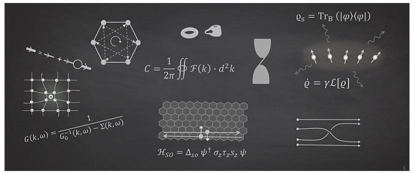
Física da Matéria Condensada

Margarida Telo da Gama



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Do you know, I always thought unicorns were fabulous monsters, too? I never saw one alive before!'

Well, now that we have seen each other,' said the unicorn, 'if you'll believe in me, I'll believe in you.

Is that a bargain ?

Lewis Carroll, Through the looking glass

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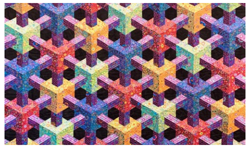
PROGRAMA (OUTLINE)



1. INTRODUÇÃO
2. ESTRUTURA CRISTALINA
3. ESTRUTURAS DOS SÓLIDOS
4. DIFRAÇÃO E DIFUSÃO ELÁSTICA DE ONDAS
5. LIGAÇÕES QUIMICAS
6. VIBRAÇÕES ATÓMICAS
7. TERMODINÂMICA DE FONÕES
8. ESTADOS ELECTRÓNICOS
9. TERMODINÂMICA DE ELECTRÕES EM METAIS
10. CONDUTIVIDADE ELÉCTRICA E TÉRMICA
11. ELECTRÕES EM SEMICONDUTORES

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BIBLIOGRAFIA

1. Fundamentals of Solid State Physics, J. R. Christman, Wiley, 1988.
2. Solid State Physics, N. W. Ashcroft and N. D. Mermin, Holt, 1976.
3. Introduction to Solid State Physics, 5th ed., C. Kittel, Wiley, 1976.
4. Solid State Physics, An Introduction to Principles of Materials Science, H. Ibach and H. Luth, Springer, 1995.
5. Solid State Physics, H. E. Hall, Wiley, 1974

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AVALIAÇÃO

- Exame
- Contínua: entrega da resolução escrita de 1-3 problemas das séries seguida da resolução no quadro durante as TPs (20%) e exame final (80%)

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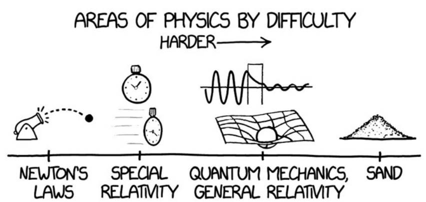

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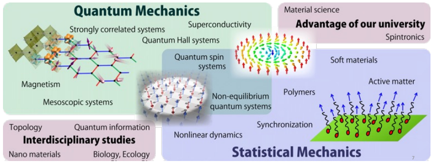
1. Introduction



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What is condensed matter ?

Collective properties that emerge from the interactions of many particles:

- Quantum or classical Dynamics to calculate the energy spectrum (states) - E_N
- Statistical Mechanics to calculate the occupation probability of each state – $P(E_N)$

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What is condensed matter physics ?

Properties of materials in terms of the interacting building blocks:

- Hard condensed matter: electrons & nuclei
- Soft condensed matter: polymers, colloids …

Response to external fields:

- Linear
- Non-linear

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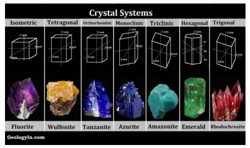
1. Crystal structure: Lattices



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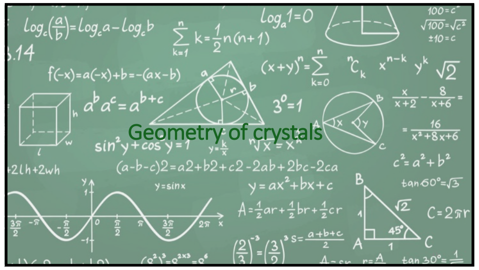

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Ideal solid

Periodic structure where the atoms are placed regularly with the medium exhibiting symmetry of translation.

Mathematically, there is symmetry of translation, in 3d, when there are, 3 no coplanar, vectors such that the medium is invariant for a translation

$$T = n_1\mathbf{a}+n_2\mathbf{b}+n_3\mathbf{c}$$

for all integers n_i

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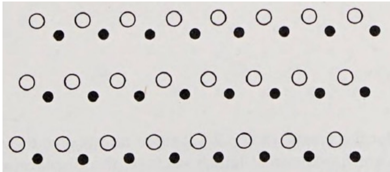
2D crystalline solid: the basis of two atoms is repeated periodically



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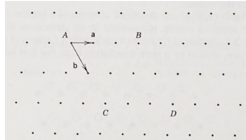
Lattice points give the positions of the basis
a and **b** are fundamental lattice vectors

Displacement of any lattice point is $n_1\mathbf{a}+n_2\mathbf{b}$



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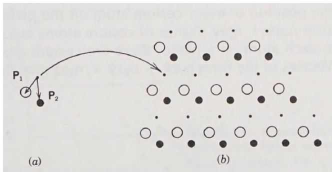
Basis and basis vectors (a) lattice points and atomic positions (b)



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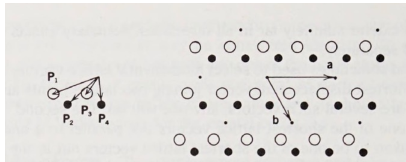
Another basis and the same lattice



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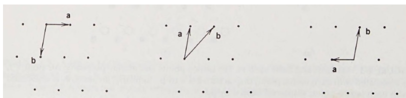
Primitive lattice vectors correspond to the smallest possible basis



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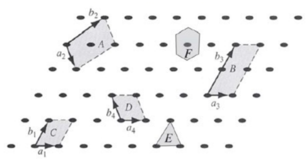
Lattice vectors and unit cells



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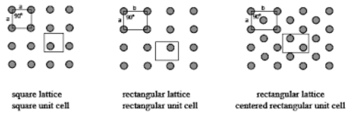
Unit cells



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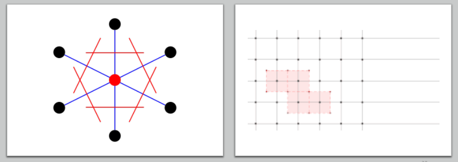
Wigner-Seitz cell



