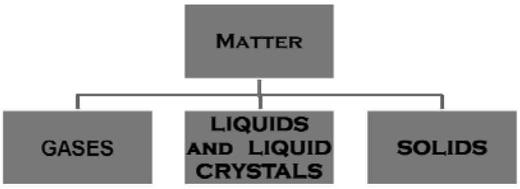
Solid State Physics

Jian GONG

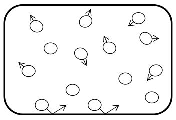
2009. 09-2010. 01

matter



Gases

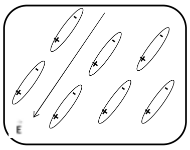
- Gases have atoms or molecules that do not bond to one another in a range of pressure, temperature and volume.
- These molecules haven't any particular order and move freely within a container.

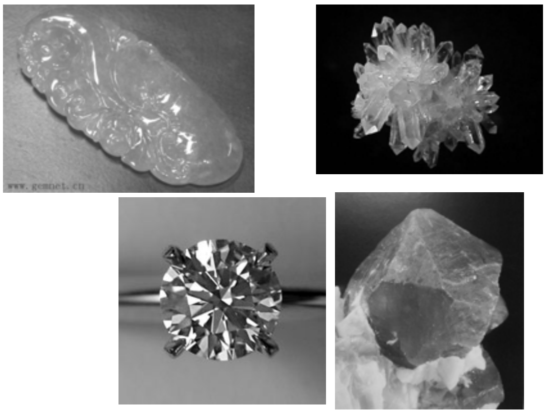


Liquids and Liquid Crystals

- Similar to gases, liquids haven't any atomic/molecular order and they assume the shape of the containers.
- Applying low levels of thermal energy can easily break the existing weak bonds.

Solid ?





Solid State Physics

The purpose of this course is to present a survey of the phenomena exhibited by solid state systems and an introduction to the fundamental physical principles, mathematic concepts, and experimental techniques important in the study of solid state material.

Course information

- **Textbook: Charles Kittel "Introduction to solid state physics" 7th , 1995.**
- **Instructor : 1) Jian Gong (Lecture)**
  STB 0605
  Tel: 4992967
  2) Haiyun Xue (HW & Question)
  Tel: ?

Homework, Quizzes, and Exam

Your course grade will be determined as follows:

- **20% from homework**
  Homework assignments will be given out in class.
- **10% from quizzes**
  The quizzes will be held at the beginning of class after a topic has been concluded.
- **70% from final exam**
  The final exam will contain questions that may come from any topic which has been covered in class.

Schedule

Chapter One, Crystal structure

Chapter Two, Reciprocal lattice

Chapter Three, Crystal Binding and Elastic Constants

Chapter Four, Phonons I: Crystal vibration

Chapter Five, Phonons II: Thermal properties

Chapter Six, Free electron Fermi gas

Chapter Seven, Energy bands

Chapter Eight, Semiconductor crystals

Chapter Nine, Fermi surfaces and metals

Final Exam.

Phenomena

➨ Mechanical
    structure
    strength
➨Thermal
    heat capacity
    heat conduction
    phase transition
➨Electrical
    insulators
    metals
    semiconductors
    superconductors
➨Optical
    reflection, refraction
➨Magnetic
    ferromagnetism

Principles

➨ Newton's laws
➨ Maxwell's EM equation
➨ Thermodynamics and statistical mechanics
➨ Quantum mechanics
    Schrodinger equation
    Pauli exclusion principle
➨ Order and symmetry

Reference

- **Introduction to solid state physics, Charles Kittel 1995.**
- **Solid state physics**, Giuseppe Grosso ,2006.
- **Solid state physics, Ashcroft, Neil W, 2004.**
- 固体物理学, 黄昆,
- 固体物理学, 方俊鑫,陆栋, **1980.**
- 固体物理学, 阎守胜, **2003.**
- 固体物理,韦丹, **2007.**

What is a "Solid"?

A material that keeps its shape.

- can be deformed by stresses
- returns to the original shape if it is not strained too much

---- differs from "Fluid"

Structure difference ?

The atomic scale nature of materials has known for less than 100 years.

The mechanical properties, especially strength against large strains, have been part of human advances for thousands of years.

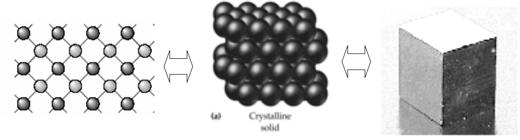
ELEMENTARY CRYSTALLOGRAPHY

SOLID MATERIALS

- CRYSTALLINE
  - Single Crystal
- POLYCRYSTALLINE
- AMORPHOUS (Non-crystalline)

Crystalline Solid

- Crystalline Solid is the solid form of a substance in which the ***atoms or molecules*** are arranged in a definite, repeating pattern in three dimension.
- Single crystals, ideally have a high degree of order, or regular geometric periodicity, throughout the ***entire volume of the material***.
- Single crystal has an atomic structure that repeats periodically across its whole volume. Even at infinite length scales, each atom is related to every other equivalent atom in the structure by translational symmetry



What is "Solid State Physics"?

- **The body of knowledge is about the fundamental phenomena and classifications of solid.**

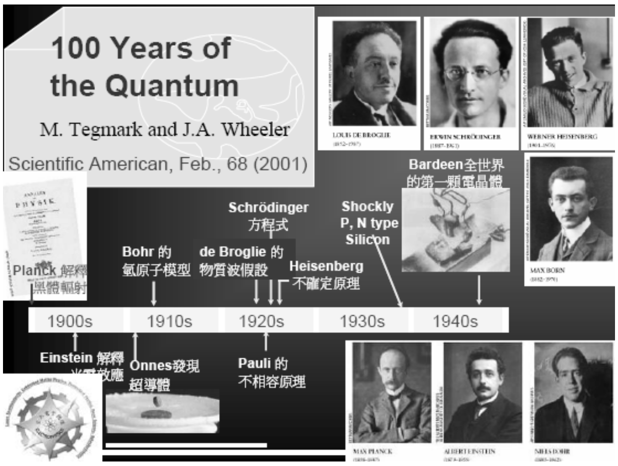
?

A characteristic behavior exhibited by classes of solids.

Such as ductile vs. brittle materials
metals vs. insulators
superconductors
ferromagnetic material

The basic understanding of such "fundamental phenomena"has only occurred in the last 80 years.

Due to "quantum mechanics"



100 Years of the Quantum

M. Tegmark and J.A. Wheeler

Scientific American, Feb., 68 (2001)

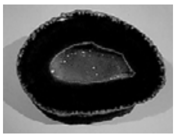
Aim of Solid State Physics

- Solid state physics (SSP) explains the properties of solid materials as found on earth.
- The properties are expected to follow from Schrödinger's eqn. for a collection of atomic nuclei and electrons interacting with electrostatic forces.
- The fundamental laws governing the behaviour of solids are known and well tested.

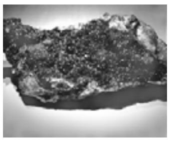
Chapter One
Crystal structure

- Periodic arrays of atom
- Fundamental types of lattices
- Index system for crystal planes
- Simple crystal structure

Drusy Quartz in Geode



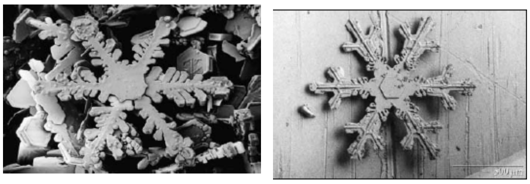
Tabular Orthoclase Feldspar

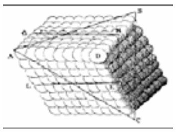


Encrusting Smithsonite

Peruvian Pyrite

Snow crystal



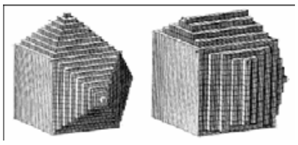


Calcite($CaCO_3$) crystal is made from spherical particles.

Christiaan Huygen, Leiden1690

A crystal is made from spherical particles.

Robert Hooke, London 1745



depicted by RenéHaüy,

Paris, 1822

the most efficient way to stack spheres

Nature, 3 July 2003

- X-rays were discovered in 1895 by the German physicist Wilhelm Conrad Röntgen and were so named because their nature was unknown at the time.
- He was awarded the Nobel prize for physics in 1901.

Wilhelm Conrad Röntgen
(1845-1923)

Bertha Röntgen's Hand 8 Nov, 1895

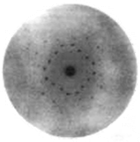
Periodic arrays of atom

In 1912

Interference effects with Rontgen rays, Laue-1914

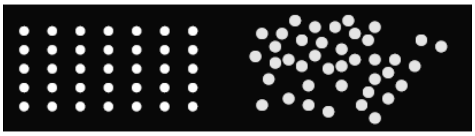
1. The crystals are composed of a periodic array of atoms.

2. the studies have been extended to include amorphous or glasses and liquids.



In 1912 ZnS

Solid: Crystal vs. Amorphous (glassy)



Ordered array of atoms **Disordered arrangement**

Competition between attractive (binding) force and repulsive force.

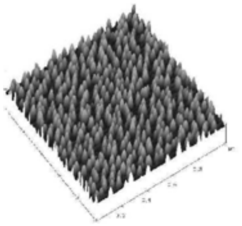
Regular array lowers system energy.

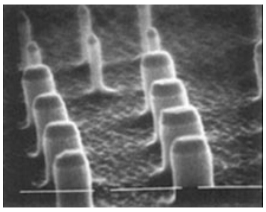
Complicated !--difficult to predict the structure of materials

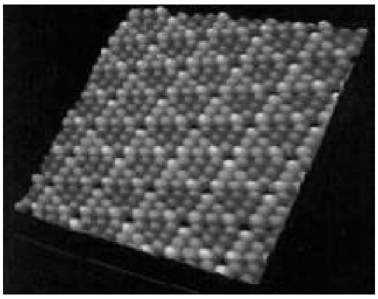
Crystal structure

- Importance: structure plays a major role in determining physical properties of solids
- Determination: X-ray and neutron scattering are key tools for determining crystal structure.

  Also microscopic techniques such SEM, TEM (bulk) STM,AFM…(surface)

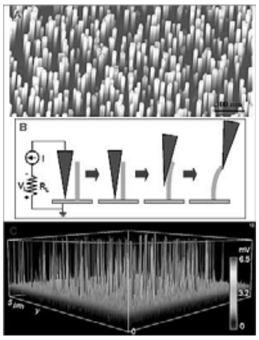






Si surface : G.Binning and H.Rohrer STM in 1986

Z. L. Wang



- Deviation: There is no perfect crystal.

  Many key properties depend on deviation more.

  Defects – imperfection in crystal

  Phonons- lattice vibrations

Review

ELEMENTARY CRYSTALLOGRAPHY

SOLID MATERIALS

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  - Single Crystal
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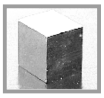
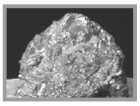
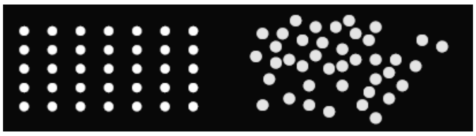




Solid: Crystal vs. Amorphous (glassy)



Ordered array of atoms **Disordered arrangement**

Competition between attractive (binding) force and repulsive force.

Regular array lowers system energy.

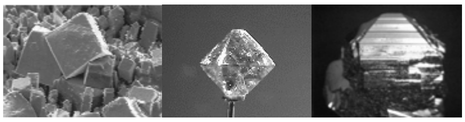
For SSP

■ Symmetry of a crystal can have a profound influence on its properties.

■ Any crystal structure should be specified completely, concisely and unambiguously.

■ Structures should be classified into different types according to the symmetries they possess.

crystal structure ?



Deals with the geometric description of crystals and their internal arrangement.

⇩

The branch of science **crystallography**

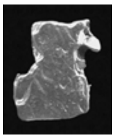
ELEMENTARY

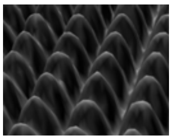
- A basic knowledge of crystallography is essential for solid state physicists;
  - to specify any crystal structure and
  - to classify the solids into different types according to the symmetries they possess.
- Symmetry of a crystal can have a profound influence on its properties.
- We will concern in this course with solids with simple structures.

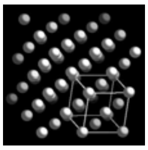
CONTENTS

- Periodic arrays of atom
  - lattice translation vectors
  - Basis and crystal structure
  - Primitive lattice cell
- Fundamental types of lattices
  - 2D lattice types
  - 3D lattice type

What is crystal (space) lattice?


Platinum


Platinum surface


Crystal lattice and structure of Platinum

one replaces each atom by a geometrical point located at the equilibrium position of that atom.

a. Lattice translation vectors

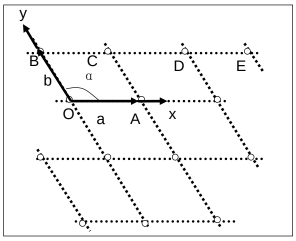
Crystal
periodic array of atoms: point lattice + basis


Point lattice –mathematical points in space

Lattice +basis=crystal structure

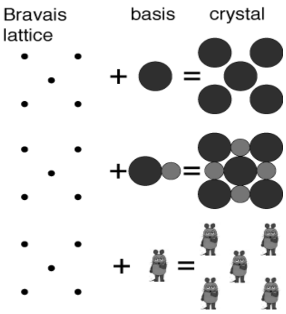
crystal structure

- An infinite array of points in space,
- Each point has identical surroundings to all others.
- Arrays are arranged exactly in a periodic manner.



● Crystal structure can be obtained by attaching atoms, groups of atoms or molecules which are called basis (motif) to the lattice sides of the lattice point.

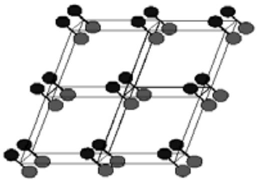
different choices for the basis



Lattice +basis=crystal structure

Attention

- Don't mix up atoms with lattice points
- Lattice points are infinitesimal points in space
- Lattice points do not necessarily lie at the centre of atoms



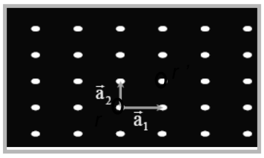
To describe a CS, there three important question to answer:

1. What is the lattice?
2. What choice of a_1, a_2, a_3 do we wish to make?
3. What is the basis?

Lattice?

Translation vectors

$(\vec{a}_1, \vec{a}_2, \vec{a}_3)$

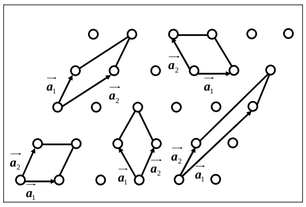


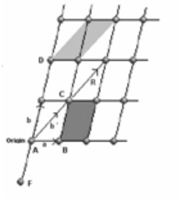
From the point *r*

$\vec{r}' = \vec{r} + u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$

$u_1, u_2, u_3 \in$ integer

$\vec{a}_1, \vec{a}_2, \vec{a}_3$ = lattice vector





The choice of lattice vectors is not unique. Thus one could equally well take the <u>vectors a and b' as a lattice vectors.</u>

Crystal axes

↑

Smallest valume ⇨ Primitive translation vectors

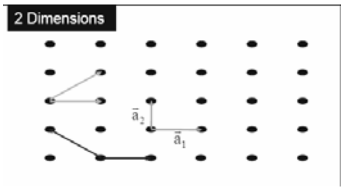
b. Primitive Lattice Cell

A cell will fill all space by the repetition of suitable crystal translation operations. ----A minimum volume cell.

