC(hex)	i	3.0		AgI		-	2.8
Te	d	0.33		Cu ₂ O	d	2.172	
ZnSb		0.56	0.56	TiO ₂		3.03	-

[&]quot;HgTe is a semimetal; the bands overlap.

Propriedades óticas de metais:

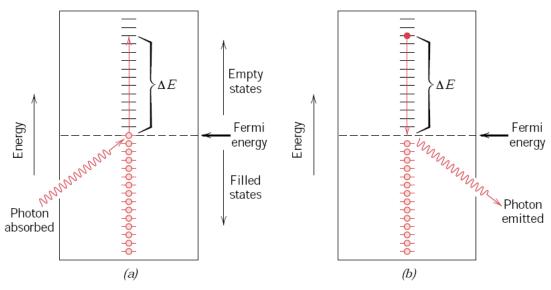


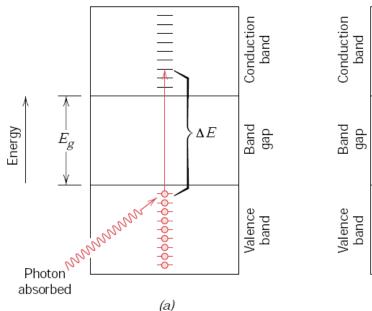
FIGURE 19.4 (a) Schematic representation of the mechanism of photon absorption for metallic materials in which an electron is excited into a higher-energy unoccupied state. The change in energy of the electron ΔE is equal to the energy of the photon. (b) Reemission of a photon of light by the direct transition of an electron from a high to a low energy state.

Propriedades óticas de semicondutores e isolantes:

Absorção de fótons:

$$h\nu > E_g$$

$$\frac{hc}{\lambda} > E_g$$



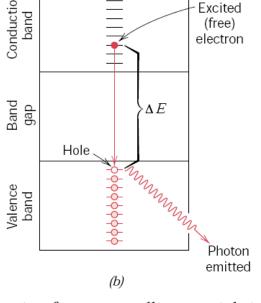
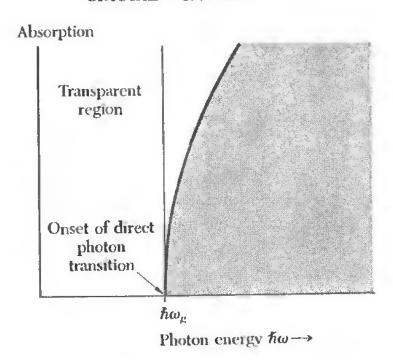
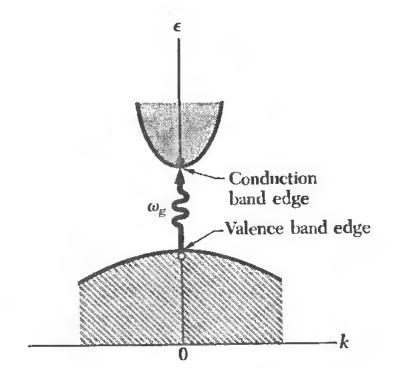


FIGURE 19.5 (a) Mechanism of photon absorption for nonmetallic materials in which an electron is excited across the band gap, leaving behind a hole in the valence band. The energy of the photon absorbed is ΔE , which is necessarily greater than the band gap energy E_g . (b) Emission of a photon of light by a direct electron transition across the band gap.