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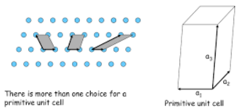
Volume of a unit cell



Volume of a unit cell
|c . a x b|

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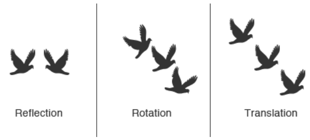
Rigid symmetry operations: Point & spatial



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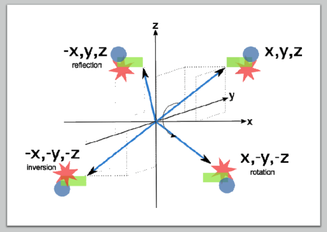
Point symmetries

Mirror, rotation and inversion



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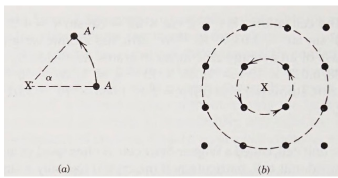
Rotational symmetry



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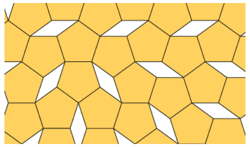
Crystals do not have 5-fold rotational axes



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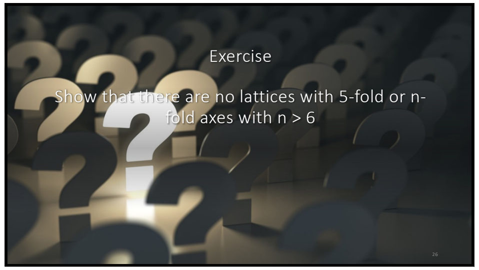

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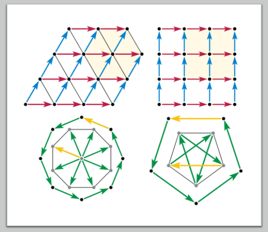
Lattice proof



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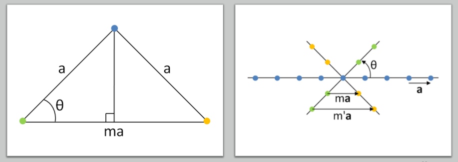
Geometric proof



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Rigid symmetries are not independent

For example, a 2-fold axis perpendicular to a mirror plane implies inversion symmetry (prove this).

Small number of symmetry groups in 2 and 3 dimensions.

Point symmetry groups: Crystallographic systems

Spatial symmetry groups: Bravais lattices

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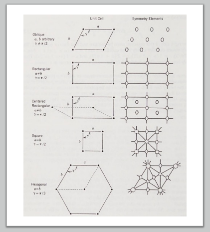

2D
Unit cells and symmetry groups

5 Bravais lattices
4 crystallographic systems

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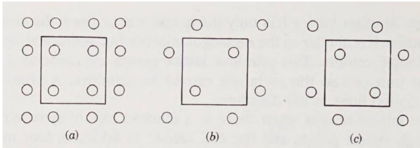

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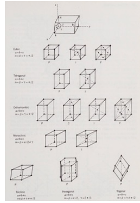
3D
Unit cells and symmetry groups

14 Bravais lattices
7 crystallographic systems



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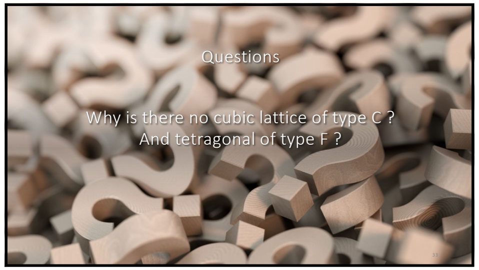

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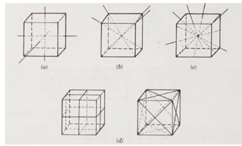
Symmetry axes and planes of a cube



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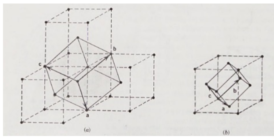
Primitive translation vectors and primitive cells for bcc and fcc



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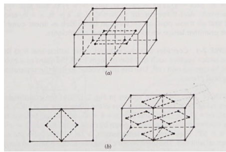
Stacking of square lattices to form bcc and fcc



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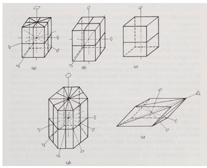
Symmetry elements of unit cells



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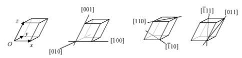
Directions



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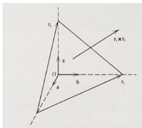
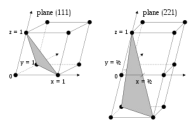
Crystallograpic planes:
Miller indices





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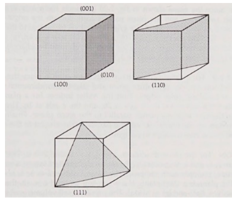
Planes of cubic lattices



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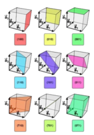
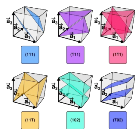
Planes of cubic lattices





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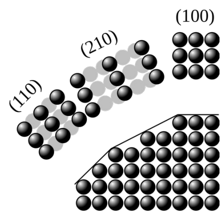
Dense crystallographic planes



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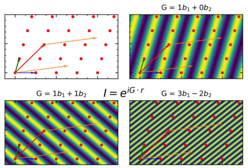
Reciprocal lattice



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Reciprocal lattice vectors

$$\vec{b}_1 = 2\pi \cdot \frac{\vec{a}_2 \times \vec{a}_3}{V}$$
$$\vec{b}_2 = 2\pi \cdot \frac{\vec{a}_3 \times \vec{a}_1}{V}$$
$$\vec{b}_3 = 2\pi \cdot \frac{\vec{a}_1 \times \vec{a}_2}{V}$$

- As we have seen above, the reciprocal lattice of a Bravais lattice is again a Bravais lattice.
- The reciprocal latticeof a reciprocal lattice is the (original) direct lattice.
- The length of the reciprocal lattice vectors is proportional to the reciprocal of the length of the direct lattice vectors. This is where the term reciprocal lattice arises from.