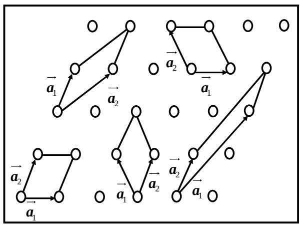
⊗ One lattice point per primitive cell.

$$A_{cell} = |\vec{a}_1 \times \vec{a}_2| = |\vec{a}_1||\vec{a}_2||\sin\phi|$$

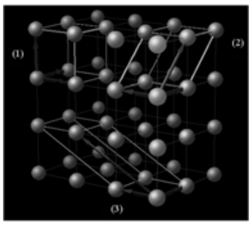
Same for all primitive cells



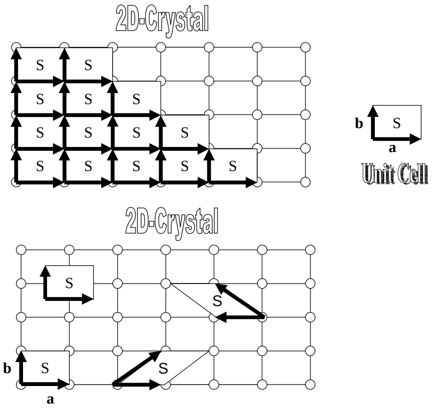
⊗ Not unique.



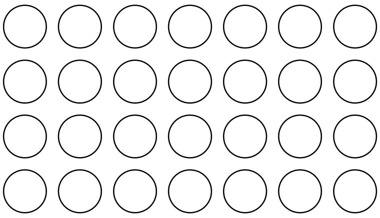
Not unique (2D)



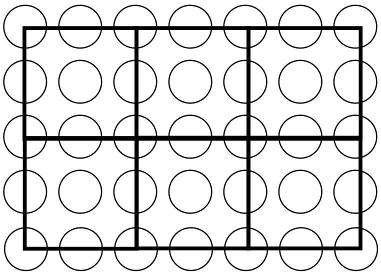
Not unique (3D)



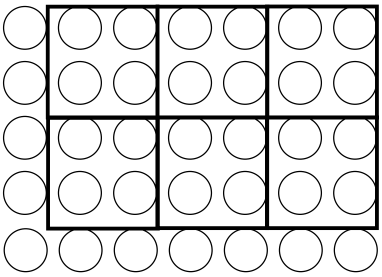
2D Unit Cell example -(NaCl)



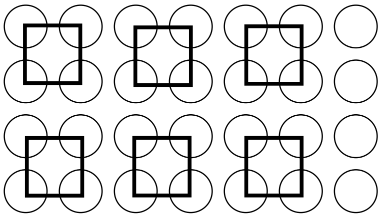
We define <u>**lattice points**</u> ; these are points with *identical environments*



it doesn't matter if you start from Na or Cl



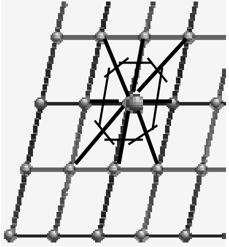
lattice points need not be atoms

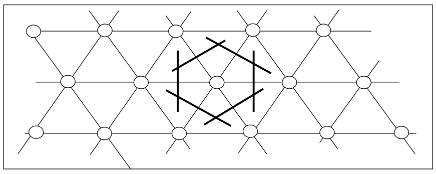


This is NOT a unit cell even though they are all the same - empty space is not allowed!

Wigner-Seitz Primitive cell in 2D (or 3D)

- Draw lines to connect a given lattice point to all nearby lattice points.
- Draw bisecting lines (or planes) to the previous lines.
- The smallest area (or volume) enclosed.





Highest symmetry

An atom --- the center of unit cell

All the space of the crystal
may be filled by these primitive cells

c. Fundamental types of Bravais lattices

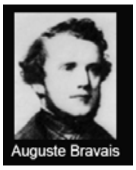
Bravais lattices

Basis $\longrightarrow$ One atom

Based on symmetries :

Translational – same if translate by a vector

$$\vec{T} = u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$$

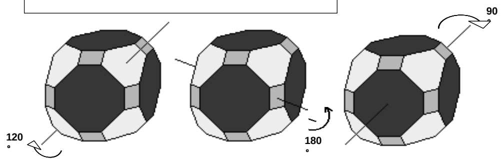


Auguste Bravais

Operation	Element
Rotation	Axis
Reflection	Plane
Inversion	Point
Rotoinversion	Axes

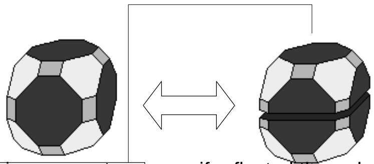
2) Rotational–same if lattice is rotated by an angle about a point

2-fold	by 180° ⬮	4-fold	by 90° ■
3-fold	by 120° ▲	6-fold	by 60° ⬢

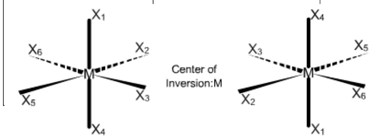


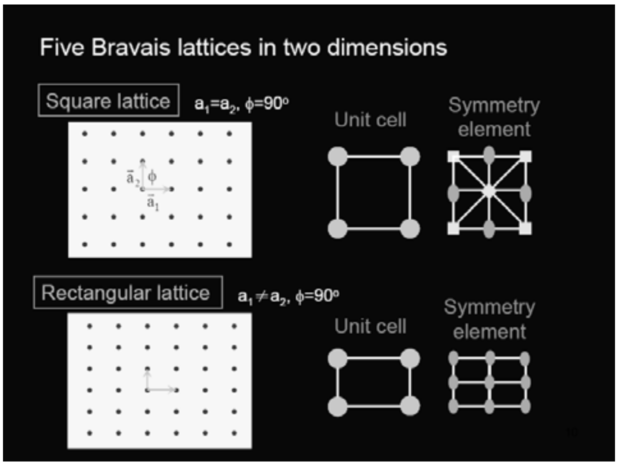
- The axis is called n-fold if the angle of rotation is 2 π /n.

3) Mirror symmetry –same if reflected about a plane



4) Inversion symmetry –same if reflected through a point (equivalent to rotation 180 and mirror ⊥ rotational axis





Five Bravais lattices in two dimensions

Square lattice $a_1=a_2$, $\phi=90°$

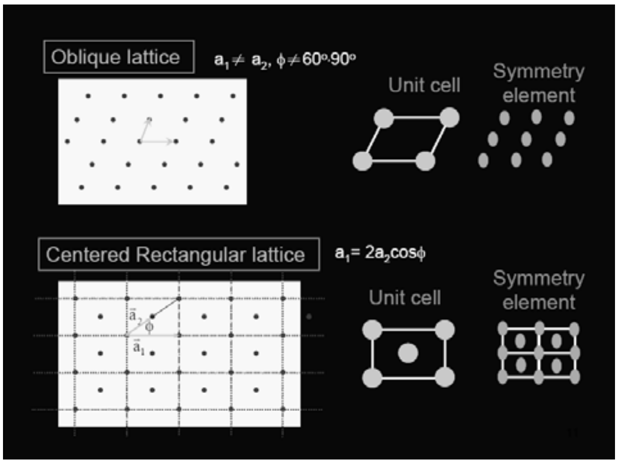
Unit cell

Symmetry element

Rectangular lattice $a_1 \neq a_2$, $\phi=90°$

Unit cell

Symmetry element



Oblique lattice $a_1 \neq a_2$, $\phi \neq 60°, 90°$

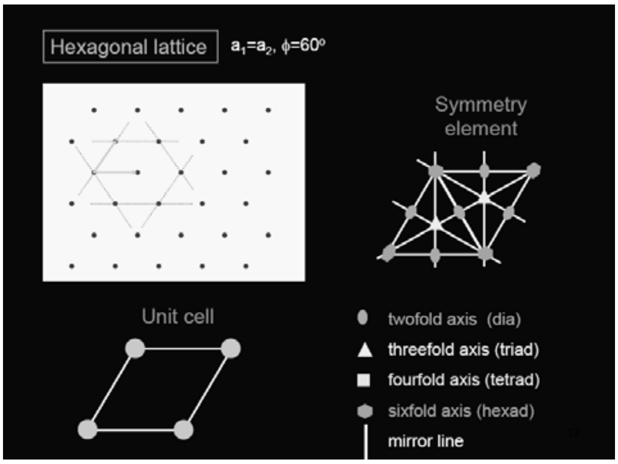
Unit cell

Symmetry element

Centered Rectangular lattice $a_1 = 2a_2 \cos\phi$

Unit cell

Symmetry element



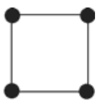
Hexagonal lattice $a_1=a_2$, $\phi=60°$

Symmetry element

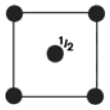
Unit cell

- ● twofold axis (dia)
- ▲ threefold axis (triad)
- ■ fourfold axis (tetrad)
- ⬢ sixfold axis (hexad)
- | mirror line

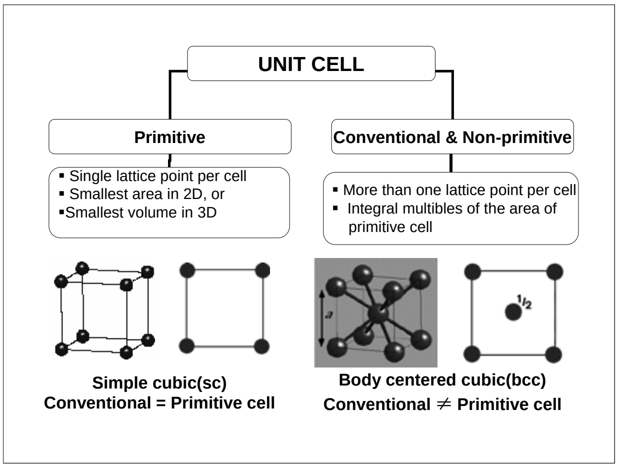
A Bravais lattice is a lattice in which every lattice point has exactly the same environment.



unit cell =Primitive cell



unit cell ≠ Primitive cell



UNIT CELL

Primitive

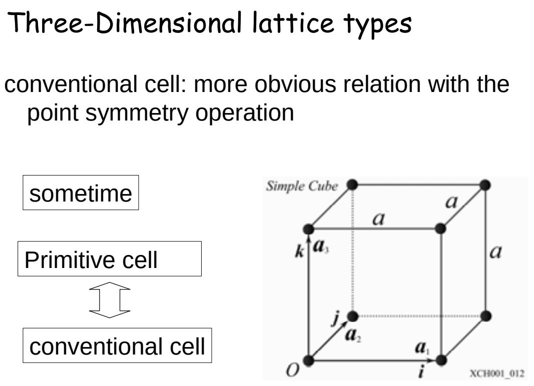
- Single lattice point per cell
- Smallest area in 2D, or
- Smallest volume in 3D

Conventional & Non-primitive

- More than one lattice point per cell
- Integral multibles of the area of primitive cell

Simple cubic(sc)
Conventional = Primitive cell

Body centered cubic(bcc)
Conventional ≠ Primitive cell



Three-Dimensional lattice types

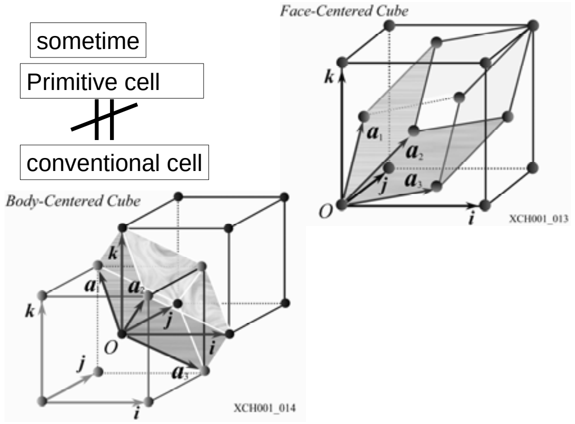
conventional cell: more obvious relation with the point symmetry operation

sometime

Primitive cell

⇕

conventional cell

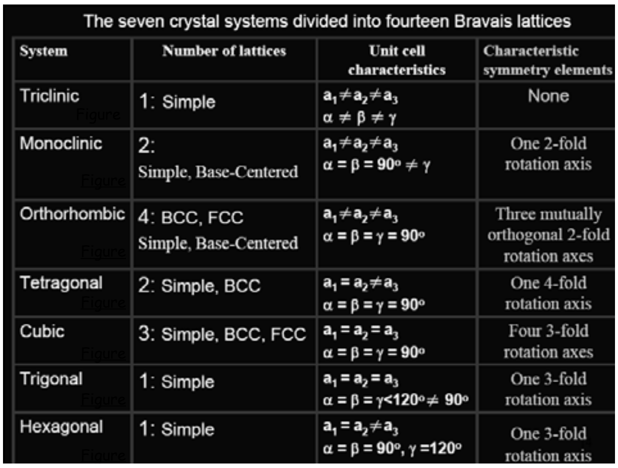


sometime

Primitive cell

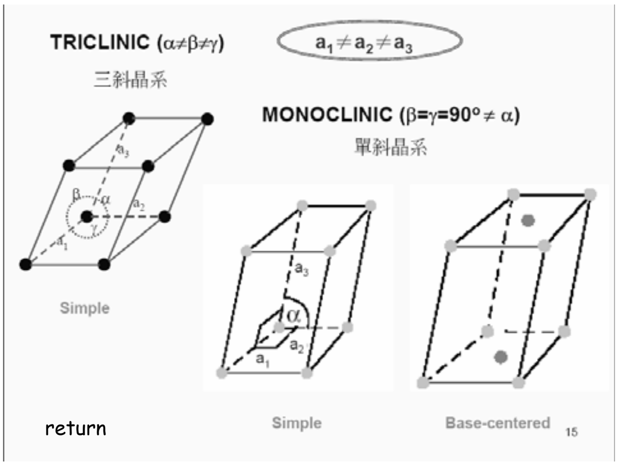
≠

conventional cell



The seven crystal systems divided into fourteen Bravais lattices

System	Number of lattices	Unit cell characteristics	Characteristic symmetry elements
Triclinic Figure	1: Simple	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$	None
Monoclinic Figure	2: Simple, Base-Centered	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = 90^\circ \neq \gamma$	One 2-fold rotation axis
Orthorhombic Figure	4: BCC, FCC Simple, Base-Centered	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$	Three mutually orthogonal 2-fold rotation axes
Tetragonal Figure	2: Simple, BCC	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$	One 4-fold rotation axis
Cubic Figure	3: Simple, BCC, FCC	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90^\circ$	Four 3-fold rotation axes
Trigonal Figure	1: Simple	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120^\circ \neq 90^\circ$	One 3-fold rotation axis
Hexagonal Figure	1: Simple	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	One 3-fold rotation axis



TRICLINIC ($\alpha \neq \beta \neq \gamma$) $a_1 \neq a_2 \neq a_3$

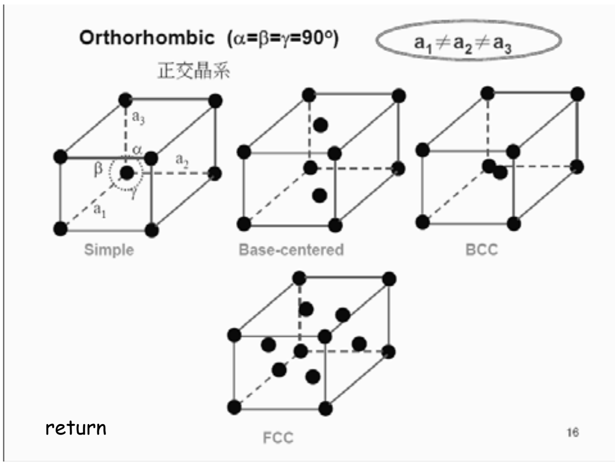
三斜晶系

MONOCLINIC ($\beta = \gamma = 90^\circ \neq \alpha$)