Propriedades óticas de semicondutores e isolantes:

CRYSTAL WITH DIRECT GAP





Propriedades óticas de semicondutores e isolantes:

InSb: $E_g = 0.23 \text{ eV } (T = 0 \text{ K}).$

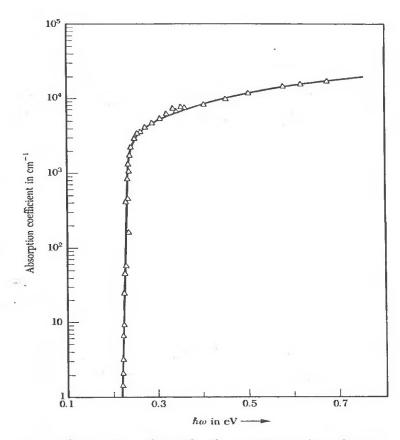
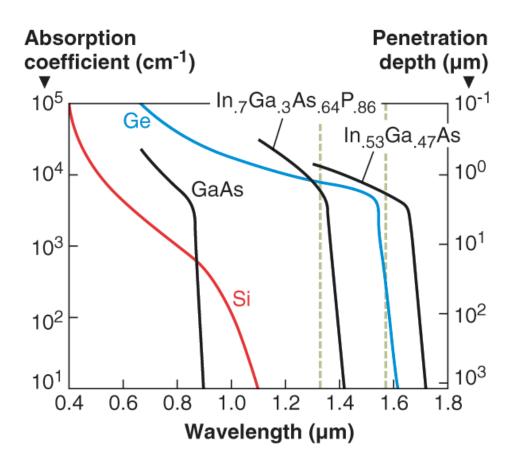


Figure 6 Optical absorption in pure indium antimonide, InSb. The transition is direct because both conduction and valence band edges are at the center of the Brillouin zone, $\mathbf{k}=0$. Notice the sharp threshold. (After G. W. Gobeli and H. Y. Fan.)

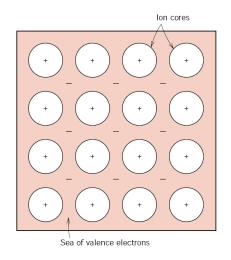
Introduction to Solid State Physics, Kittel, 1996.

Propriedades óticas de semicondutores e isolantes:



http://www.laserfocusworld.com/articles/print/volume-43/issue-5/features/semiconductor-detectors-germanium-on-silicon-approaches-iii-v-semiconductors-in-performance.html

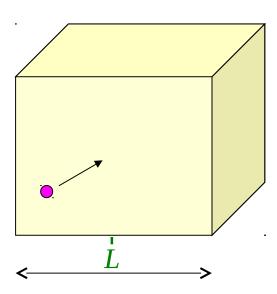
Aplicação do modelo de partícula em uma "caixa" - elétrons livres em metais:



$$-\frac{\square^2}{2m}\nabla^2\psi(\square) + \emptyset \quad (\square)\psi(\square) = \mathcal{E} \quad \psi(\square)$$

$$/\!/ (/\!\!\! -) = 0$$

$$\psi_{\ell}\Box(\ell) = \sqrt{\frac{1}{\ell}}e^{-\ell\ell}$$



Fundamentals of Materials Science and Engineering, Callister.

Condições de contorno periódicas:

$$\psi_{k}^{\square}(\not\vdash + \not\vdash) = \psi_{k}^{\square}(\not\vdash) \qquad k^{\square} = \frac{2\pi}{2\pi} (\pi_{k}, \pi_{k}, \pi_{k}, \pi_{k})$$

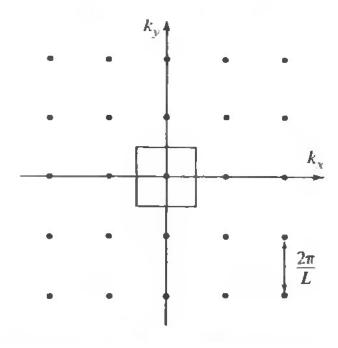
$$\bigwedge^{\square} = \frac{2\pi}{\sqrt{2\pi}} (\Lambda_{\chi}, \Lambda_{\chi}, \Lambda_{\chi})$$

$$n_i = 0, \pm 1, \pm 2, \dots$$

Energia total:
$$\mathcal{E}\left(k\right) = \frac{\prod^2 k^2}{2m}$$

Figure 2.2

Points in a two-dimensional k-space of the form $k_x = 2\pi n_x L$, $k_y = 2\pi n_y L$. Note that the area per point is just $(2\pi L)^2$. In d dimensions the volume per point is $(2\pi L)^d$.