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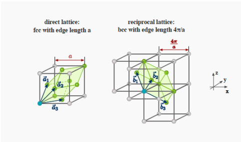
Reciprocal lattice of an fcc lattice



$$\vec{b}_1 = \frac{8\pi}{a^3} \cdot \vec{a}_2 \times \vec{a}_3 = \frac{4\pi}{a} \cdot \left(-\frac{\hat{x}}{2} + \frac{\hat{y}}{2} + \frac{\hat{z}}{2}\right)$$
$$\vec{b}_2 = \frac{8\pi}{a^3} \cdot \vec{a}_3 \times \vec{a}_1 = \frac{4\pi}{a} \cdot \left(\frac{\hat{x}}{2} - \frac{\hat{y}}{2} + \frac{\hat{z}}{2}\right)$$
$$\vec{b}_3 = \frac{8\pi}{a^3} \cdot \vec{a}_1 \times \vec{a}_2 = \frac{4\pi}{a} \cdot \left(\frac{\hat{x}}{2} + \frac{\hat{y}}{2} - \frac{\hat{z}}{2}\right)$$

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3. Structures of solids

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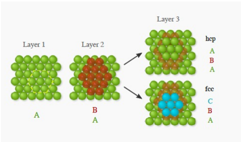
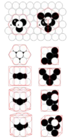
Close packed structures





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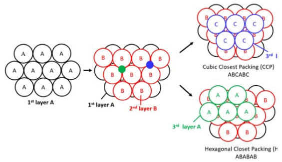
Close packed structures



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Close packed structures

Snowballs stacked in preparation for a snowball fight. The front pyramid is hexagonal close-packed and rear is face-centered cubic.

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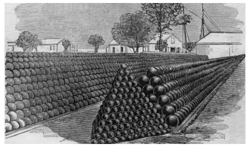
The cannon ball mathematical problem (1587)



Cannonballs piled on a triangular *(front)* and rectangular *(back)* base, both fcc lattices.

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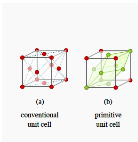
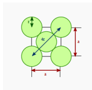
Close packed density: fcc lattice





$$\varrho = \frac{n \cdot V_{\mathrm{sph}}}{V_{\mathrm{uc}}} = \frac{4 \cdot \frac{4}{3}\pi \cdot \left(\frac{\sqrt{2}}{4}\right)^3 a^3}{a^3} = \frac{\sqrt{2}\pi}{6} \approx 74\%$$

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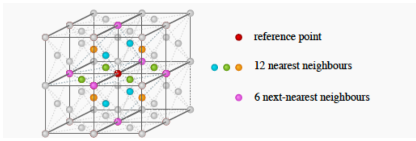
Nearest-neighbours



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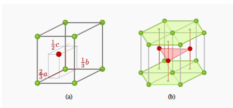
Second close packed density: hcp structure



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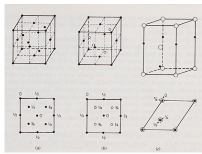
Other crystal structures: diamond, zinc blende and wurzite



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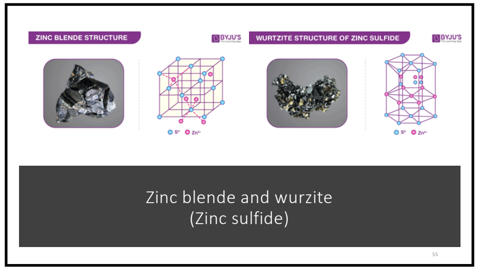

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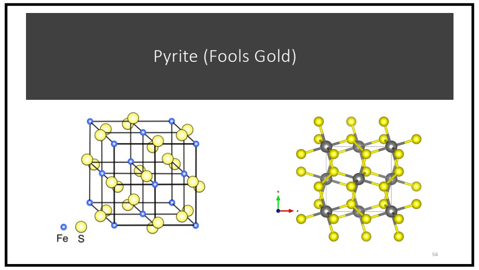

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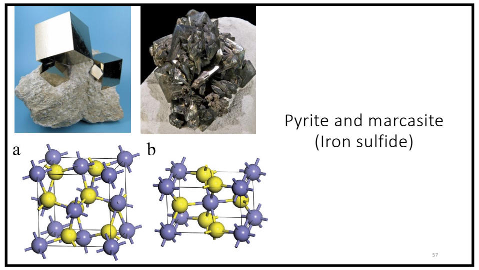

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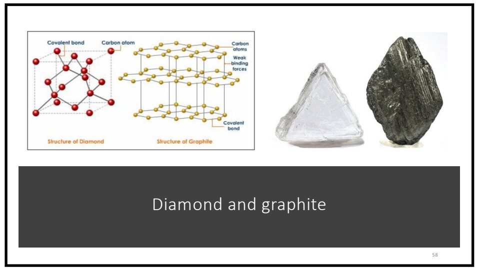

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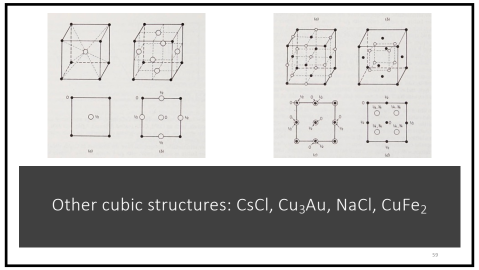

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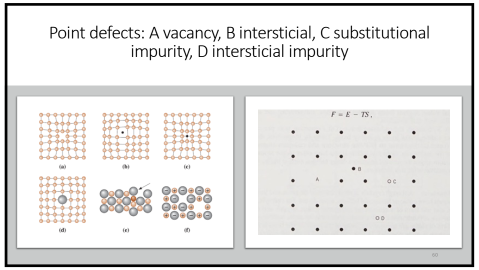

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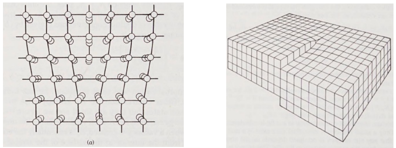

Dislocations: Edge (a) and screw (b)

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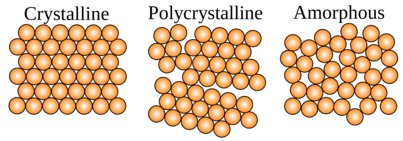
Amorphous structures