單斜晶系

return

15

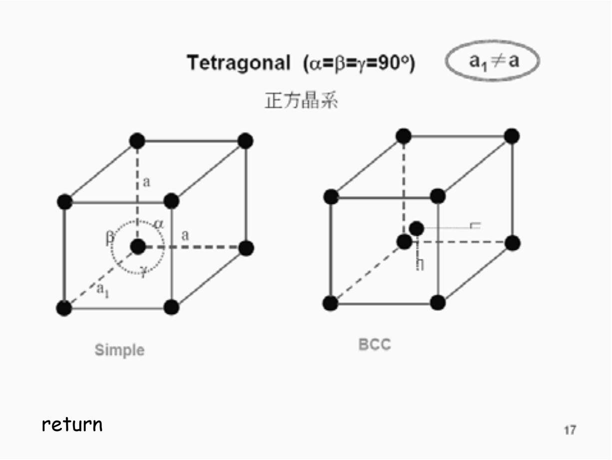


Orthorhombic ($\alpha = \beta = \gamma = 90^\circ$) $a_1 \neq a_2 \neq a_3$

正交晶系

return

16

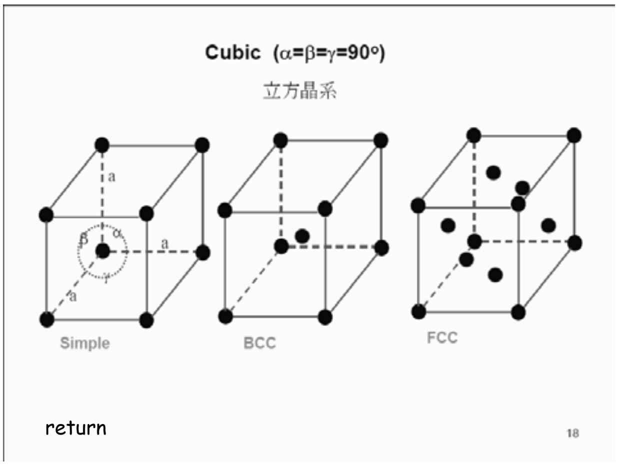


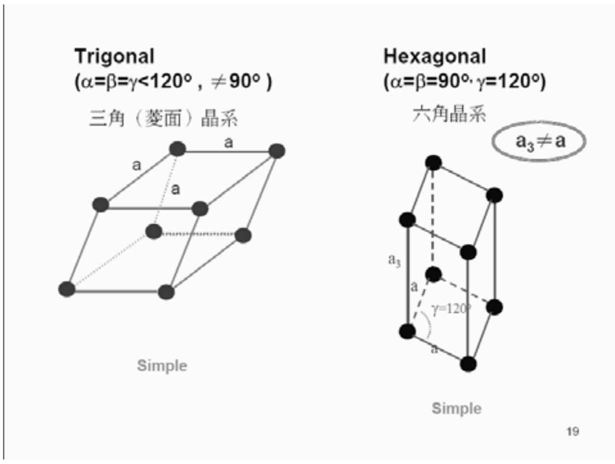
Tetragonal ($\alpha = \beta = \gamma = 90^\circ$) $a_1 \neq a$

正方晶系

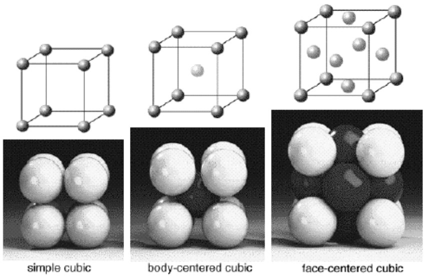
return

17

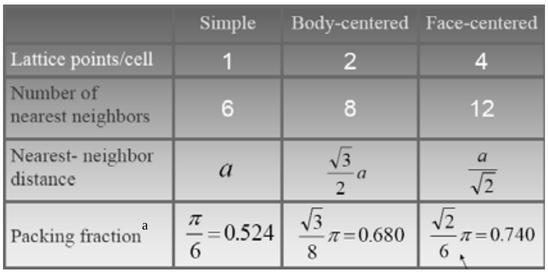




Three common Unit Cell in 3D



Characteristics of cubic lattices



	Simple	Body-centered	Face-centered
Lattice points/cell	1	2	4
Number of nearest neighbors	6	8	12
Nearest- neighbor distance	a	$\frac{\sqrt{3}}{2}a$	$\frac{a}{\sqrt{2}}$
Packing fraction[a]	$\frac{\pi}{6}=0.524$	$\frac{\sqrt{3}}{8}\pi=0.680$	$\frac{\sqrt{2}}{6}\pi=0.740$

[a] The packing fraction is the maximum proportion of the available volume that can be filled with hard spheres.

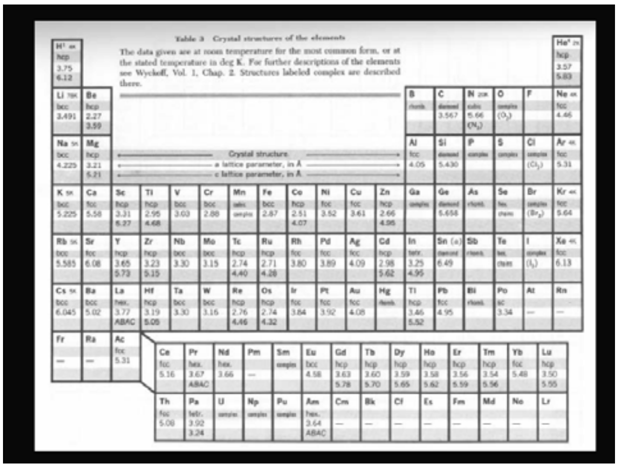


Table 3 Crystal structures of the elements

The data given are at room temperature for the most common form, or at the stated temperature in deg K. For further descriptions of the elements see Wyckoff, Vol. 1, Chap. 2. Structures labeled complex are described there.

H^1 4K hcp 3.75 6.12																	He^4 2K hcp 3.57 5.83
Li 78K bcc 3.491	Be hcp 2.27 3.59											B rhomb.	C diamond 3.567	N 20K cubic 5.66 (N_2)	O complex (O_2)	F	Ne 4K fcc 4.46
Na 5K bcc 4.225	Mg hcp 3.21 5.21	Crystal structure a lattice parameter, in Å c lattice parameter, in Å										Al fcc 4.05	Si diamond 5.430	P complex	S complex	Cl complex (Cl_2)	Ar 4K fcc 5.31
K 5K bcc 5.225	Ca fcc 5.58	Sc hcp 3.31 5.27	Ti hcp 2.95 4.68	V bcc 3.03	Cr bcc 2.88	Mn cubic complex	Fe bcc 2.87	Co hcp 2.51 4.07	Ni fcc 3.52	Cu fcc 3.61	Zn hcp 2.66 4.95	Ga complex	Ge diamond 5.658	As rhomb.	Se hex. chains	Br complex (Br_2)	Kr 4K fcc 5.64
Rb 5K bcc 5.585	Sr fcc 6.08	Y hcp 3.65 5.73	Zr hcp 3.23 5.15	Nb bcc 3.30	Mo bcc 3.15	Tc hcp 2.74 4.40	Ru hcp 2.71 4.28	Rh fcc 3.80	Pd fcc 3.89	Ag fcc 4.09	Cd hcp 2.98 5.62	In tetr. 3.25 4.95	Sn (α) diamond 6.49	Sb rhomb.	Te hex. chains	I complex (I_2)	Xe 4K fcc 6.13
Cs 5K bcc 6.045	Ba bcc 5.02	La hex. 3.77 ABAC	Hf hcp 3.19 5.05	Ta bcc 3.30	W bcc 3.16	Re hcp 2.76 4.46	Os hcp 2.74 4.32	Ir fcc 3.84	Pt fcc 3.92	Au fcc 4.08	Hg rhomb.	Tl hcp 3.46 5.52	Pb fcc 4.95	Bi rhomb.	Po sc 3.34	At —	Rn —
Fr —	Ra —	Ac fcc 5.31															
			Ce fcc 5.16	Pr hex. 3.67 ABAC	Nd hex. 3.66	Pm —	Sm complex	Eu bcc 4.58	Gd hcp 3.63 5.78	Tb hcp 3.60 5.70	Dy hcp 3.59 5.65	Ho hcp 3.58 5.62	Er hcp 3.56 5.59	Tm hcp 3.54 5.56	Yb fcc 5.48	Lu hcp 3.50 5.55	
			Th fcc 5.08	Pa tetr. 3.92 3.24	U complex	Np complex	Pu complex	Am hex. 3.64 ABAC	Cm —	Bk —	Cf —	Es —	Fm —	Md —	No —	Lr —	

Review

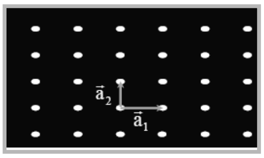
- What is lattice?

periodic array of atoms = point lattice + basis

$\vec{r}' = \vec{r} + u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$

$u_1, u_2, u_3 \in \text{integer}$

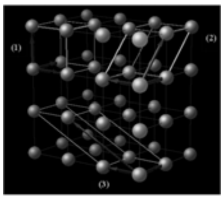
$\vec{a}_1, \vec{a}_2, \vec{a}_3 = \text{lattice vector}$



- **Primitive Lattice Cell**

⊗ One lattice point per primitive cell.
⊗ A minimum volume cell
⊗ Not unique.

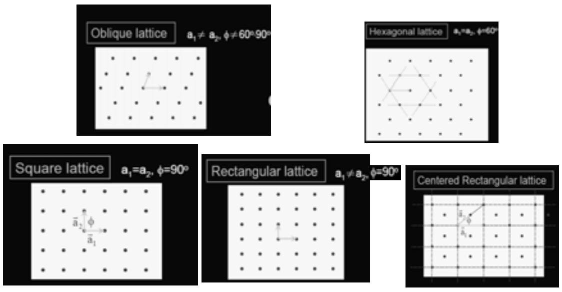
Wigner-Seitz Primitive cell

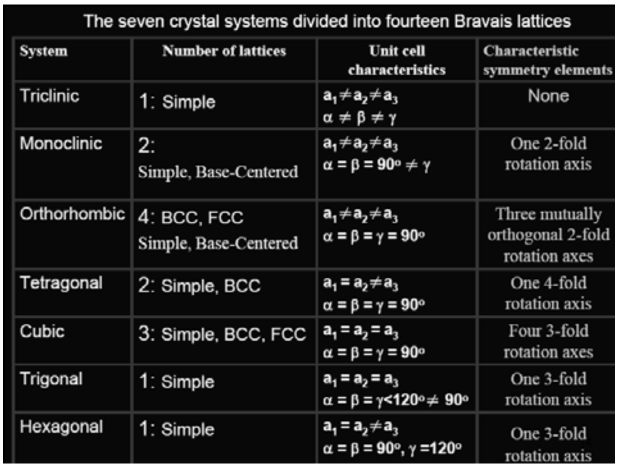


- **Bravais lattices**

a lattice in which every lattice point has exactly the same environment.

Five Bravais lattices in two dimension





The seven crystal systems divided into fourteen Bravais lattices

System	Number of lattices	Unit cell characteristics	Characteristic symmetry elements
Triclinic	1: Simple	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$	None
Monoclinic	2: Simple, Base-Centered	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = 90° \neq \gamma$	One 2-fold rotation axis
Orthorhombic	4: BCC, FCC Simple, Base-Centered	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90°$	Three mutually orthogonal 2-fold rotation axes
Tetragonal	2: Simple, BCC	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90°$	One 4-fold rotation axis
Cubic	3: Simple, BCC, FCC	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90°$	Four 3-fold rotation axes
Trigonal	1: Simple	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120° \neq 90°$	One 3-fold rotation axis
Hexagonal	1: Simple	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90°, \gamma = 120°$	One 3-fold rotation axis

---

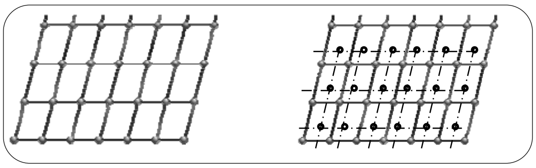
Crystal Lattice

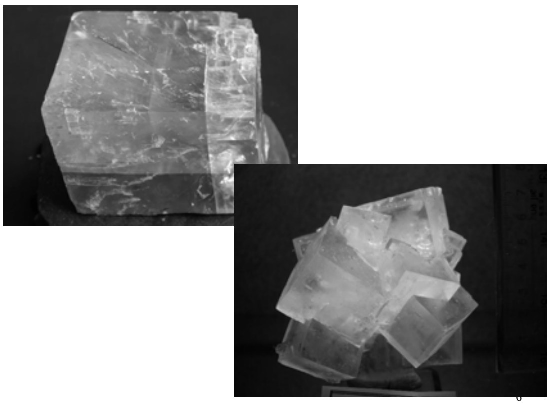
Bravais Lattice (BL)

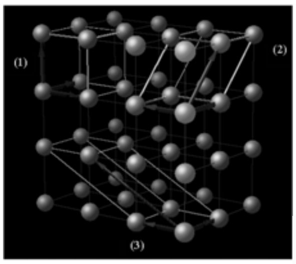
- All atoms are of the same kind
- All lattice points are equivalent

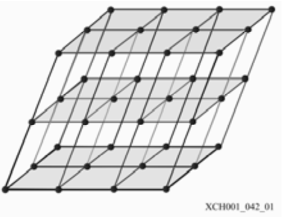
Non-Bravais Lattice (non-BL)

- Atoms can be of different kind
- Some lattice points are not equivalent
- A combination of two or more BL









III. Directions and planes in crystals

a. Crystal Directions

- **We choose one lattice point on the line as an origin, say the point O. Choice of origin is completely arbitrary, since every lattice point is identical.**

- **Then we choose the lattice vector joining O to any point on the line, say point T. This vector can be written as;**

  $R = n_1 a + n_2 b + n_3 c$
- **To distinguish a lattice <u>direction</u> from a lattice <u>point</u>, the triple is enclosed in square brackets [...] is used.$[n_1 n_2 n_3]$**
- **$[n_1 n_2 n_3]$ is the <u>smallest reduced integer</u> of the <u>*same relative ratios*</u>.**

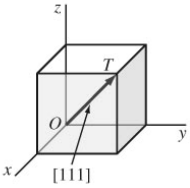
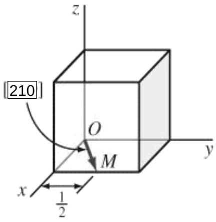
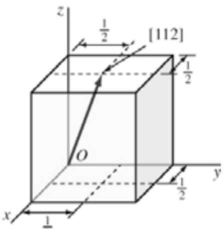


Fig. Shows [111] direction

Examples

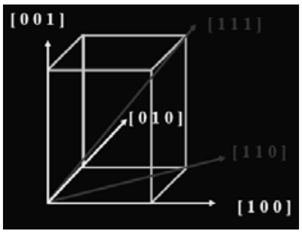




X = 1 , Y = ½ , Z = 0
[1 ½ 0] ⟹ [2 1 0]

X = ½ , Y = ½ , Z = 1
[½ ½ 1] ⟹ [1 1 2]

Cubic has highest symmetric directions

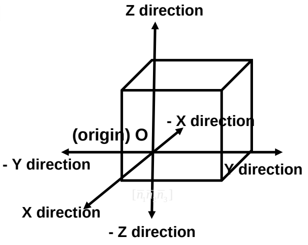


Negative directions

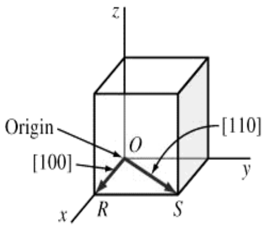
- When we write the direction $[n_1 n_2 n_3]$ depend on the origin, negative directions can be written as

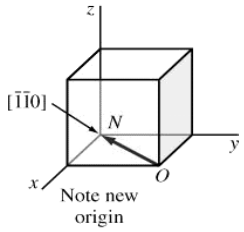
  $[\bar{n}_1 \bar{n}_2 \bar{n}_3]$

  $R = n_1 a + n_2 b + n_3 c$
- Direction must be smallest integers



Examples 1

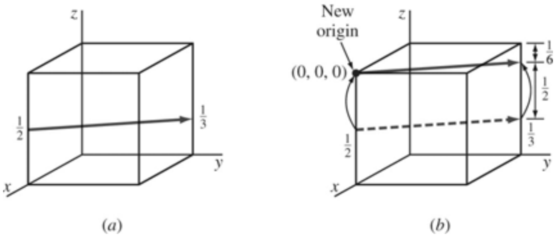




X = 1 , Y = 0 , Z = 0 ⟹ [1 0 0]

X = -1 , Y = -1 , Z = 0 ⟹ $[\bar{1}\bar{1}0]$

Examples 2



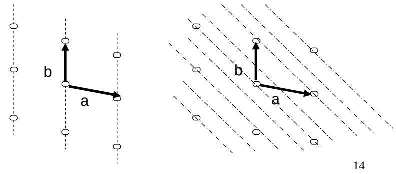
We can move vector to the origin.