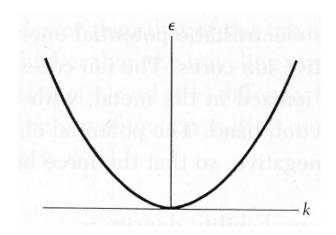
Volume por ponto no espaço k:

Solid State Physics, Ashcroft / Mermin, 1976.

$$\Delta V_k = \left(\frac{2\pi}{L}\right)^3 = \frac{8\pi^3}{V}$$

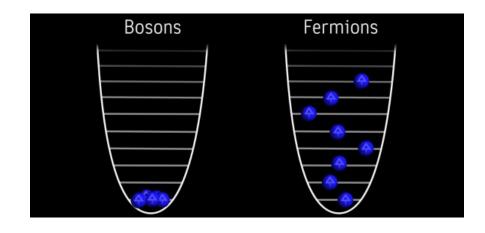
Elétrons livres em metais:

$$\mathcal{E}\left(k\right) = \frac{\square^2 k^2}{2m_e}$$



Máxima energia – energia e velocidade de Fermi:

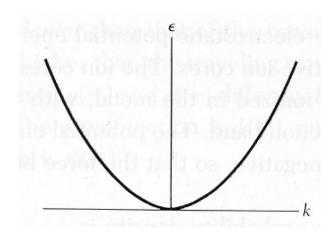
$$E_F = \frac{\mathsf{h}^2 k_F^2}{2m_e} \qquad v_F = \frac{\mathsf{h} k_F}{m_e}$$



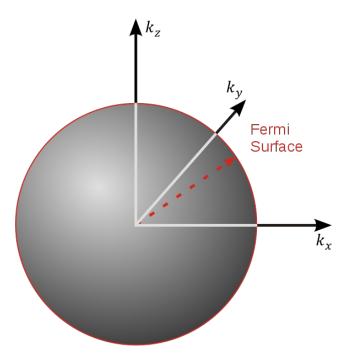
http://www.learner.org/courses/physics/visual/visual.html?shortname=BEC_fermi

Energia e superfície de Fermi:

$$E_F = \frac{\mathsf{h}^2 k_F^2}{2m_e}$$



Esfera de Fermi:

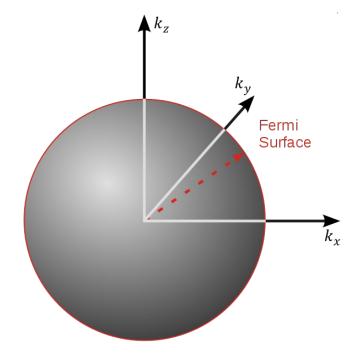


http://en.wikipedia.org/wiki/Fermi_energy

Preenchimento de estados no espaço *k*:

$$N_{el\acute{e}trons}(\Omega) = 2 \times \frac{\Omega}{\Delta V_k}$$

$$\Delta m_s = \pm 1/2$$



http://en.wikipedia.org/wiki/Fermi_energy

Relação entre energia de Fermi e concentração de elétrons:

$$N = 2 \times \left(\frac{4\pi k_F^3}{3} \frac{1}{7} \left(\frac{V}{8\pi^3} \right) \right) \qquad E_F = (3\pi^2 n)^{2/3} \frac{h^2}{2m_e}$$

Table 1 Calculated free electron Fermi surface parameters for metals at room temperature (Except for Na, K, Rb, Cs at 5 K and Li at 78 K)