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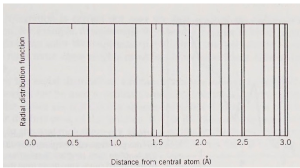
Radial distribution function of crystalline fcc structure



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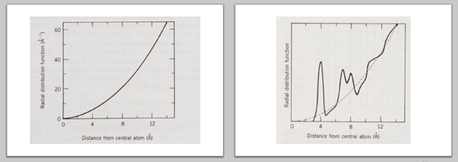
Radial distribution function of amorphous structures



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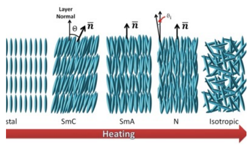
Liquid crystalline order



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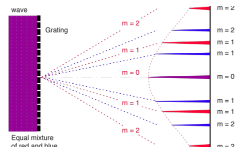
4. Diffraction



66

Scattering from a sample

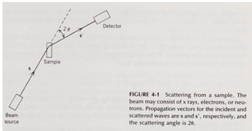
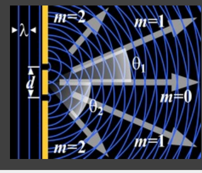
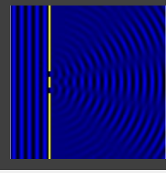


FIGURE 4-1 Scattering from a sample. The beam may consist of x rays, electrons, or neutrons. Propagation vectors for the incident and scattered waves are s and s', respectively, and the scattering angle is 2θ.

67





Two slits

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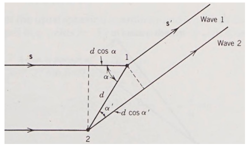
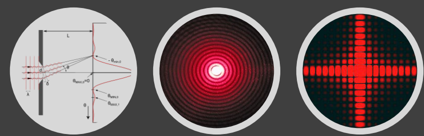
Scattering from two particles



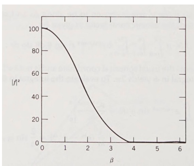
69

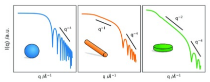


Diffraction from an aperture

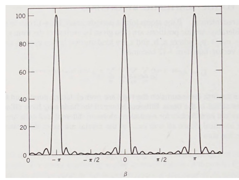
70

Form factor





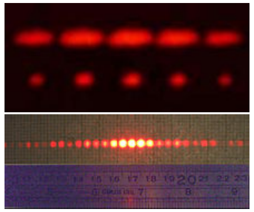
71



$\beta = \frac{1}{2}\Delta\mathbf{s}\cdot\mathbf{a}$ and $g(\beta) = \sin^2(N\beta)/\sin^2(\beta)$

Scattering function for N=10

72



Diffraction patterns for two, five and one hundred and fifty slits

73

Laue scattering condition

$$\Delta \mathbf{s} = h\mathbf{A} + k\mathbf{B} + \ell\mathbf{C}.$$

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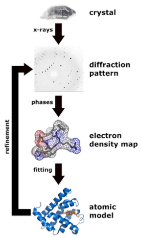
NOBEL PRIZE IN PHYSICS, 1914

Max von Laue



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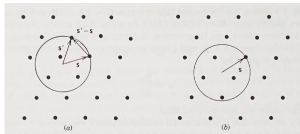
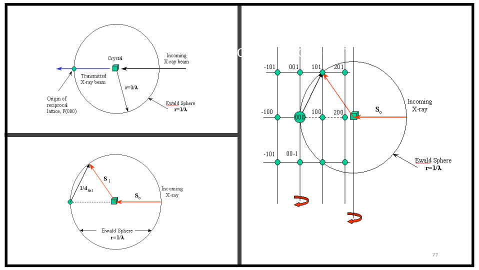
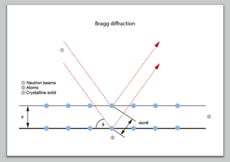
Ewald construction

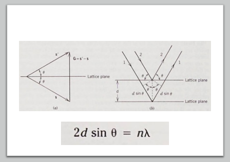


76



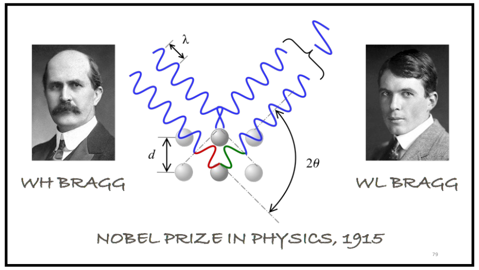
77





Bragg scattering

78



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Structure factor

$$F = \sum_m f_m e^{-2\pi i (u_m h + v_m k + w_m \ell)} .$$

80

Structure factor

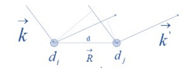
The amplitude of the rays scattered at d_1, d_2, d_3…. are in the ratios :

$$e^{-iK \cdot d_j}$$

The net ray scattered by the entire cell:

$$S_k = \sum_{j=1}^{n} e^{-iK \cdot d_j}$$

$$I_{(hkl)} \propto |S_k|^2$$



$$\vec{K} = \vec{k}' - \vec{k}$$

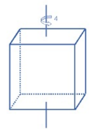
Phase difference: $K \cdot (d_i - d_j)$

The amplitude of the two rays differ: $e^{iK \cdot (d_i - d_j)}$

81

Structure factor SC

For simple cubic: (0,0,0)



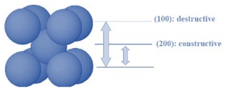
$$S_k = e^{-iK \cdot 0} = 1$$

82

Structure factor BCC

For BCC: (0,0,0), (1/2, ½, ½)…. Two point basis

S=2, when h+k+l even
S=0, when h+k+l odd, **systematical absence**



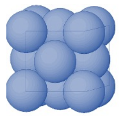
For BCC: (0,0,0), (1/2, ½, ½)…. Two point basis

$$S_k = \sum_{j=1}^{2} e^{-iK \cdot d_j} = e^{-iK \cdot 0} + e^{-iK \cdot \frac{1}{2}(\vec{x}+\vec{y}+\vec{z})}$$
$$= 1 + e^{-i\pi(h+k+l)}$$
$$= 1 + (-1)^{h+k+l}$$