X =-1 , Y = 1 , Z = -1/6
[-1 1 -1/6] ⇨ $[\bar{6}6\bar{1}]$

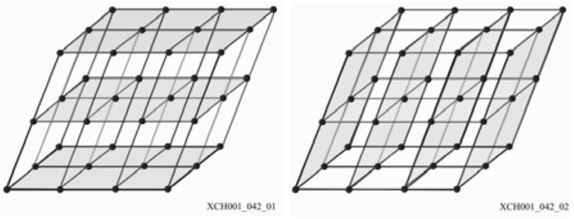
Crystal planes

- Within a crystal lattice it is possible to identify sets of equally spaced parallel planes. These are called lattice planes.
- In the figure density of lattice points on each plane of a set is the same and all lattice points are contained on each set of planes**.**

The set of planes in 2D lattice.



Same lattice , two crystal planes



Miller Indices

Miller Indices are a symbolic vector representation for the orientation of an atomic plane in a crystal lattice.

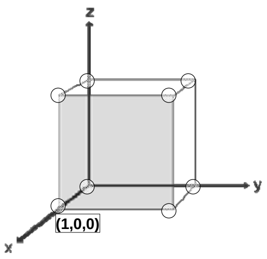
Notes:

1) Determine the intercepts of the plane along each of the three crystallographic directions

2) Take the reciprocals of the intercepts

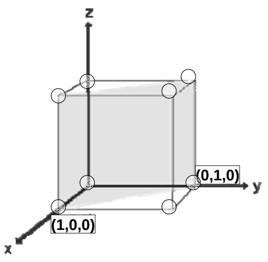
3) If fractions result, multiply each by the denominator of the smallest fraction

Example-1



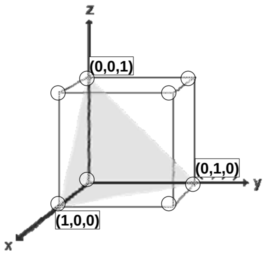
Axis	X	Y	Z
Intercept points	1	∞	∞
Reciprocals	1/1	1/ ∞	1/ ∞
Smallest Ratio	1	0	0
Miller İndices (100)			

Example-2



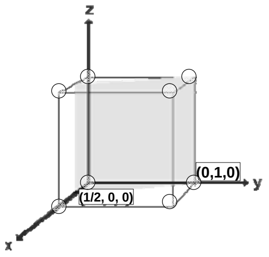
Axis	X	Y	Z
Intercept points	1	1	∞
Reciprocals	1/1	1/ 1	1/ ∞
Smallest Ratio	1	1	0
Miller İndices (110)			

Example-3



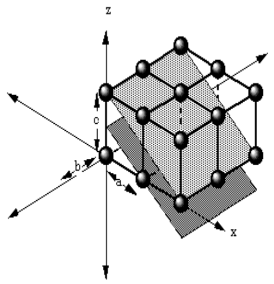
Axis	X	Y	Z
Intercept points	1	1	1
Reciprocals	1/1	1/ 1	1/ 1
Smallest Ratio	1	1	1
Miller İndices (111)			

Example-4



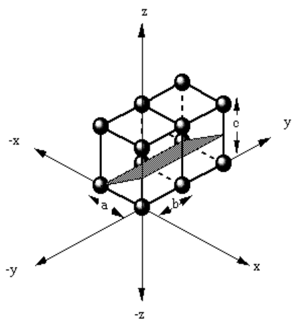
Axis	X	Y	Z
Intercept points	1/2	1	∞
Reciprocals	1/(½)	1/ 1	1/ ∞
Smallest Ratio	2	1	0
Miller İndices (210)			

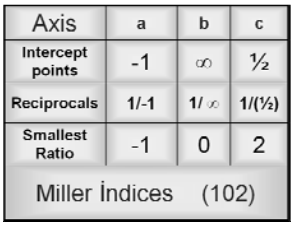
Example-5



Axis	a	b	c
Intercept points	1	∞	½
Reciprocals	1/1	1/ ∞	1/(½)
Smallest Ratio	1	0	2
Miller İndices (102)			

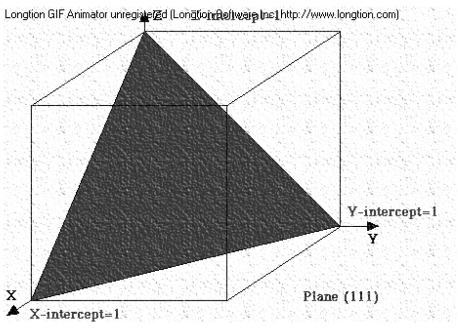
Example-6



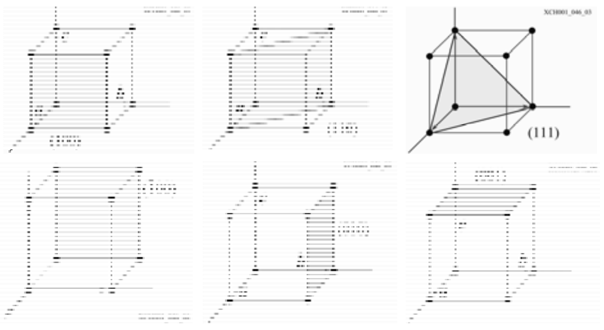


Axis	a	b	c
Intercept points	-1	∞	½
Reciprocals	1/-1	1/ ∞	1/(½)
Smallest Ratio	-1	0	2
Miller İndices (102)			

Example-7



Six kinds of planes in cubic crystal



Coordination Number

- Coordination Number (CN) : The Bravais lattice points closest to a given point are the nearest neighbours.
- Because the Bravais lattice is periodic, all points have the same number of nearest neighbours or coordination number. It is a property of the lattice.
- A simple cubic has coordination number 6; a body-centered cubic lattice, 8; and a face-centered cubic lattice,12.

Atomic Packing Factor

- Atomic Packing Factor (APF) is defined as the volume of atoms within the unit cell divided by the volume of the unit cell.

$$\text{APF} = \frac{\text{Volume of Atoms in Unit Cell}}{\text{Volume of Unit Cell}}$$

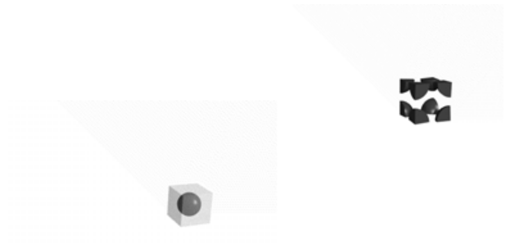
Most common crystal structures :

1. Simple Cubic lattice

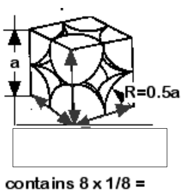
conventional cell : 1 atom/cube

6 nearest neighbors

Simple Cubic lattice

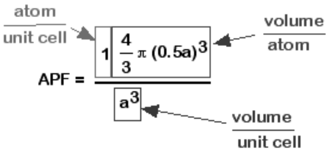


Packing Factor of SC



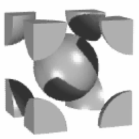
contains 8 x 1/8 =
1atom/unit cell

APF = 0.52 for simple cubic



$$\text{APF} = \frac{1 \cdot \frac{4}{3}\pi(0.5a)^3}{a^3}$$

2. Body Centered Cubic lattice



Conventional cell : 2 atoms/ cube

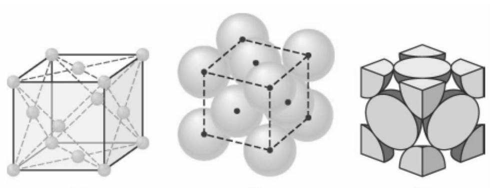
Not a primitive lattice

8 nearest neighbors

Alkali metals : Li, Na, K, Rb, Cs
Ferromagnetic metals : Cr, Fe
Transition metals : Nb, V, Ta, Mo, W

- BCC lattice + single atom basis
- SC lattice + basis of 2 atoms at (0,0,0) and (1/2,1/2,1/2)

Face Centered Cubic (FCC)?



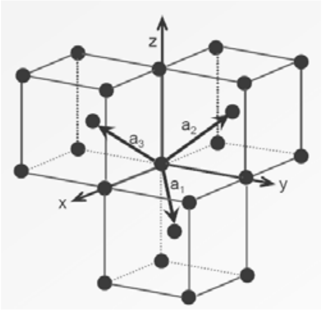
Packing Factor

Numbers of nearest neighbors

Primitive translation vector

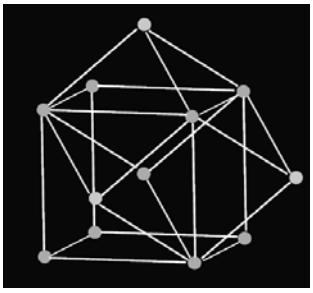
The angle between two adjacent edges

Edge



Primitive translation vector

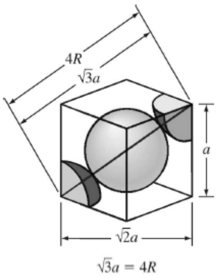
Body-centered Cubic lattice



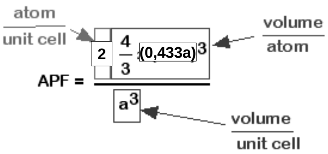
Primitive cell :
Rhombohedron

1. Edge $\frac{\sqrt{3}}{2}a$
2. the angle between two adjacent edges is 109°28’

Packing Factor of BCC



$$APF_{BCC} = \frac{V_{atoms}}{V_{unit\ cell}} = 0.68$$



$$APF = \frac{2\ \frac{4}{3}\pi(0{,}433a)^3}{a^3}$$

Review

1. Directions and planes in crystals

Miller Indices

Notes:

1) Determine the intercepts of the plane along each of the three crystallographic directions

2) Take the reciprocals of the intercepts

3) If fractions result, multiply each by the denominator of the smallest fraction

2. Coordination Number

number of nearest neighbours

SCC 6

BCC 8

3. Atomic Packing Factor

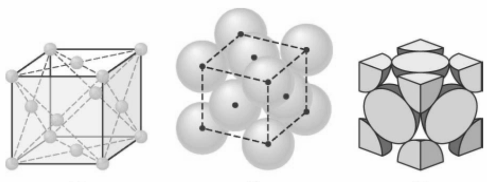
$$\text{APF} = \frac{\text{Volume of Atoms in Unit Cell}}{\text{Volume of Unit Cell}}$$

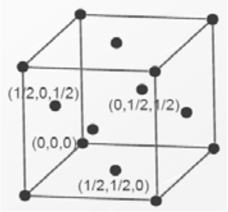
SCC 0.52

BCC 0.68

3. Face Centered Cubic lattice :

- There are atoms at the corners of the unit cell and at the center of each face.
- Face centered cubic has 4 atoms so its non primitive cell.
- Many of common metals (Cu,Ni,Pb..etc) crystallize in FCC structure.





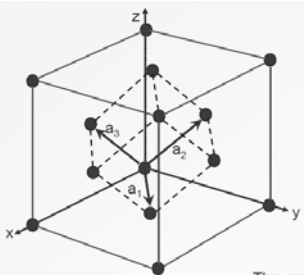
Conventional cell : 4 atoms/ cube

Not a primitive lattice

12 nearest neighbors

Noble metals : Cu, Ag, Au
Transition metals : Ni, Pd, Pt,
Inert gas solids : Ne, Ar, Kr, Xe

- FCC lattice + single atom basis
- SC lattice + basis of 4 atoms at (0,0,0), (1/2,1/2,0) (1/2,0,1/2),and (0,1/2,1/2)



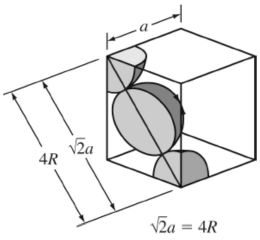
Primitive translation vector

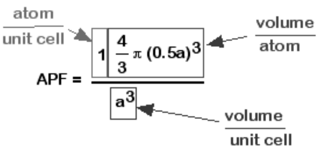
Rhombohedral Primitive cell

The angle between two adjacent edges : 60º
Edge : $\frac{\sqrt{2}}{2}$

Packing Factor of FCC

$$APF_{FCC} = \frac{V_{atoms}}{V_{unit\ cell}} = 0.74$$

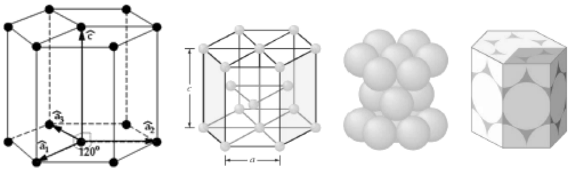




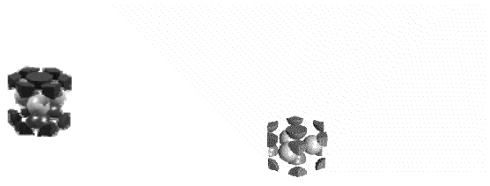
$$\text{APF} = \frac{\underset{\text{atom / unit cell}}{1}\ \underset{\text{volume / atom}}{\frac{4}{3}\pi(0.5a)^3}}{\underset{\text{volume / unit cell}}{a^3}}$$

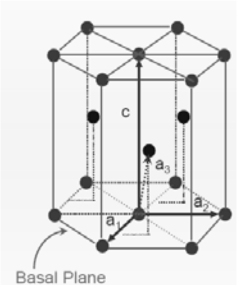
4. Hexagonal Close-Packed lattice

- A crystal system in which three equal coplanar axes intersect at an angle of 60 , and a perpendicular to the others, is of a different length.



HEXAGONAL SYSTEM





a_1, a_2, and c do not construct a primitive lattice
a_1, a_2, and a_3 construct a primitive lattice

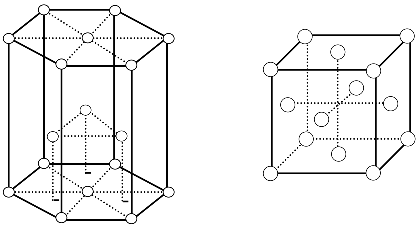
12 nearest neighbors

Transition metals : Sc, Y, Ti, Zr, Co…
IIA metals : Be, Mg

Hexgonal lattice + basis of 2 atoms at (0,0,0) and (2/3,1/3,1/2)

Close-Packed lattice

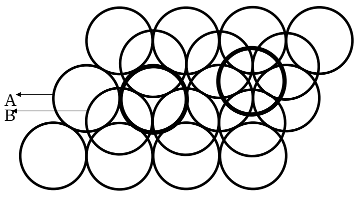
Hexagonal Close-Packed lattice	HCP
Cubic Close-Packed lattice	FCC



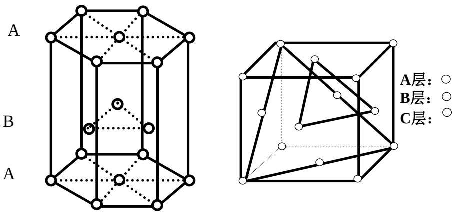
1th step: Spheres are arranged in a single closed-packed layer A by placing each sphere in contact with six others.