Valency	Metal	Electron concentration, in cm ⁻³	Radius a parameter r_{s}	Fermi wavevector, in cm ⁻¹	Fermi velocity, in cm s ⁻¹	Fermi energy, in eV	Fermi temperature $T_F \equiv \epsilon_F/k_B$, in deg K
1	Li	4.70×10^{22}	3.25	1.11×10^{8}	1.29×10^{8}	4.72	$5.48 \times 10^{\circ}$
Α.	Na	2.65	3.93	0.92	1.07	3.23	3.75
	K	1.40	4.86	0.75	0.86	2.12	2.46
	Rb	1.15	5.20	0.70	0.81	1.85	2.15
	Cs	0.91	5.63	0.64	0.75	1.58	1.83
	Cu	8.45	2.67	1.36	1.57	7.00	8.12
	Ag	5.85	3.02	1.20	1.39	5.48	6.36
	Au	5.90	3.01	1.20	1.39	5.51	6.39
2	Ве	24.2	1.88	1.93	2.23	14.14	16.41
_	Mg	8.60	2.65	1.37	1.58	7.13	8.27
	Ca	4.60	3.27	1.11	1.28	4.68	5.43
	Sr	3.56	3.56	1.02	1.18	3.95	4.58
	Ba	3.20	3.69	0.98	1.13	3.65	4.24
Part Street	Zn	13.10	2.31	1.57	1.82	9.39	10.90
	Cd	9.28	2.59	1.40	1.62	7.46	8.66
3	Al	18.06	2.07	1.75	2.02	11.63	13.49
3	Ga	15.30	2.19	1.65	1.91	10.35	12.01
	In	11.49	2.41	1.50	1.74	8.60	9.98
4	Pb	13.20	2.30	1.57	1.82	9.37	10.87
-1	$\operatorname{Sn}(w)$	14.48	2.23	1.62	1.88	10.03	11.64

^aThe dimensionless radius parameter is defined as $r_s = r_0/a_H$, where a_H is the first Bohr radius and r_0 is the radius of a sphere that contains one electron.

Condução elétrica em metais – Lei de Ohm:

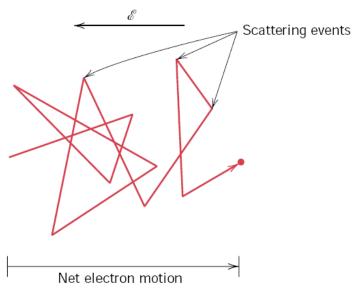


FIGURE 12.7 Schematic diagram showing the path of an electron that is deflected by scattering events.

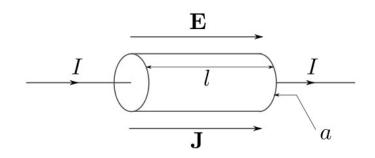
Velocidade de deriva:

$$\mathbf{r}_{d} = -\frac{eE\tau}{m_{e}}$$

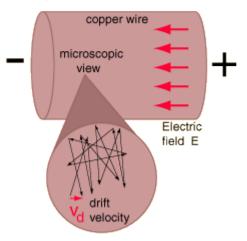
Fundamentals of Materials Science and Engineering , Callister.

tempo médio de colisão

Condução elétrica em metais – Lei de Ohm:



The electron moves at the Fermi speed, and has only a tiny drift velocity superimposed by the applied electric field.



http://en.wikipedia.org/wiki/Ohm's_law

$$\int_{-\infty}^{\infty} = \sigma \xi^{\square}$$

$$\int_{-\infty}^{\infty} = -n \, e \, V_{\alpha} = \left(\frac{n \, e^{2} \tau}{m_{e}^{2}}\right)^{\square} \Rightarrow \sigma = \frac{n \, e^{2} \tau}{m_{e}^{2}}$$

http://hyperphysics.phy-astr.gsu.edu/hbase/electric/ohmmic.html

Variação com a temperatura:

$$\sigma(7) = \frac{n e^{2} \tau(7)}{m_{e}}$$

Dependência da condutividade elétrica com a temperatura:

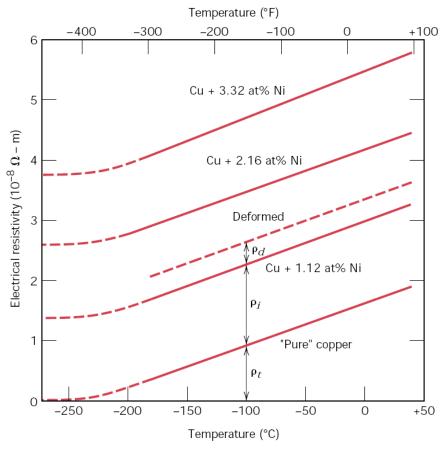


FIGURE 12.8 The electrical resistivity versus temperature for copper and three copper-nickel alloys, one of which has been deformed. Thermal. impurity, and deformation contributions to the resistivity are indicated at −100°C. [Adapted from J. O. Linde, Ann. Physik, 5, 219 (1932); and C. A. Wert and R. M. Thomson, Physics of Solids, 2nd edition. McGraw-Hill Book Company, New York, 1970.]

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Dependência da condutividade elétrica com a temperatura:

Table 12.1 Room-Temperature Electrical Conductivities for Nine Common Metals and Alloys

Metal	Electrical Conductivity $[(\Omega - m)^{-1}]$
Silver	6.8×10^{7}
Copper	6.0×10^{7}
Gold	4.3×10^{7}
Aluminum	3.8×10^{7}
Iron	1.0×10^{7}
Brass (70 Cu-30 Zn)	1.6×10^{7}
Platinum	0.94×10^{7}
Plain carbon steel	0.6×10^{7}
Stainless steel	0.2×10^{7}

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Bandas de energia em sólidos

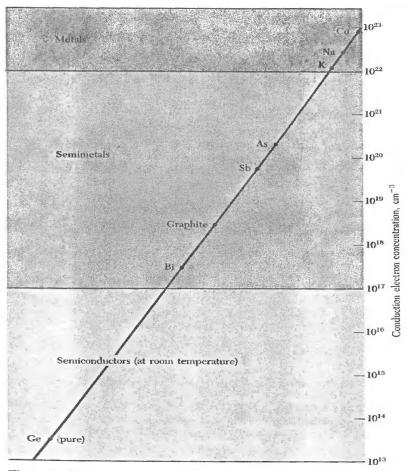
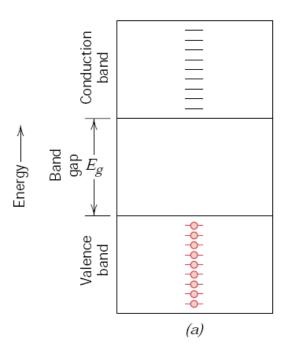
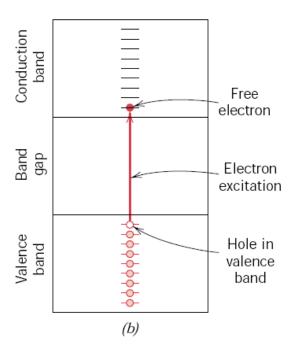


Figure I Carrier concentrations for metals, semimetals, and semiconductors. The semiconductor range may be extended upward by increasing the impurity concent in ion, and the range can be extended downward to merge eventually with the insulator range.

FIGURE 12.6

For an insulator or semiconductor, occupancy of electron states (a) before and (b) after an electron excitation from the valence band into the conduction band, in which both a free electron and a hole are generated.