S=2, when h+k+l even
S=0, when h+k+l odd, systematical absence

83

Structure factor FCC



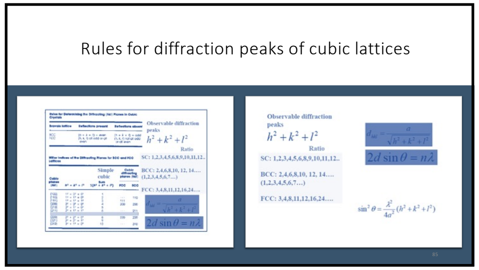
FCC

S=4 when h+k, k+l, h+l all even (h,k, l all even/odd)

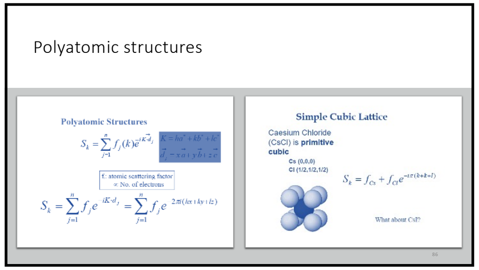
S=0, otherwise

$$S_k = 1 + e^{-i\pi(h+k)} + e^{-i\pi(h+l)} + e^{-i\pi(l+k)}$$

84



85



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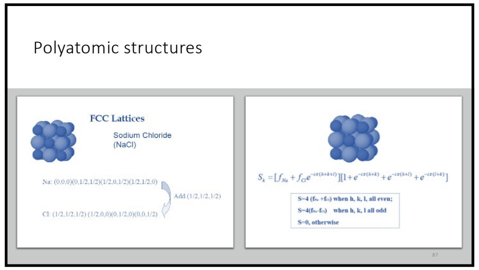

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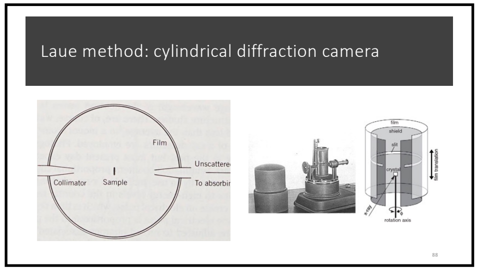
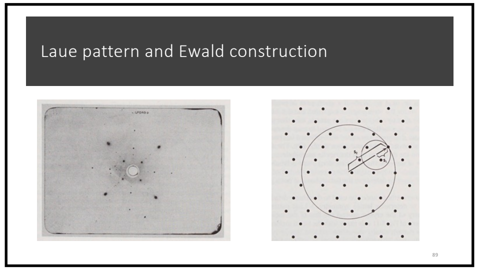


88



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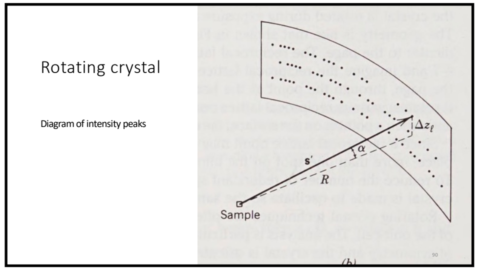

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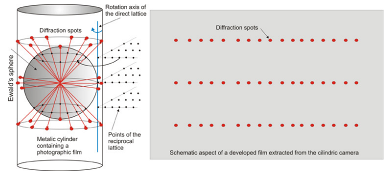
Rotating crystal



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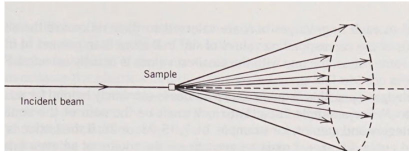
Powder sample



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Powder pattern

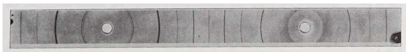

FIGURE 4-16 Powder pattern for tungsten. Each ring corresponds to a different scattering angle. The pattern consists of two sets of rings, for beams scattered in the back (on the left) and forward (on the right) directions, respectively. (From Walter Kiszenick, unpublished. Used with permission.)

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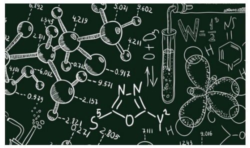
5. Bonding



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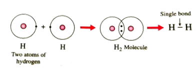
Hydrogen molecule



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Schroedinger's equation

$$H\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

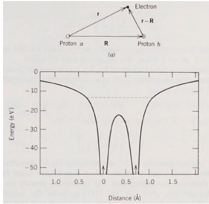
Time evolution

$$\frac{-\hbar^2}{2m}\frac{\partial^2\Psi(x)}{\partial x^2} + U(x)\Psi(x) = E\Psi(x)$$

Time independent equation

96

Molecular H_2 ion



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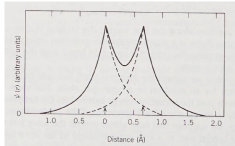
Bonding wave function



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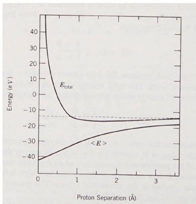
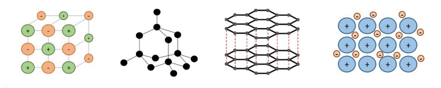
Energy



99

Ionic, covalent, van der Waals and metallic bonding



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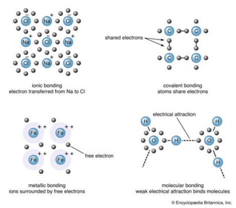
Bonding mechanisms



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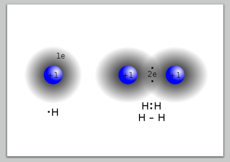
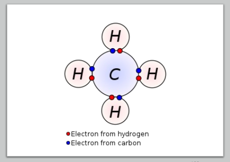
Covalent bonding





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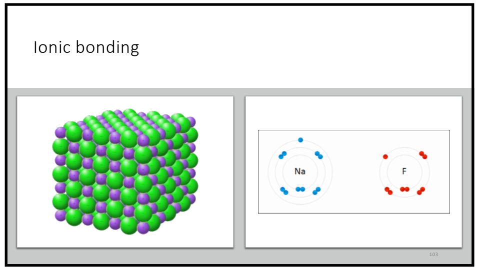
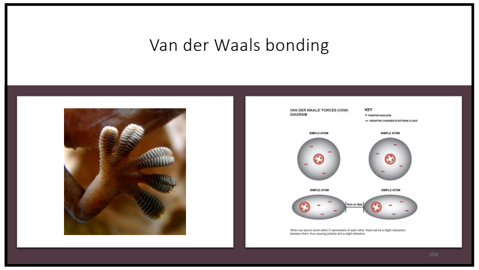