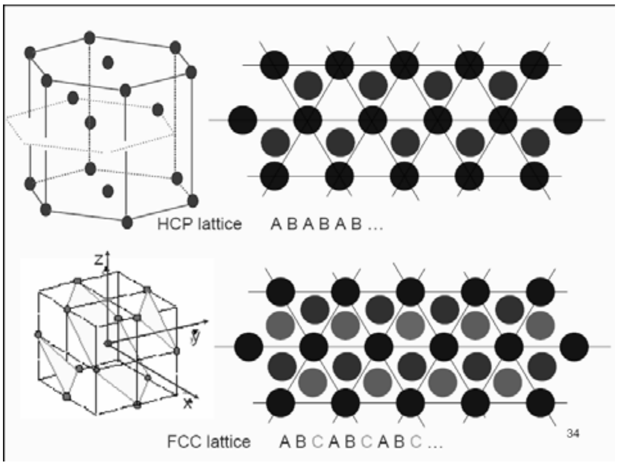
2th step: A second similar layer bottom B may be added by placing each sphere of B in contact with there spheres of the bottom layer.

3th step: A third layer C may be added in two way.



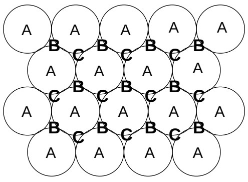
HCP (-A-B-) **FCC (A-B-C)**

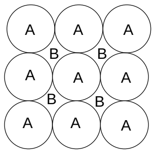




Packing

Close pack





Sequence ABABAB..
-hexagonal close pack

Sequence ABCABCAB..
-face centered cubic close pack

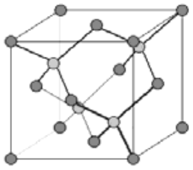
Sequence AAAA…
- simple cubic

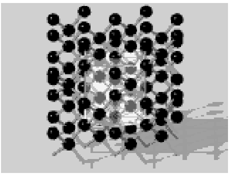
Sequence ABAB…
- body centered cubic

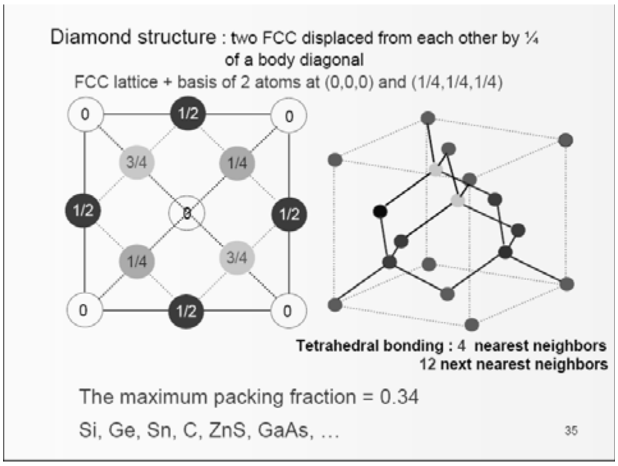
Close pack

5 Diamond Structure

- The diamond lattice is consist of two interpenetrating face centered bravais lattices.
- There are eight atom in the structure of diamond.
- Each atom bonds covalently to 4 others equally spread about atom in 3d.







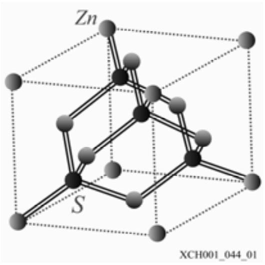
Diamond structure : two FCC displaced from each other by ¼ of a body diagonal

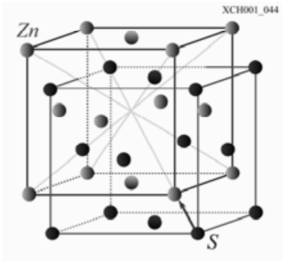
FCC lattice + basis of 2 atoms at (0,0,0) and (1/4,1/4,1/4)

Tetrahedral bonding : 4 nearest neighbors
12 next nearest neighbors

The maximum packing fraction = 0.34

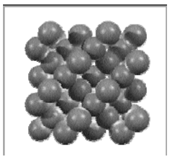
Si, Ge, Sn, C, ZnS, GaAs, …



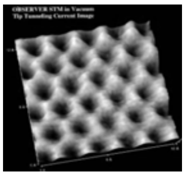


Some atoms form multiple stable structures:

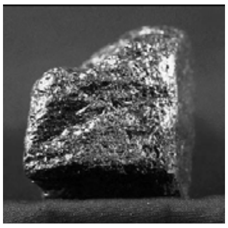
for example, C→diamond or graphite (hexagonal)



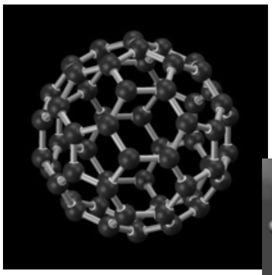
An STM image of a graphite surface clearly shows the interconnected 6-membered rings of graphite



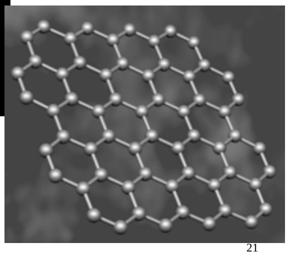
graphite



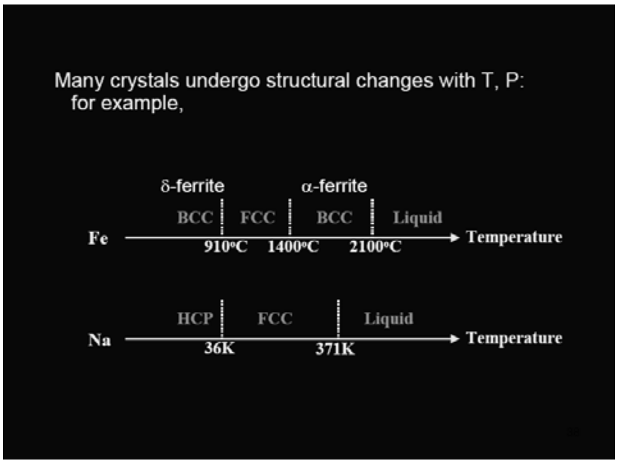
diamond



Fullerene



Graphene

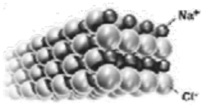


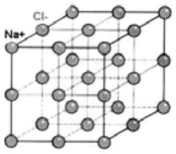
Many crystals undergo structural changes with T, P:
for example,

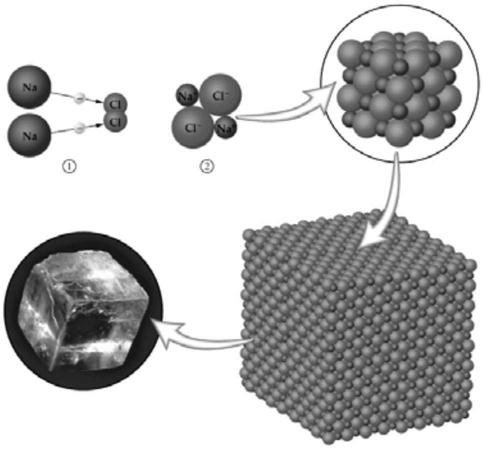
MOST IMPORTANT
CRYSTAL STRUCTURES

1. Sodium Chloride Structure

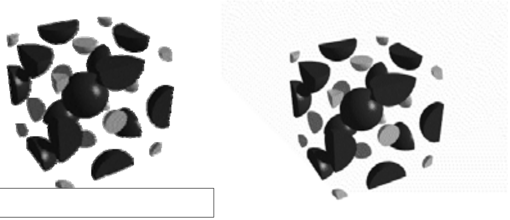
- **Sodium chloride also crystallizes in a cubic lattice, but with a different unit cell.**
- **Sodium chloride structure consists of equal numbers of sodium and chlorine ions placed at alternate points of a simple cubic lattice.**
- **Each ion has six of the other kind of ions as its nearest neighbours.**

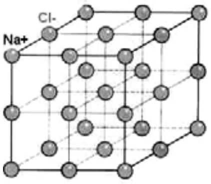






- **If we take the NaCl unit cell and remove all the red Cl ions, we are left with only the blue Na. If we compare this with the fcc / ccp unit cell, it is clear that they are identical. Thus, the Na is in a fcc sublattice.**





- This structure can be considered as a face-centered-cubic Bravais lattice with a basis consisting of a sodium ion at 0 and a chlorine ion at the center of the conventional cell,

$$a/2(\vec{x}+\vec{y}+\vec{z})$$

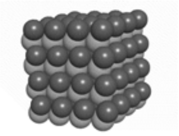
- LiF,NaBr,KCl,LiI,etc
- The lattice constants are in the order of 4-7 angstroms.

---

2. Cesium Chloride Structure Cs+Cl-

- Cesium chloride crystallizes in a cubic lattice. The unit cell may be depicted as shown. (Cs+ is teal, Cl- is gold).

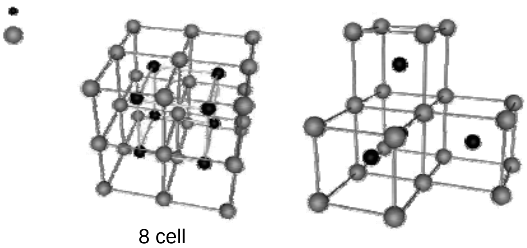
- *Cesium chloride consists of equal numbers of cesium and chlorine ions, placed at the points of a body-centered cubic lattice so that each ion has eight of the other kind as its nearest neighbors.*



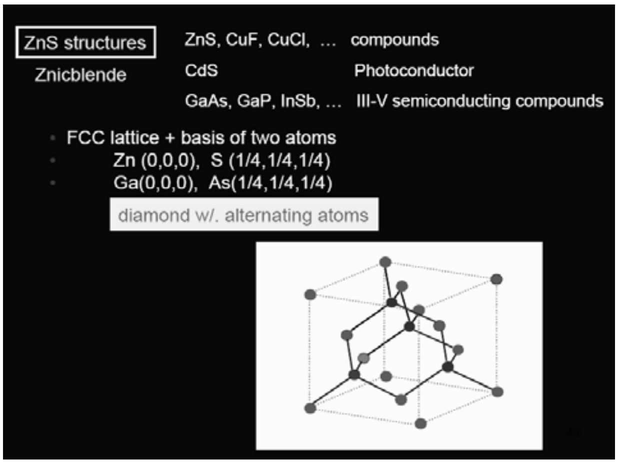
- The translational symmetry of this structure is that of the simple cubic Bravais lattice, and is described as a simple cubic lattice with a basis consisting of a cesium ion at the origin **0** and a chlorine ion at the cube center

$$a/2(\vec{x}+\vec{y}+\vec{z})$$

- CsBr,CsI crystallize in this structure.The lattice constants are in the order of 4 angstroms.



8 cell



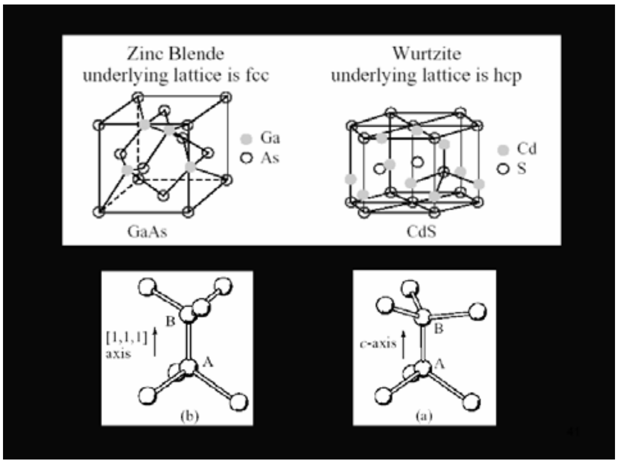
ZnS structures

Znicblende

ZnS, CuF, CuCl, …	compounds
CdS	Photoconductor
GaAs, GaP, InSb, …	III-V semiconducting compounds

- FCC lattice + basis of two atoms
- Zn (0,0,0), S (1/4,1/4,1/4)
- Ga(0,0,0), As(1/4,1/4,1/4)

diamond w/. alternating atoms



Homework

1.1, 1.2, 1.3

Chapter Two Reciprocal Lattice

Diffraction of waves by crystals

Scattered wave amplitude

Reciprocal lattice vectors

Fourier analysis of the basis

How do we determine the structure of crystal ?
----bulk and surface structures

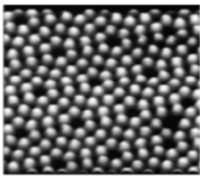
One can experimentally determine crystal structures

from real space

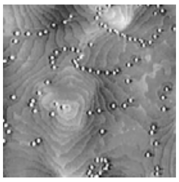
or

from diffraction to obtain the lattice structures in reciprocal space.

(1) Direct observation—see atoms directly on surface

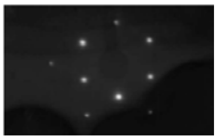


STM picture of atoms on Si(111) surface



IV-VI Quantum Dot AFM picture
From M. Pinczolits, Institute of Physics, University of Lintz and American Institute of Physics

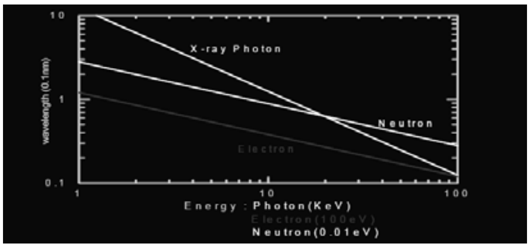
(2) Diffraction of Radiation waves ---traditional method

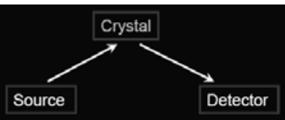


Electron diffraction pattern of(111) diamond surface

Diffraction regime: λ ~d

scattering are sensitive to the crystal structure





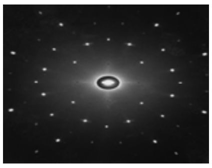
Radiations :		Detections :
1895	X-ray (Photon)	Intensity vs. Direction
1932	Neutron	Intensity vs. Energy (λ)
1897	Electrons	

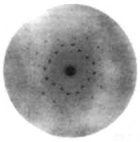
Nobel prizes
X-ray Diffraction:
Rontgen, 1901,; von Laue 1914;
Bragg, 1915
Electron microscopy/diffraction:
Ruska, Binig, &Rohrer, 1986
Neutron diffraction:
Brockhouse & Shull 1994

1912

Arnold Sommerfeld,1868-1951

Max von Laue,1879-1960





In 1912 ZnS

The Nobel Prize in Physics 2009

"for groundbreaking achievements concerning the transmission of light in fibers for optical communication"
"for the invention of an imaging semiconductor circuit – the CCD sensor"


Charles K. Kao


Willard S. Boyle


George E. Smith


Congratulations to Professor Charles K. Kao
Nobel Laureate in Physics 2009

A Short Biography of Professor Kao

1933	Born in Shanghai on 4 November
1957, 1965	Awarded the degrees of BSc and PhD from the University of London
1966	Published a paper which proposed using glass fibres as a conductor for optic communication, ushering in the era of optic fibre communication
1970	Joined CUHK as Reader and chair of the then new Department of Electronics, later appointed as the first Professor of Electronics
1985	Conferred the degree of Doctor of Science, *honoris causa*, by CUHK
1987	Became Vice-Chancellor of CUHK
1996	Retired in July from vice-chancellorship and appointed as Honorary Professor of Engineering
	A minor planet (3463) was named after him as 'Kaokuen' by the Purple Mountain Observatory of the Chinese Academy of Sciences
2009	Awarded the Nobel Prize in Physics by the Royal Swedish Academy of Sciences

Review

1. crystal structure

Periodic arrays of atom

Lattice +basis=crystal structure

lattice translation vectors

$$\vec{r}\,' = \vec{r} + u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$$

$$u_1, u_2, u_3 \in \text{integer}$$

$$\vec{a}_1, \vec{a}_2, \vec{a}_3 = \text{lattice vector}$$

---

2. Primitive Lattice Cell

- ⊗ One lattice point per primitive cell.
- ⊗ A minimum volume cell
- ⊗ Not unique.

3. Bravais lattices

2D 3D

4. Directions and planes in crystals

Crystal Directions

Crystal plane Miller Indices

5. Most common crystal structures

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How do we determine the structure of crystal ?
----bulk and surface structures

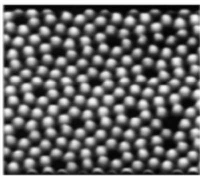
One can experimentally determine crystal structures

from real space

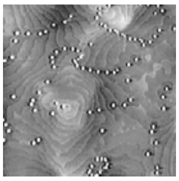
or

from diffraction to obtain the lattice structures in reciprocal space.