Portadores de carga (elétrons / buracos):

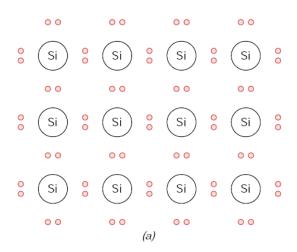
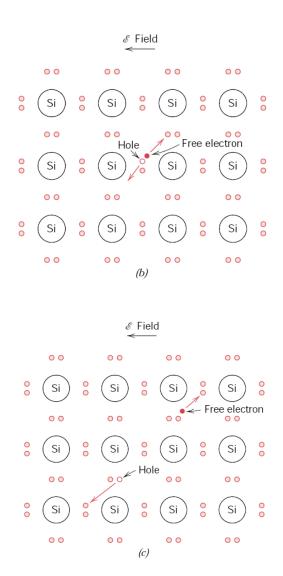
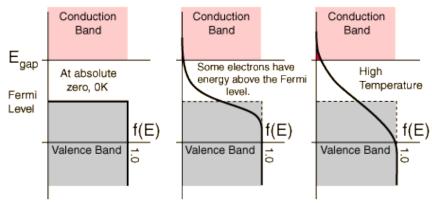


FIGURE 12.10 Electron bonding model of electrical conduction in intrinsic silicon: (a) before excitation; (b) and (c) after excitation (the subsequent free-electron and hole motions in response to an external electric field).



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Excitação térmica de portadores de carga (elétrons / buracos):



No electrons can be above the valence band at 0K, since none have energy above the Fermi level and there are no available energy states in the band gap. At high temperatures, some electrons can reach the conduction band and contribute to electric current. Função de Fermi:

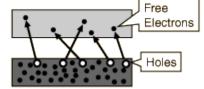
$$f(E,T) = \frac{1}{e^{(E-E_F)/k_BT} + 1}$$

Variação da condutividade elétrica com a temperatura:

$$\sigma_{\rm intr}(T) \cong \sigma_0 e^{-E_g/2k_BT}$$

Conduction band

Valence Band

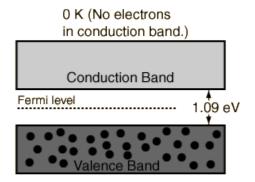


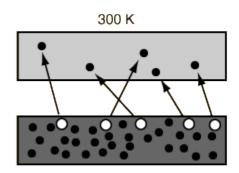
http://hyperphysics.phy-astr.gsu.edu/hbase/solids/intrin.html

Table 12.2 Band Gap Energies, Electron and Hole Mobilities, and Intrinsic Electrical Conductivities at Room Temperature for Semiconducting Materials

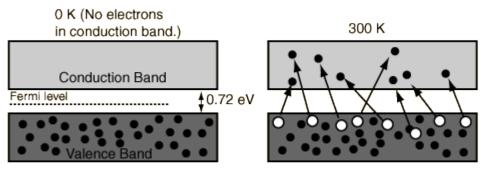
	Band Gap	Electrical Conductivity	Electron Mobility	Hole Mobility
Material	(eV)	$[(\Omega - m)^{-1}]$	$(m^2/V-s)$	$(m^2/V-s)$
		Element	tal	
Si	1.11	$4 imes 10^{-4}$	0.14	0.05
Ge	0.67	2.2	0.38	0.18
		III-V Comp	oounds	
GaP	2.25		0.05	0.002
GaAs	1.42	10^{-6}	0.85	0.45
InSb	0.17	2×10^4	7.7	0.07
		II-VI Comp	oounds	
CdS	2.40		0.03	_
ZnTe	2.26	_	0.03	0.01

Exemplos de semicondutores





Silício



Germânio

http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html

Dopagem do tipo *n* (portadores – elétrons):

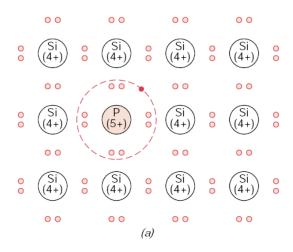
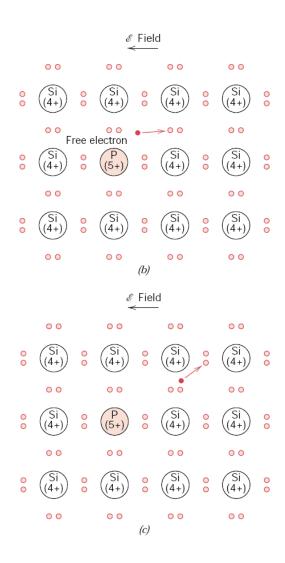