103



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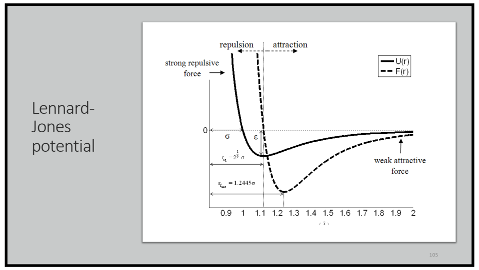

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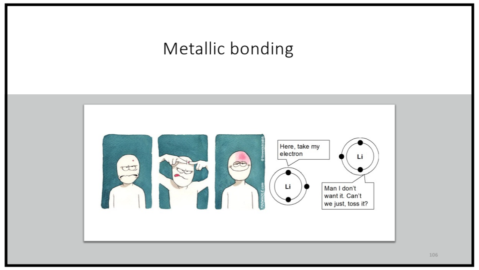

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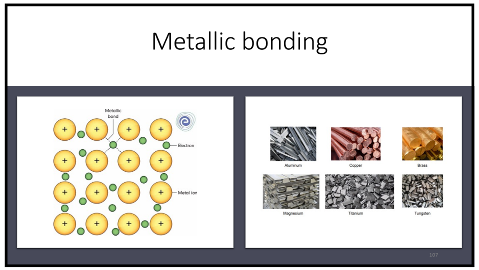

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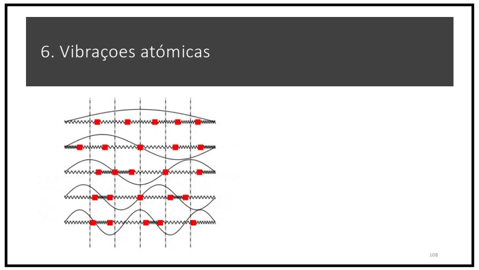

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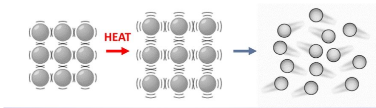
Vibrations



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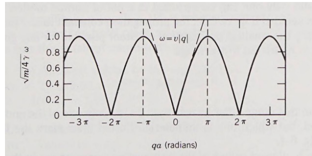
Dispersion relation: 1d lattice



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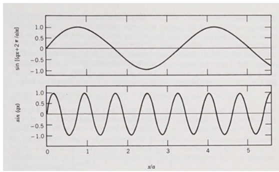
N normal modes: 1d lattice



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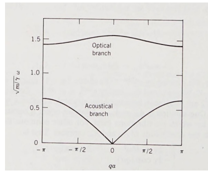
1d lattice with basis of two atoms



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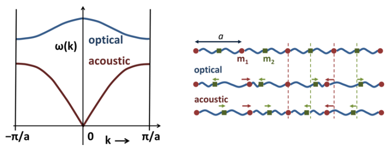
1d lattice with basis of two atoms



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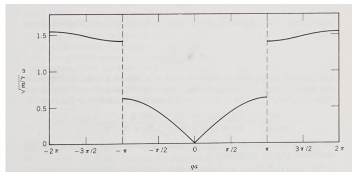
1d lattice with basis of two atoms: extended zone



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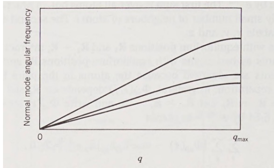
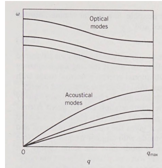
3d lattice



115

3d lattice with basis of two atoms



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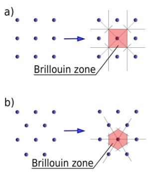
Brioullin zone



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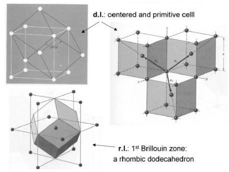
Brioullin zone (bcc lattice)



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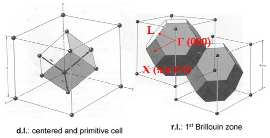
Brioullin zone (fcc lattice)



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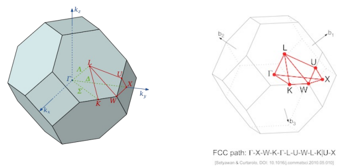
Brioullin zone



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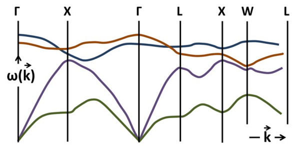
3d lattice with basis of two atoms



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Crystal momentum

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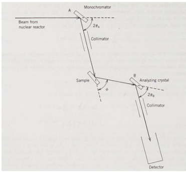
Triple axis neutron spectrometer



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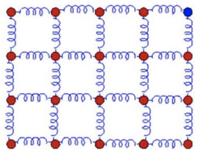
7. Termodinâmica de fonões



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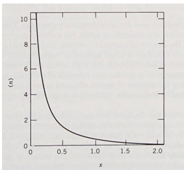
Number of phonons as a funtion of $x = \beta\hbar\omega$



$$\langle n \rangle \longrightarrow e^{-\beta\hbar\omega}$$

$$\langle E \rangle \longrightarrow \hbar\omega e^{-\beta\hbar\omega} + \tfrac{1}{2}\hbar\omega\,,$$

$$\langle n \rangle \longrightarrow \frac{1}{\beta\hbar\omega} = \frac{k_B T}{\hbar\omega}$$

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Constant frequency surface

FIGURE 8-2 A schematic representation of constant frequency surfaces in reciprocal space. A Brillouin zone is shown and each contour is defined by propagation vectors such that $\omega(\mathbf{q})$ = constant. Different surfaces are associated with different values of ω.