(1) Direct observation—see atoms directly on surface

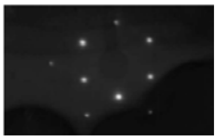


STM picture of atoms
on Si(111) surface



IV-VI Quantum Dot AFM picture
From M. Pinczolits, Institute of Physics, University of Lintz and American Institute of Physics

(2) Diffraction of Radiation waves ---traditional method

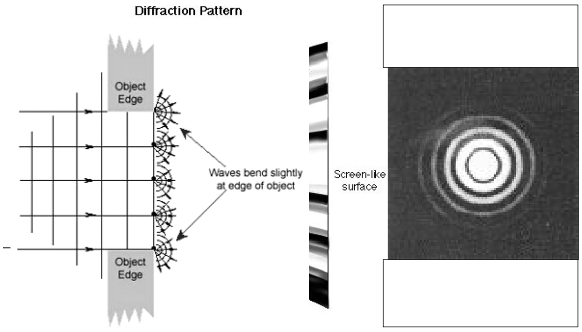


Electron diffraction pattern of(111) diamond surface

Diffraction regime: λ ~d

scattering are sensitive to the crystal structure

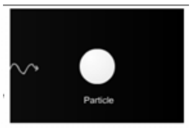
LIGHT INTERFERENCE



Diffraction from a particle and solid

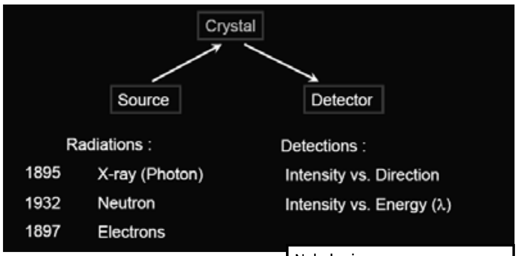
Single particle

- To understand diffraction we also have to consider what happens when a wave interacts with a single particle**.** The particle scatters the incident beam uniformly in **all** directions



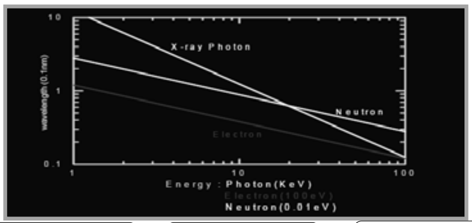
Solid material

- What happens if the beam is incident on solid material? If we consider a crystalline material, the scattered beams may add together in a few directions and reinforce each other to give **diffracted** beams



Radiations :		Detections :
1895	X-ray (Photon)	Intensity vs. Direction
1932	Neutron	Intensity vs. Energy (λ)
1897	Electrons	

Nobel prizes
X-ray Diffraction:
Rontgen, 1901,; von Laue 1914; Bragg, 1915
Electron microscopy/diffraction:
Ruska, Binig, &Rohrer, 1986
Neutron diffraction:
Brockhouse & Shull 1994



X-Ray	**Neutron**	**Electron**
λ = 1A°	λ = 1A°	λ = 2A°
E ~ 10^4 eV	E ~ 0.08 eV	E ~ 150 eV
interact with electron Penetrating	interact with nuclei Highly Penetrating	interact with electron Less Penetrating

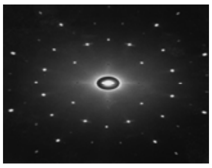
X-RAY

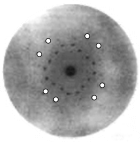
- X-rays were discovered in 1895 by the German physicist Wilhelm Conrad Röntgen and were so named because their nature was unknown at the time.
- He was awarded the Nobel prize for physics in 1901.


Wilhelm Conrad Röntgen
(1845-1923)


Arnold Sommerfeld,1868-1951


Max von Laue,1879-1960




In 1912 ZnS

X-Ray Diffraction & Bragg Equation

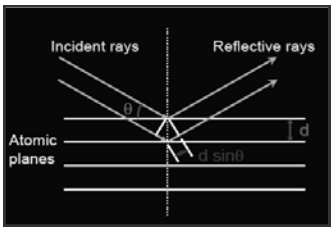
- English physicists Sir W.H. Bragg and his son Sir W.L. Bragg developed a relationship in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence (theta, θ).This observation is an example of X-ray **wave interference.**


Sir William Henry Bragg (1862-1942),
William Lawrence Bragg (1890-1971)

- 1915, the father and son were awarded the Nobel prize for physics *"for their services in the analysis of crystal structure by means of Xrays".*

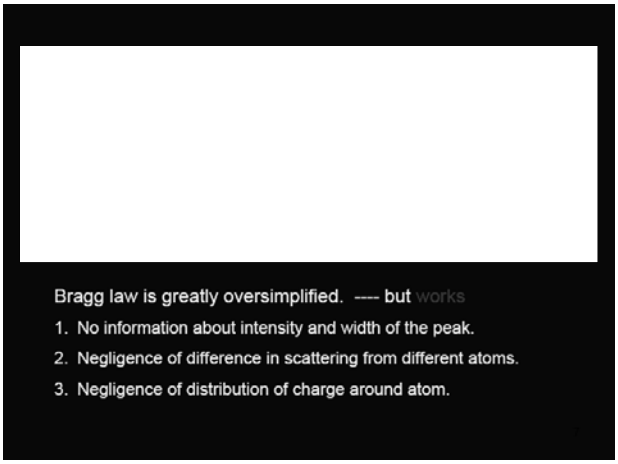
Diffraction of waves by crystals

Bragg presented a simple explanation of the diffracted beams from a crystal

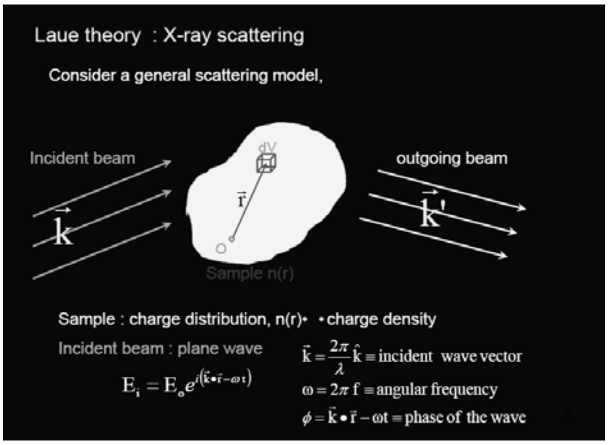


condition for constructive interference from a crystal

$$2d\sin\theta = n\lambda$$ Bragg Law


Bragg law is greatly oversimplified. ---- but works

1. No information about intensity and width of the peak.
2. Negligence of difference in scattering from different atoms.
3. Negligence of distribution of charge around atom.


Laue theory : X-ray scattering

Consider a general scattering model,

Sample : charge distribution, n(r)• •charge density

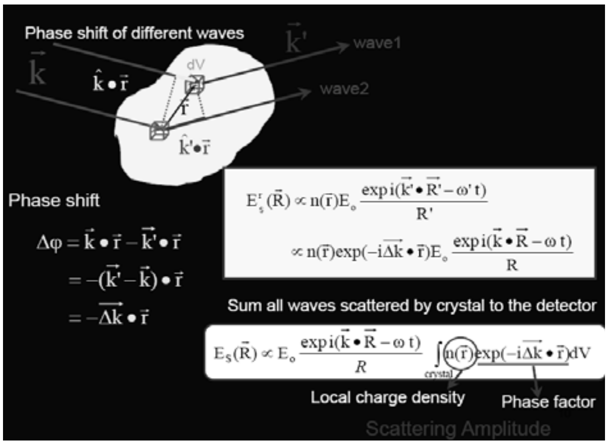
Incident beam : plane wave

$$E_i = E_o e^{i(\vec{k}\bullet\vec{r}-\omega t)}$$

$\vec{k} = \frac{2\pi}{\lambda}\hat{k} \equiv$ incident wave vector

$\omega = 2\pi f \equiv$ angular frequency

$\phi = \vec{k}\bullet\vec{r} - \omega t \equiv$ phase of the wave



Phase shift of different waves

Phase shift

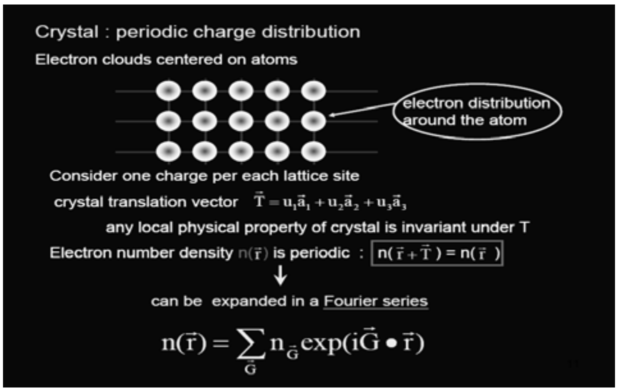
$$\Delta\varphi = \vec{k}\bullet\vec{r} - \vec{k}'\bullet\vec{r} = -(\vec{k}'-\vec{k})\bullet\vec{r} = -\overrightarrow{\Delta k}\bullet\vec{r}$$

$$E_s'(\vec{R}) \propto n(\vec{r})E_o \frac{\exp i(\vec{k}'\bullet\vec{R}' - \omega' t)}{R'} \propto n(\vec{r})\exp(-i\overrightarrow{\Delta k}\bullet\vec{r})E_o \frac{\exp i(\vec{k}\bullet\vec{R} - \omega t)}{R}$$

Sum all waves scattered by crystal to the detector

$$E_S(\vec{R}) \propto E_o \frac{\exp i(\vec{k}\bullet\vec{R} - \omega t)}{R} \int_{crystal} \underbrace{n(\vec{r})}_{\text{Local charge density}} \underbrace{\exp(-i\overrightarrow{\Delta k}\bullet\vec{r})}_{\text{Phase factor}} dV$$

Scattering Amplitude



Crystal : periodic charge distribution

Electron clouds centered on atoms

Consider one charge per each lattice site

crystal translation vector $\vec{T} = u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$

any local physical property of crystal is invariant under T

Electron number density $n(\vec{r})$ is periodic : $\boxed{n(\vec{r}+\vec{T}) = n(\vec{r})}$

↓

can be expanded in a Fourier series

$$n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} \exp(i\vec{G}\bullet\vec{r})$$

Recall in one dimension

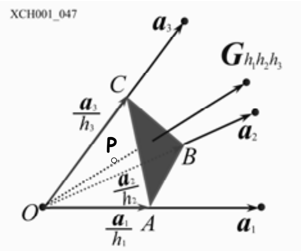
$$n(x) = \sum_p n_p \exp(i\frac{2\pi p}{a}x)$$

p : integer, n_p : complex constants

Fourier coefficient $n_p = \frac{1}{a}\int_0^a dx\ n(x)\ \exp(-i\frac{2\pi p}{a}x)$

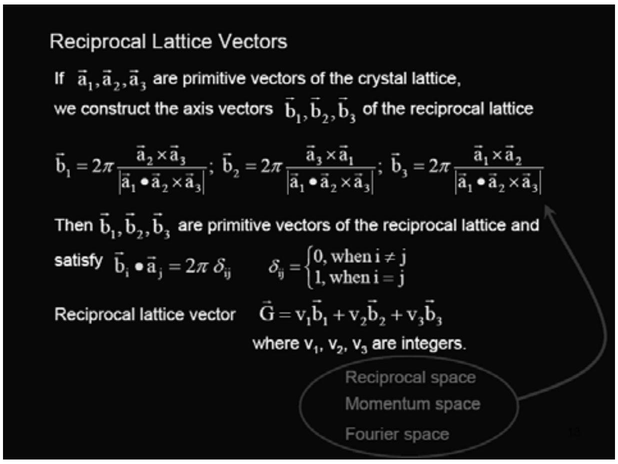
$\frac{2\pi p}{a}$ is a point in the reciprocal lattice or Fourier space of the crystal.

Reciprocal lattices Vectors



$OP = \rho$

$\rho d = 2\pi$



Reciprocal Lattice Vectors

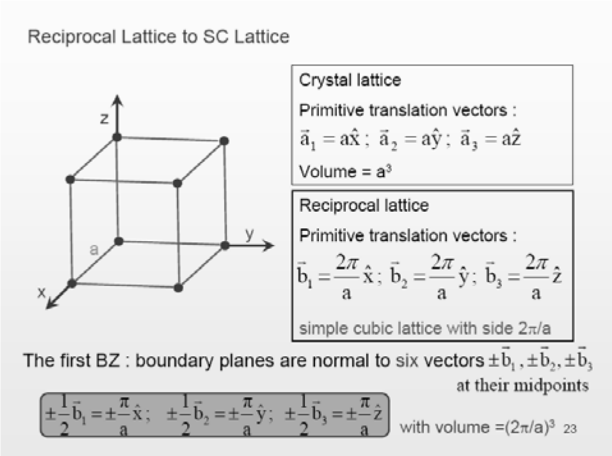
If $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are primitive vectors of the crystal lattice,
we construct the axis vectors $\vec{b}_1, \vec{b}_2, \vec{b}_3$ of the reciprocal lattice

$$\vec{b}_1 = 2\pi\frac{\vec{a}_2\times\vec{a}_3}{|\vec{a}_1\bullet\vec{a}_2\times\vec{a}_3|};\ \vec{b}_2 = 2\pi\frac{\vec{a}_3\times\vec{a}_1}{|\vec{a}_1\bullet\vec{a}_2\times\vec{a}_3|};\ \vec{b}_3 = 2\pi\frac{\vec{a}_1\times\vec{a}_2}{|\vec{a}_1\bullet\vec{a}_2\times\vec{a}_3|}$$

Then $\vec{b}_1, \vec{b}_2, \vec{b}_3$ are primitive vectors of the reciprocal lattice and
satisfy $\vec{b}_i\bullet\vec{a}_j = 2\pi\,\delta_{ij}$ $\delta_{ij} = \begin{cases} 0, \text{when } i \neq j \\ 1, \text{when } i = j \end{cases}$

Reciprocal lattice vector $\vec{G} = v_1\vec{b}_1 + v_2\vec{b}_2 + v_3\vec{b}_3$
where v_1, v_2, v_3 are integers.