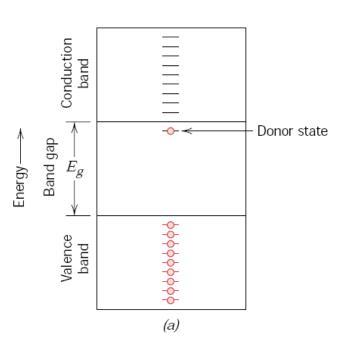
Figure 12.11 Extrinsic *n*-type semiconduction model (electron bonding). (a) An impurity atom such as phosphorus, having five valence electrons, may substitute for a silicon atom. This results in an extra bonding electron, which is bound to the impurity atom and orbits it. (b) Excitation to form a free electron. (c) The motion of this free electron in response to an electric field.

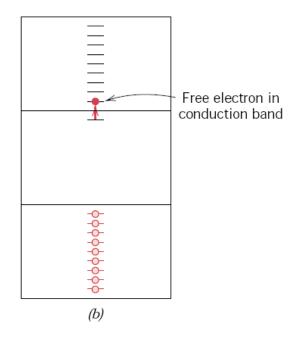


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Dopagem do tipo *n* (portadores – elétrons):

FIGURE 12.12 (a)
Electron energy band scheme for a donor impurity level located within the band gap and just below the bottom of the conduction band. (b)
Excitation from a donor state in which a free electron is generated in the conduction band.





Dopagem do tipo p (portadores – buracos):

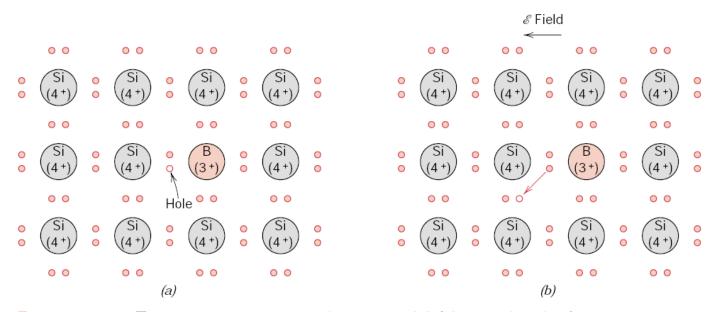


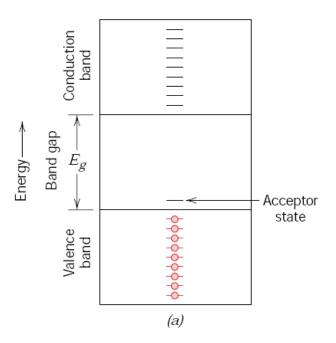
FIGURE 12.13 Extrinsic *p*-type semiconduction model (electron bonding). (a) An impurity atom such as boron, having three valence electrons, may substitute for a silicon atom. This results in a deficiency of one valence electron, or a hole associated with the impurity atom. (b) The motion of this hole in response to an electric field.

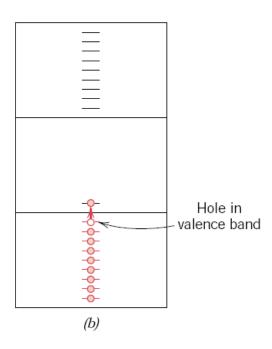
Dopagem do tipo *p* (portadores – buracos):

FIGURE 12.14

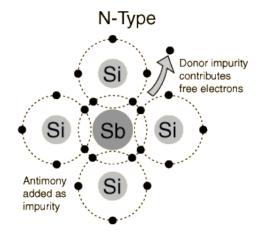
(a) Energy band scheme for an acceptor impurity level located within the band gap and just above the top of the valence band.