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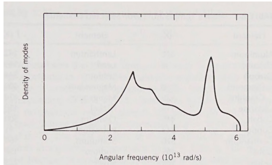
Density of modes



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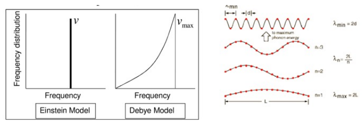
Models of Einstein and Debye



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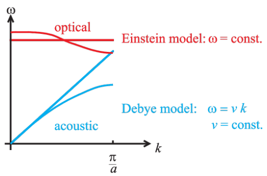
Models of Einstein and Debye



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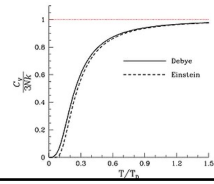
Models of Einstein and Debye



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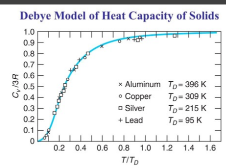
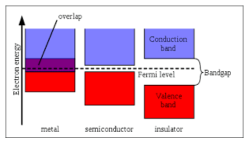
Model of Debye for various metals



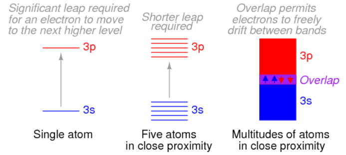
131

8. Estados electrónicos



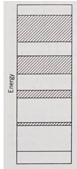
132

Overlap of atomic states



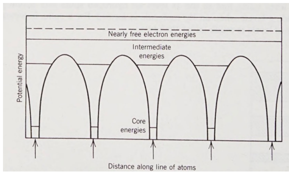
133

Bands



134

Electronic energy along a line of atoms



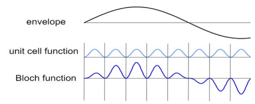
135

Bloch's theorem

we can rewrite the Bloch theorem equation $\psi(x+a) = \exp(ika)\psi(x)$ alternative form

$$\psi(x) = u(x)\exp(ikx)$$

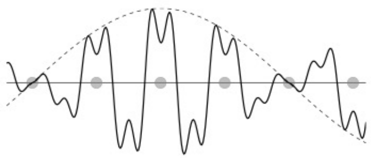
where $u(x)$ is periodic with the lattice periodicity.



Concept of the Bloch functions. We can think of the $\exp(ikx)$ as being an example of an "envelope" function that multiplies the unit cell function $u(x)$

136

Bloch function



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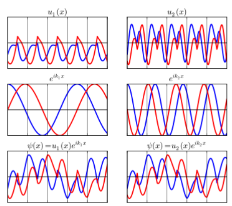
Bloch functions



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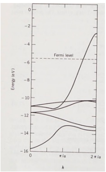
Bands of copper in the 100 direction



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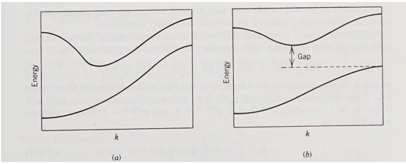
Band overlap



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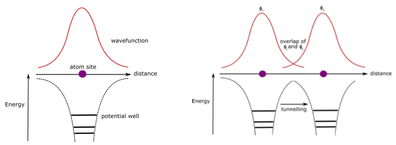
Recap: Covalent Bonding



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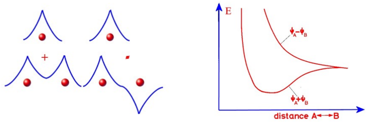
Bonding and anti-bonding states & energies



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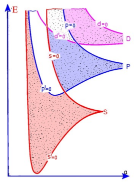
Many atoms: bands



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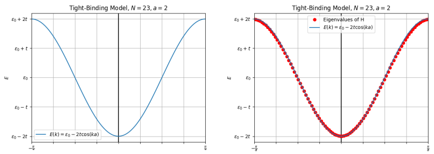
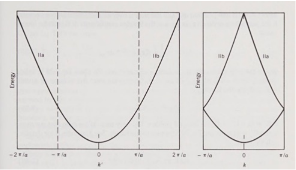
Exercise: tight binding model in 1d



Simon, S. H. (2013). *The Oxford solid state basics*. Oxford, UK: Oxford Univ. Press.

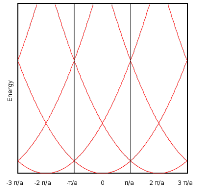
144

Free electron bands in 1d



145

Free electron bands in 1d



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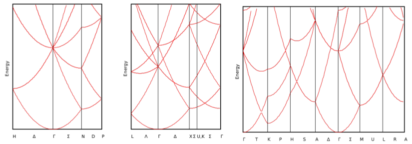
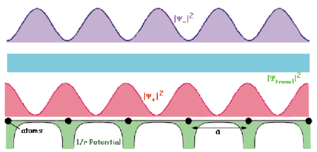
Free electron bands for bcc, fcc and hexagonal closed packed



147

Bragg reflection of free electrons

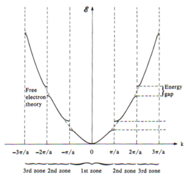


$$e^{ikx} - e^{-ikx}$$
$$\sim \sin(kx)$$

$$e^{ikx} + e^{-ikx}$$
$$\sim \cos(kx)$$

148

Band gaps of nearly free electrons in 1d



149

Nearly free electron bands in 1d

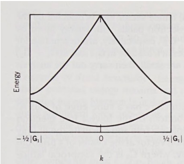
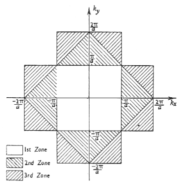


FIGURE 7-7 Energy as a function of propagation vector magnitude for nearly free electrons. The propagation vector is taken to be parallel to reciprocal lattice vector $\mathbf{G}_1$, which is bisected by a Brillouin zone boundary. The curves are similar to those of Fig. 7-6*b* but gaps occur at $\mathbf{k} = \pm\frac{1}{2}\mathbf{G}_1$. The gap width depends on the Fourier component $U(\mathbf{G}_1)$ of the potential energy function.