Reciprocal space
Momentum space
Fourier space



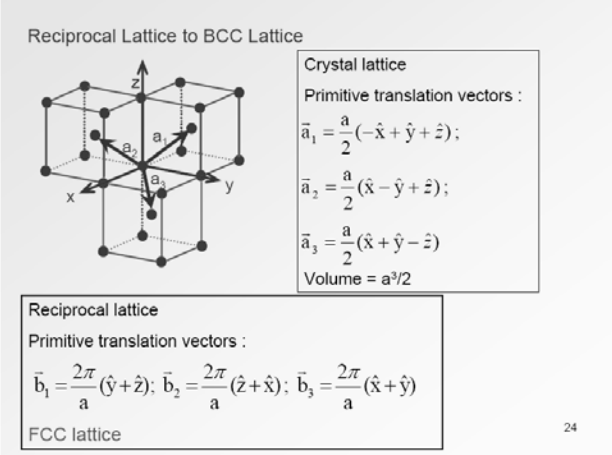
Reciprocal Lattice to SC Lattice

Crystal lattice
Primitive translation vectors :
$\vec{a}_1 = a\hat{x};\ \vec{a}_2 = a\hat{y};\ \vec{a}_3 = a\hat{z}$
Volume = a^3

Reciprocal lattice
Primitive translation vectors :
$\vec{b}_1 = \frac{2\pi}{a}\hat{x};\ \vec{b}_2 = \frac{2\pi}{a}\hat{y};\ \vec{b}_3 = \frac{2\pi}{a}\hat{z}$
simple cubic lattice with side $2\pi/a$

The first BZ : boundary planes are normal to six vectors $\pm\vec{b}_1, \pm\vec{b}_2, \pm\vec{b}_3$ at their midpoints

$\boxed{\pm\frac{1}{2}\vec{b}_1 = \pm\frac{\pi}{a}\hat{x};\ \ \pm\frac{1}{2}\vec{b}_2 = \pm\frac{\pi}{a}\hat{y};\ \ \pm\frac{1}{2}\vec{b}_3 = \pm\frac{\pi}{a}\hat{z}}$ with volume $=(2\pi/a)^3$



Reciprocal Lattice to BCC Lattice

Crystal lattice

Primitive translation vectors :

$$\vec{a}_1 = \frac{a}{2}(-\hat{x}+\hat{y}+\hat{z});$$
$$\vec{a}_2 = \frac{a}{2}(\hat{x}-\hat{y}+\hat{z});$$
$$\vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}-\hat{z})$$

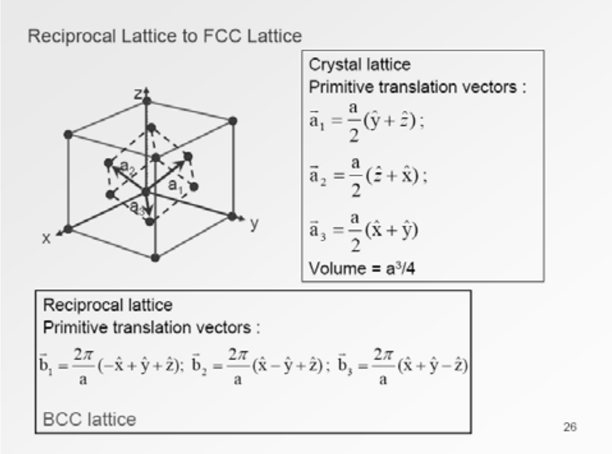
Volume = $a^3/2$

Reciprocal lattice

Primitive translation vectors :

$$\vec{b}_1 = \frac{2\pi}{a}(\hat{y}+\hat{z});\ \vec{b}_2 = \frac{2\pi}{a}(\hat{z}+\hat{x});\ \vec{b}_3 = \frac{2\pi}{a}(\hat{x}+\hat{y})$$

FCC lattice



Reciprocal Lattice to FCC Lattice

Crystal lattice
Primitive translation vectors :

$$\vec{a}_1 = \frac{a}{2}(\hat{y}+\hat{z});$$
$$\vec{a}_2 = \frac{a}{2}(\hat{z}+\hat{x});$$
$$\vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y})$$

Volume = $a^3/4$

Reciprocal lattice
Primitive translation vectors :

$$\vec{b}_1 = \frac{2\pi}{a}(-\hat{x}+\hat{y}+\hat{z});\ \vec{b}_2 = \frac{2\pi}{a}(\hat{x}-\hat{y}+\hat{z});\ \vec{b}_3 = \frac{2\pi}{a}(\hat{x}+\hat{y}-\hat{z})$$

BCC lattice

Role of reciprocal lattice in X-ray diffraction

$$E_s = E_i * F$$

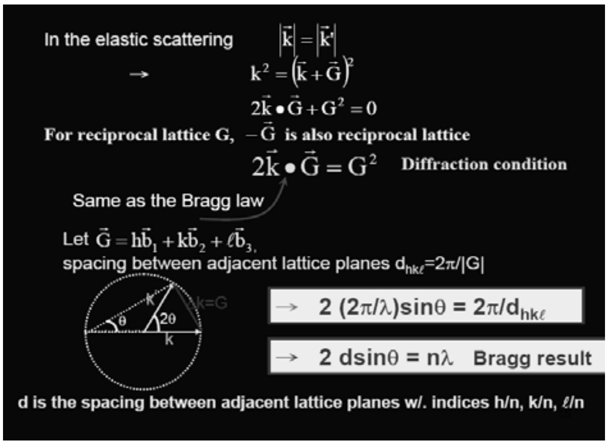
scattering amplitude $F = \int dV\, n(\vec{r}) \exp[i(\vec{k}-\vec{k}')\bullet\vec{r}]$

$\because$ periodic function $n(\vec{r}) = \sum_G n_G \exp(i\vec{G}\bullet\vec{r})$

$$\rightarrow F = \sum_G n_G \int dV \exp\{i[\vec{G}-(\vec{k}'-\vec{k})]\bullet\vec{r}\}$$
$$= \sum_G n_G \int dV \exp\{i[\vec{G}-\overrightarrow{\Delta k}]\bullet\vec{r}\}$$

where scattering vector $\overrightarrow{\Delta k} = \vec{k} - \vec{k}'$ is the change in wavevector

Therefore, $F = \begin{cases} Vn_G & \text{when } \Delta\vec{k} = \vec{G} \\ 0 & \text{when } \Delta\vec{k} \neq \vec{G} \end{cases}$



In the elastic scattering $|\vec{k}| = |\vec{k}'|$

$\rightarrow$ $k^2 = (\vec{k}+\vec{G})^2$

$2\vec{k}\bullet\vec{G} + G^2 = 0$

For reciprocal lattice G, $-\vec{G}$ is also reciprocal lattice

$2\vec{k}\bullet\vec{G} = G^2$ **Diffraction condition**

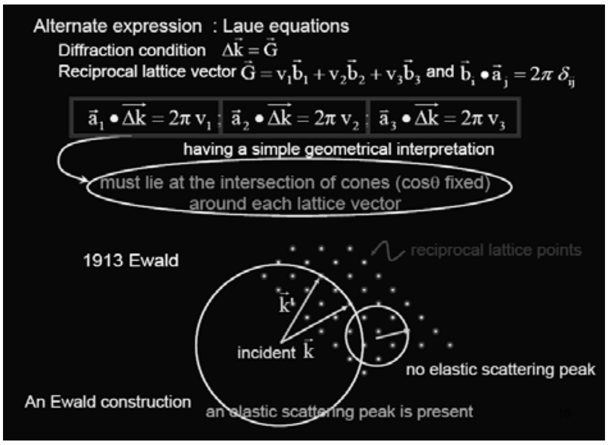
Same as the Bragg law

Let $\vec{G} = h\vec{b}_1 + k\vec{b}_2 + \ell\vec{b}_3$,
spacing between adjacent lattice planes $d_{hk\ell} = 2\pi/|G|$

$\rightarrow$ **$2\,(2\pi/\lambda)\sin\theta = 2\pi/d_{hk\ell}$**

$\rightarrow$ **$2\,d\sin\theta = n\lambda$ Bragg result**

d is the spacing between adjacent lattice planes w/. indices h/n, k/n, ℓ/n



Alternate expression : Laue equations

Diffraction condition $\Delta\vec{k} = \vec{G}$

Reciprocal lattice vector $\vec{G} = v_1\vec{b}_1 + v_2\vec{b}_2 + v_3\vec{b}_3$ and $\vec{b}_i\bullet\vec{a}_j = 2\pi\,\delta_{ij}$

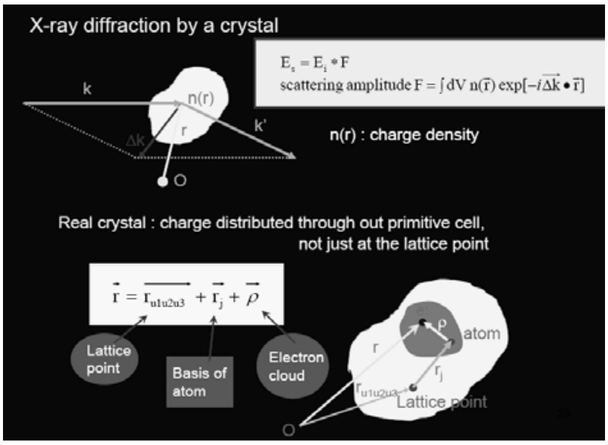
$\vec{a}_1\bullet\overrightarrow{\Delta k} = 2\pi\, v_1$; $\vec{a}_2\bullet\overrightarrow{\Delta k} = 2\pi\, v_2$; $\vec{a}_3\bullet\overrightarrow{\Delta k} = 2\pi\, v_3$

having a simple geometrical interpretation

must lie at the intersection of cones (cosθ fixed) around each lattice vector

1913 Ewald

An Ewald construction



X-ray diffraction by a crystal

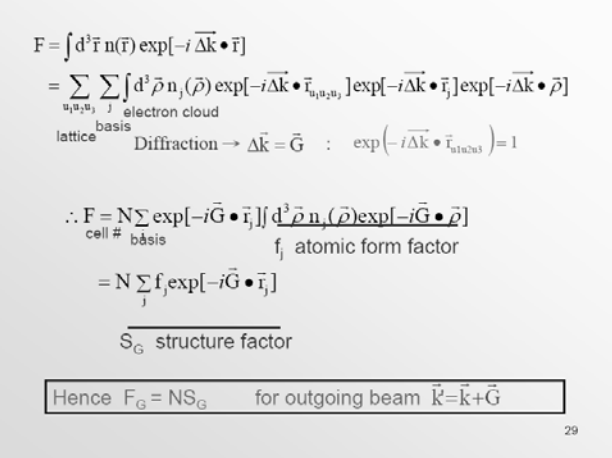
$$E_s = E_i * F$$

scattering amplitude $F = \int dV\, n(\vec{r}) \exp[-i\overrightarrow{\Delta k}\bullet\vec{r}]$

n(r) : charge density

Real crystal : charge distributed through out primitive cell,
not just at the lattice point

$$\vec{r} = \overrightarrow{r_{u1u2u3}} + \vec{r}_j + \vec{\rho}$$



$$F = \int d^3\vec{r}\, n(\vec{r}) \exp[-i\,\overrightarrow{\Delta k}\bullet\vec{r}]$$

$$= \underbrace{\sum_{u_1u_2u_3}}_{\text{lattice}} \underbrace{\sum_j}_{\text{basis}} \underbrace{\int d^3\vec{\rho}\, n_j(\vec{\rho})}_{\text{electron cloud}} \exp[-i\overrightarrow{\Delta k}\bullet\vec{r}_{u_1u_2u_3}]\exp[-i\overrightarrow{\Delta k}\bullet\vec{r}_j]\exp[-i\overrightarrow{\Delta k}\bullet\vec{\rho}]$$

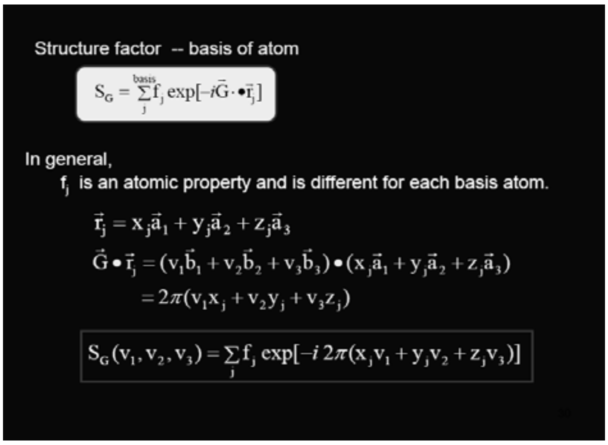
$$\text{Diffraction} \rightarrow \Delta\vec{k} = \vec{G} \quad : \quad \exp\left(-i\overrightarrow{\Delta k}\bullet\vec{r}_{u1u2u3}\right) = 1$$

$$\therefore F = \underset{\text{cell \#}}{N}\sum_{\text{basis}}\exp[-i\vec{G}\bullet\vec{r}_j]\underbrace{\int d^3\vec{\rho}\, n_j(\vec{\rho})\exp[-i\vec{G}\bullet\vec{\rho}]}_{f_j \text{ atomic form factor}}$$

$$= N\overline{\sum_j f_j \exp[-i\vec{G}\bullet\vec{r}_j]}$$

S_G structure factor

$$\boxed{\text{Hence } F_G = NS_G \quad \text{for outgoing beam } \vec{k}' = \vec{k} + \vec{G}}$$



Structure factor -- basis of atom

$$\boxed{S_G = \sum_j^{\text{basis}} f_j \exp[-i\vec{G}\cdot\bullet\vec{r}_j]}$$

In general,

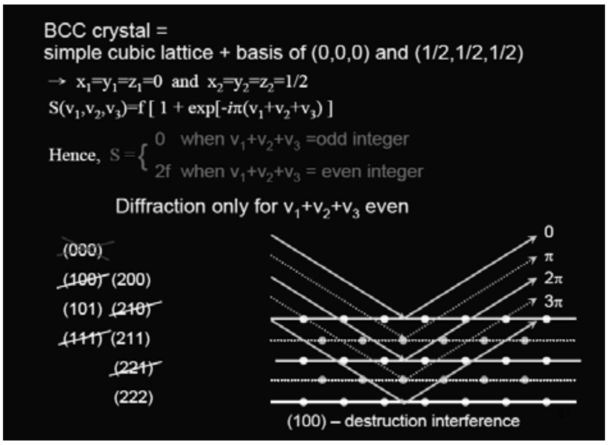
f_j is an atomic property and is different for each basis atom.

$$\vec{r}_j = x_j\vec{a}_1 + y_j\vec{a}_2 + z_j\vec{a}_3$$

$$\vec{G}\bullet\vec{r}_j = (v_1\vec{b}_1 + v_2\vec{b}_2 + v_3\vec{b}_3)\bullet(x_j\vec{a}_1 + y_j\vec{a}_2 + z_j\vec{a}_3)$$

$$= 2\pi(v_1x_j + v_2y_j + v_3z_j)$$

$$\boxed{S_G(v_1, v_2, v_3) = \sum_j f_j \exp[-i\,2\pi(x_jv_1 + y_jv_2 + z_jv_3)]}$$



BCC crystal =
simple cubic lattice + basis of (0,0,0) and (1/2,1/2,1/2)

→ $x_1=y_1=z_1=0$ and $x_2=y_2=z_2=1/2$

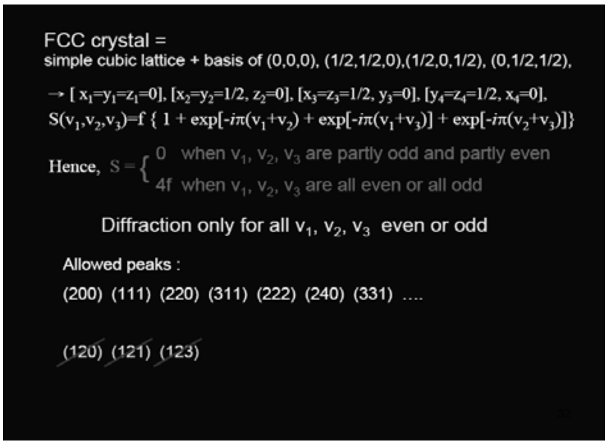
$S(v_1,v_2,v_3)=f\,[\,1 + \exp[-i\pi(v_1+v_2+v_3)\,]$

$$\text{Hence, } S = \begin{cases} 0 & \text{when } v_1+v_2+v_3 = \text{odd integer} \\ 2f & \text{when } v_1+v_2+v_3 = \text{even integer} \end{cases}$$

Diffraction only for $v_1+v_2+v_3$ even

~~(000)~~
~~(100)~~ (200)
(101) ~~(210)~~
~~(111)~~ (211)
~~(221)~~
(222)

(100) – destruction interference



FCC crystal =
simple cubic lattice + basis of (0,0,0), (1/2,1/2,0),(1/2,0,1/2), (0,1/2,1/2),

→ $[\,x_1=y_1=z_1=0]$, $[x_2=y_2=1/2,\ z_2=0]$, $[x_3=z_3=1/2,\ y_3=0]$, $[y_4=z_4=1/2,\ x_4=0]$,

$S(v_1,v_2,v_3)=f\,\{\,1 + \exp[-i\pi(v_1+v_2) + \exp[-i\pi(v_1+v_3)] + \exp[-i\pi(v_2+v_3)]\}$

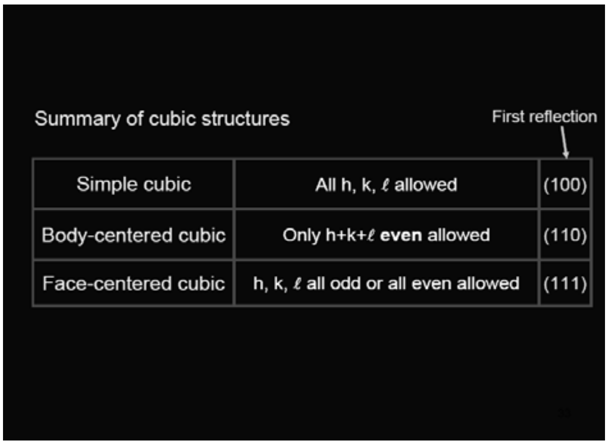
$$\text{Hence, } S = \begin{cases} 0 & \text{when } v_1, v_2, v_3 \text{ are partly odd and partly even} \\ 4f & \text{when } v_1, v_2, v_3 \text{ are all even or all odd} \end{cases}$$

Diffraction only for all v_1, v_2, v_3 even or odd

Allowed peaks :

(200) (111) (220) (311) (222) (240) (331) ….