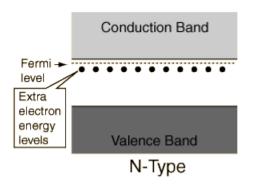
(b) Excitation of an electron into the acceptor level, leaving behind a hole in the valence band.

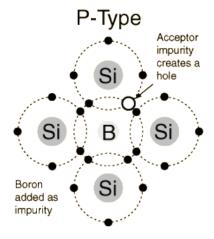


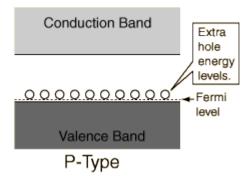


Nível de Fermi para semicondutores dopados:



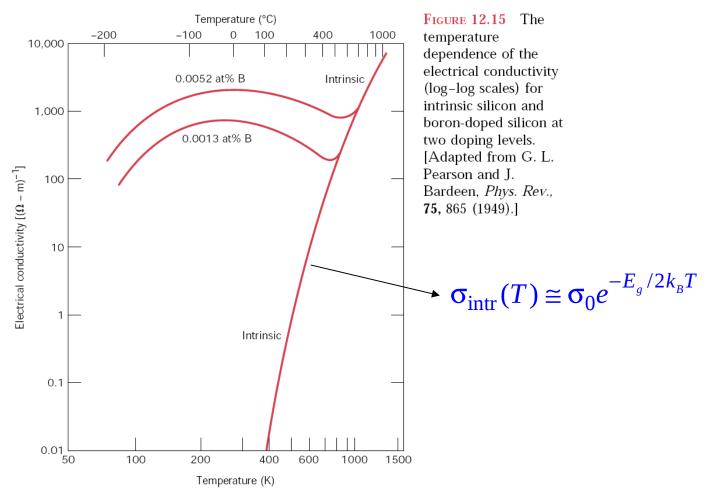






http://hyperphysics.phy-astr.gsu.edu/hbase/solids/dope.html#c2

Variação da condutividade elétrica com a temperatura:

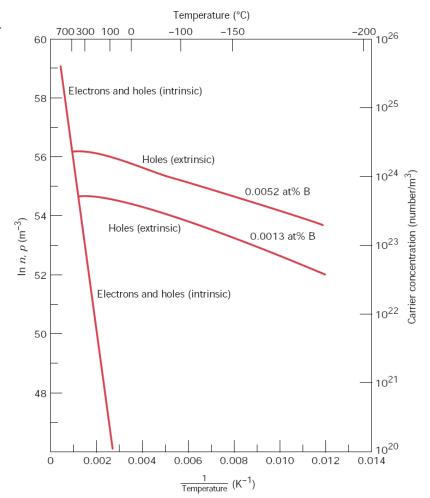


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Variação da concentração de portadores com a temperatura:

FIGURE 12.16

The logarithm of carrier (electron and hole) concentration as a function of the reciprocal of the absolute temperature for intrinsic silicon and two boron-doped silicon materials. (Adapted from G. L. Pearson and J. Bardeen, *Phys. Rev.*, **75**, 865, 1949.)



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Variação da concentração de portadores com a temperatura:

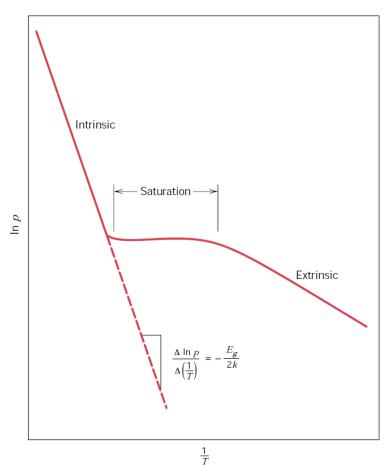


FIGURE 12.17 Schematic plot of the natural logarithm of hole concentration as a function of the reciprocal of absolute temperature for a *p*-type semiconductor that exhibits extrinsic, saturation, and intrinsic behavior.

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