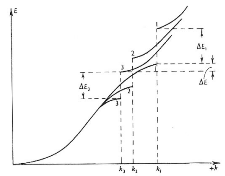
150

Brillouin zones in 2d



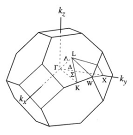
151

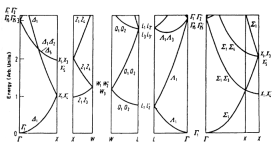
Nearly free electron bands in 2d



152

Free electron bands in 3d: Al





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Nearly free electron bands In 3d: Al

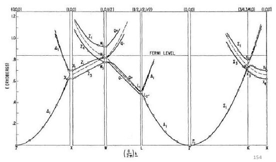
Γ- point: (0,0,0)

X- point: $\frac{2\pi}{a}$ (1,0,0)

L- point: $\frac{\pi}{a}$ (1,1,1)

K- point: $\frac{2\pi}{a}\left(\frac{3}{4},\frac{3}{4},0\right)$

W- point: $\frac{2\pi}{a}\left(1,\frac{1}{2},0\right)$



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Bands of potassium in 3 directions

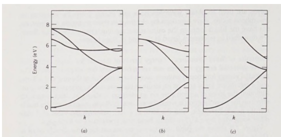

FIGURE 7-8 Electron band structure of potassium for energies near the 4s atomic level: (*a*) **k** in the [100] direction; (*b*) **k** in the [110] direction; and (*c*) **k** in the [111] direction. Some curves are incomplete. The bands shown are quite similar in form to those predicted by the nearly free electron model. (From F. S. Ham, *Phys. Rev.* **128**:82, 1962. Used with permission.)

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Bands of silicon in 3 directions

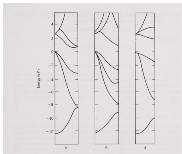

FIGURE 7-9 Electron band structure of crystalline silicon for energies near the 3s and 3*p* atomic levels: (*a*) **k** in the [100] direction; (*b*) **k** in the [110] direction; and (*c*) **k** in the [111] direction. Bands below $E = 0$ are valence bands and are associated with bonding. Higher bands are conduction bands and are important for the electrical properties of silicon. A gap exists between the valence and conduction bands. (From A. Zunger and M. L. Cohen, *Phys. Rev.* **B 20**:4082, 1979. Used with permission.)

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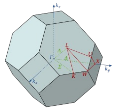
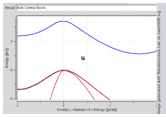
9. Termodinâmica de electrões





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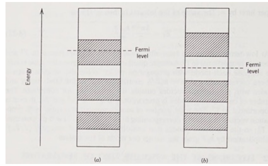
Fermi level



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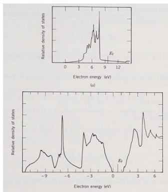
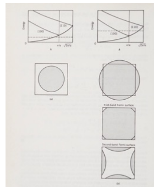
Density of states



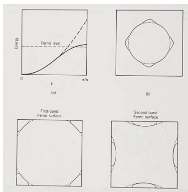
159

Fermi surface of free electrons in 2d (square)



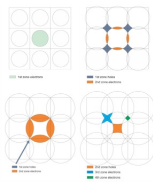
160

Fermi surface of nearly free electrons in 2d (square)



161

BZ of the square lattice: electrons & holes



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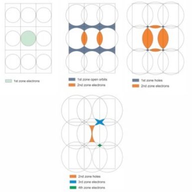
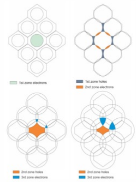
BZ of the rectangular lattice: electrons & holes



163

BZ of the face centred rectangular lattice: electrons & holes



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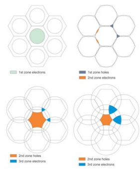
BZ of the hexagonal lattice: electrons & holes



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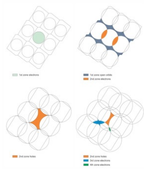
BZ of the oblique lattice: electrons & holes



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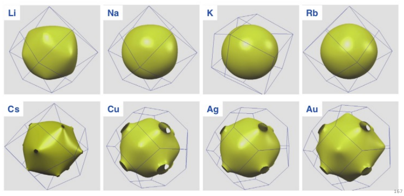
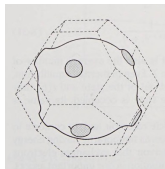
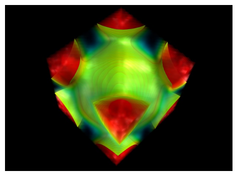
Fermi surface of alkali (bcc) and noble (fcc) metals of valence 1



167

Fermi surface of Cu (fcc valence 1)





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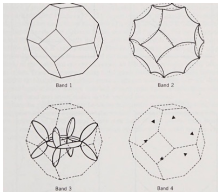
Fermi surface in 3d of Al (fcc valence 3)



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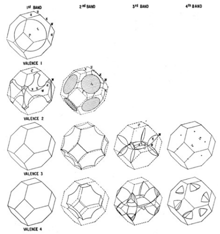
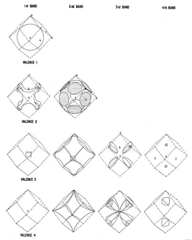
Fcc lattice



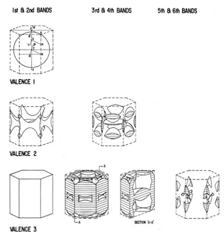
170

Bcc lattice



171

Hexagonal lattice



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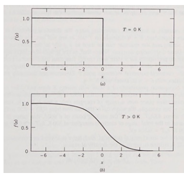
Fermi-Dirac distribution



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Electronic specific heat

$$C_{electrons} = \frac{\pi^2 N_A k^2 T}{2E_F} mole^{-1}$$

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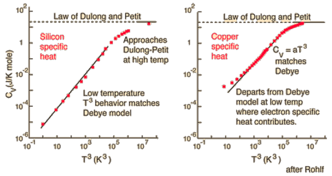
Specific heat of solids



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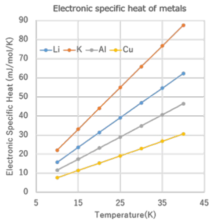

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10. Condutividade elétrica e térmica

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- https://www.doitpoms.ac.uk/tlplib/thermal_electrical/printall.php

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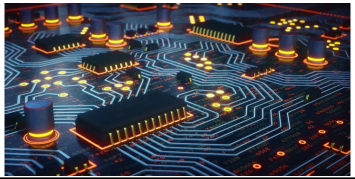
11. Electrões em semi-condutores



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