~~(120)~~ ~~(121)~~ ~~(123)~~



Summary of cubic structures

		First reflection
Simple cubic	All h, k, ℓ allowed	(100)
Body-centered cubic	Only h+k+ℓ **even** allowed	(110)
Face-centered cubic	h, k, ℓ all odd or all even allowed	(111)

Howwork

- Please calculate primitive translate vectors of crystal lattice and reciprocal lattice to BCC and FCC.

P51 2.1 &2.2

Topic:

How do we determine the structure of crystal experimentally?

Email to ndgong@imu.edu.cn

Review

1. crystal structure

Periodic arrays of atom

Lattice +basis=crystal structure

lattice translation vectors

$$\vec{r}' = \vec{r} + u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$$

$$u_1, u_2, u_3 \in \text{integer}$$

$$\vec{a}_1, \vec{a}_2, \vec{a}_3 = \text{lattice vector}$$

2. Primitive Lattice Cell

- ⊗ One lattice point per primitive cell.
- ⊗ A minimum volume cell
- ⊗ Not unique.

3. Bravais lattices

2D 3D

4. Directions and planes in crystals

Crystal Directions

Crystal plane Miller Indices

5. Most common crystal structures

X-Ray Diffraction & Bragg Equation

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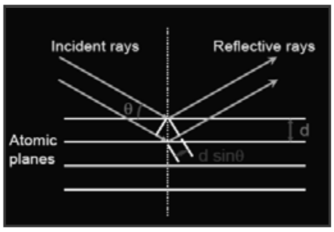
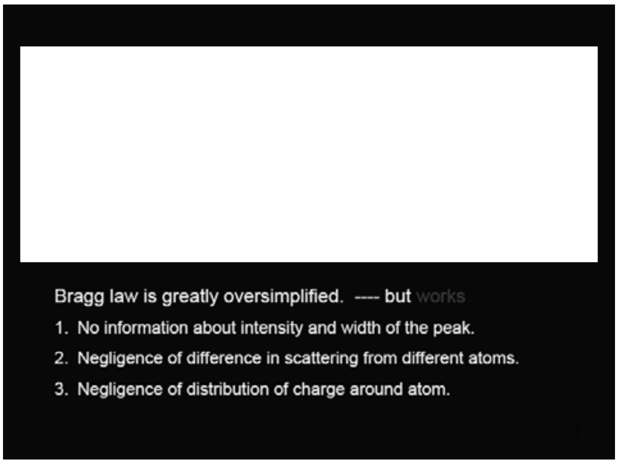
Diffraction of waves by crystals

Bragg presented a simple explanation of the diffracted beams from a crystal



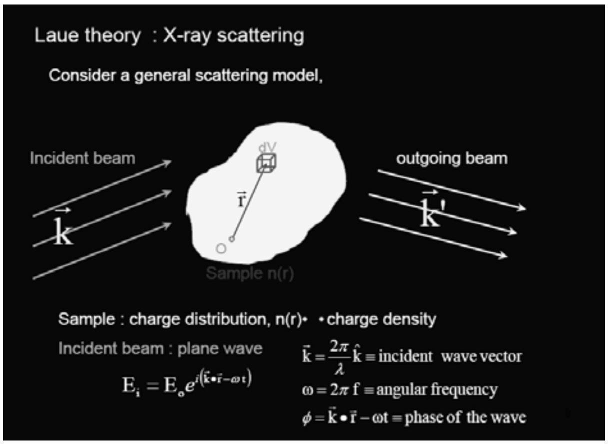
condition for constructive interference from a crystal

$$2d\sin\theta = n\lambda$$ Bragg Law



Bragg law is greatly oversimplified. ---- but works

1. No information about intensity and width of the peak.
2. Negligence of difference in scattering from different atoms.
3. Negligence of distribution of charge around atom.



Laue theory : X-ray scattering

Consider a general scattering model,

Sample : charge distribution, n(r)• •charge density

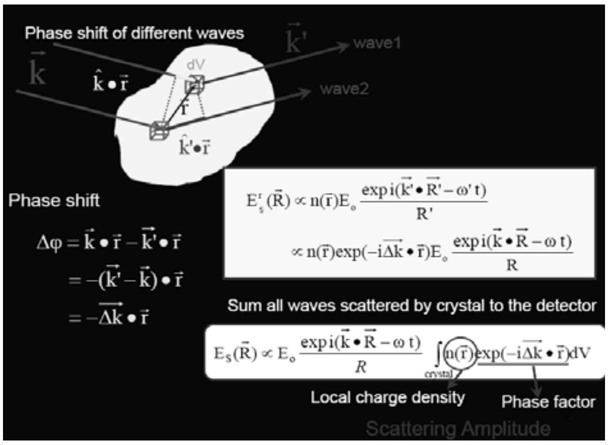
Incident beam : plane wave

$$E_i = E_o e^{i(\vec{k}\bullet\vec{r} - \omega t)}$$

$$\vec{k} = \frac{2\pi}{\lambda}\hat{k} \equiv \text{incident wave vector}$$

$$\omega = 2\pi f \equiv \text{angular frequency}$$

$$\phi = \vec{k}\bullet\vec{r} - \omega t \equiv \text{phase of the wave}$$



Phase shift of different waves

Phase shift

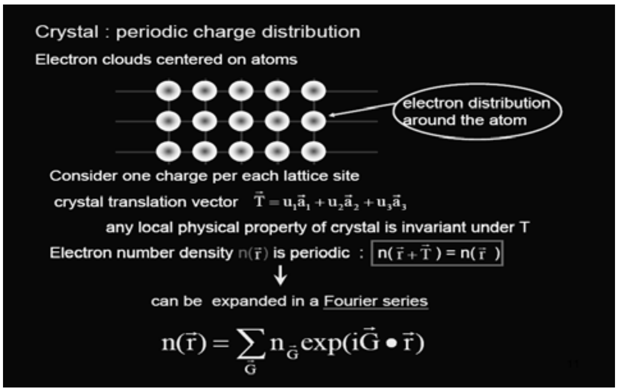
$$\Delta\varphi = \vec{k}\bullet\vec{r} - \vec{k}'\bullet\vec{r}$$
$$= -(\vec{k}' - \vec{k})\bullet\vec{r}$$
$$= -\overrightarrow{\Delta k}\bullet\vec{r}$$

$$E_s^r(\vec{R}) \propto n(\vec{r})E_o \frac{\exp i(\vec{k}'\bullet\vec{R}' - \omega' t)}{R'}$$
$$\propto n(\vec{r})\exp(-i\overrightarrow{\Delta k}\bullet\vec{r})E_o \frac{\exp i(\vec{k}\bullet\vec{R} - \omega t)}{R}$$

Sum all waves scattered by crystal to the detector

$$E_S(\vec{R}) \propto E_o \frac{\exp i(\vec{k}\bullet\vec{R} - \omega t)}{R} \int_{\text{crystal}} \underset{\text{Local charge density}}{\boxed{n(\vec{r})}}\, \underbrace{\exp(-i\overrightarrow{\Delta k}\bullet\vec{r})}_{\text{Phase factor}} dV$$

Scattering Amplitude



Crystal : periodic charge distribution

Electron clouds centered on atoms

electron distribution around the atom

Consider one charge per each lattice site

crystal translation vector $\vec{T} = u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$

any local physical property of crystal is invariant under T

Electron number density $n(\vec{r})$ is periodic : $\boxed{n(\vec{r}+\vec{T}) = n(\vec{r})}$

↓

can be expanded in a Fourier series

$$n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} \exp(i\vec{G}\bullet\vec{r})$$

Recall in one dimension

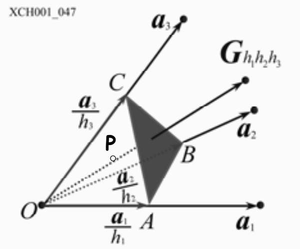
$$n(x) = \sum_p n_p \exp(i\frac{2\pi p}{a}x)$$

p : integer, n_p : complex constants

Fourier coefficient $n_p = \frac{1}{a}\int_0^a dx\ n(x)\ \exp(-i\frac{2\pi p}{a}x)$

$\frac{2\pi p}{a}$ is a point in the reciprocal lattice or Fourier space of the crystal.

Reciprocal lattices Vectors



$OP = \rho$

$\rho d = 2\pi$

Reciprocal Lattice Vectors

If $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are primitive vectors of the crystal lattice, we construct the axis vectors $\vec{b}_1, \vec{b}_2, \vec{b}_3$ of the reciprocal lattice

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

Reciprocal lattice vector

Satisfy: $\vec{a}_i\cdot\vec{b}_j = 2\pi\delta_{ij}\begin{cases} = 2\pi & (i=j) \\ = 0 & (i\neq j)\end{cases}$

$$\Leftrightarrow \boxed{\exp(i\vec{G}\bullet\vec{T}) = 1}$$

$$\Downarrow$$

$$\boxed{\exp(i\vec{G}\bullet\vec{T}) = \exp[i(n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3)\bullet(u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3)]}$$

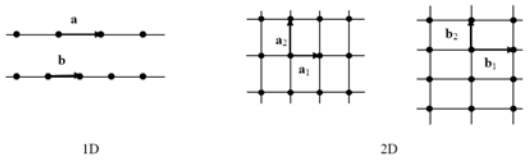
$$\Downarrow$$

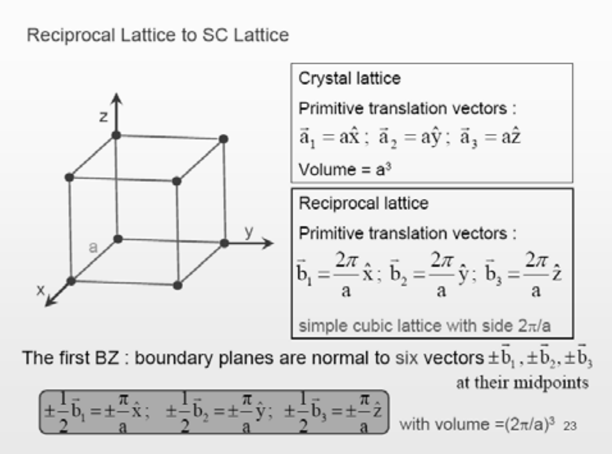
$$\boxed{\exp(i\vec{G}\bullet\vec{T}) = \exp[i(n_1u_1 + n_2u_2 + n_3u_3)]}$$

Examples

1. reciprocal lattices for 1D and 2D-rectangular structures

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij} \begin{cases} = 2\pi & (i = j) \\ = 0 & (i \neq j) \end{cases}$$





Reciprocal Lattice to SC Lattice

Crystal lattice

Primitive translation vectors :

$$\vec{a}_1 = a\hat{x}\,;\ \vec{a}_2 = a\hat{y}\,;\ \vec{a}_3 = a\hat{z}$$

Volume = a^3

Reciprocal lattice

Primitive translation vectors :

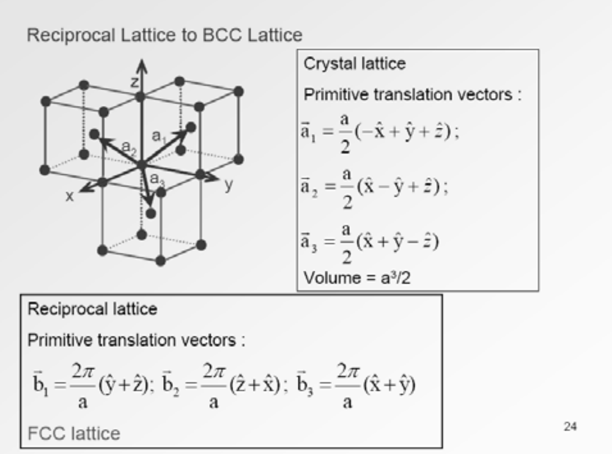
$$\vec{b}_1 = \frac{2\pi}{a}\hat{x}\,;\ \vec{b}_2 = \frac{2\pi}{a}\hat{y}\,;\ \vec{b}_3 = \frac{2\pi}{a}\hat{z}$$

simple cubic lattice with side 2π/a

The first BZ : boundary planes are normal to six vectors $\pm\vec{b}_1, \pm\vec{b}_2, \pm\vec{b}_3$ at their midpoints

$$\pm\frac{1}{2}\vec{b}_1 = \pm\frac{\pi}{a}\hat{x}\,;\quad \pm\frac{1}{2}\vec{b}_2 = \pm\frac{\pi}{a}\hat{y}\,;\quad \pm\frac{1}{2}\vec{b}_3 = \pm\frac{\pi}{a}\hat{z}$$

with volume $=(2\pi/a)^3$



Reciprocal Lattice to BCC Lattice

Crystal lattice

Primitive translation vectors :

$$\vec{a}_1 = \frac{a}{2}(-\hat{x}+\hat{y}+\hat{z})\,;$$

$$\vec{a}_2 = \frac{a}{2}(\hat{x}-\hat{y}+\hat{z})\,;$$

$$\vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}-\hat{z})$$

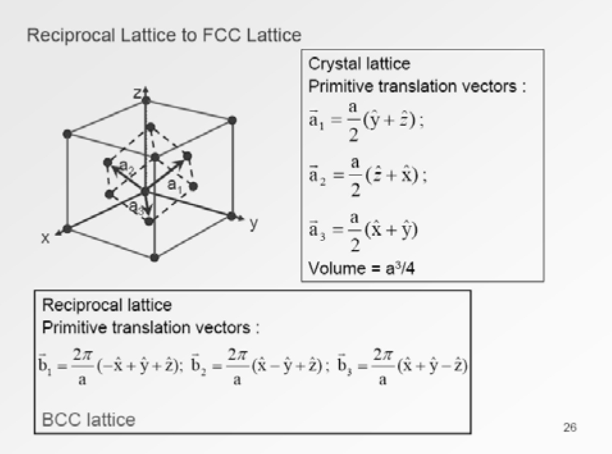
Volume = $a^3/2$

Reciprocal lattice

Primitive translation vectors :

$$\vec{b}_1 = \frac{2\pi}{a}(\hat{y}+\hat{z});\ \vec{b}_2 = \frac{2\pi}{a}(\hat{z}+\hat{x});\ \vec{b}_3 = \frac{2\pi}{a}(\hat{x}+\hat{y})$$

FCC lattice



Reciprocal Lattice to FCC Lattice

Crystal lattice

Primitive translation vectors :

$$\vec{a}_1 = \frac{a}{2}(\hat{y}+\hat{z})\,;$$

$$\vec{a}_2 = \frac{a}{2}(\hat{z}+\hat{x})\,;$$

$$\vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y})$$

Volume = $a^3/4$

Reciprocal lattice

Primitive translation vectors :

$$\vec{b}_1 = \frac{2\pi}{a}(-\hat{x}+\hat{y}+\hat{z});\ \vec{b}_2 = \frac{2\pi}{a}(\hat{x}-\hat{y}+\hat{z});\ \vec{b}_3 = \frac{2\pi}{a}(\hat{x}+\hat{y}-\hat{z})$$

BCC lattice

Role of reciprocal lattice in X-ray diffraction

$$E_S(\vec{R}) \propto E_o \frac{\exp i(\vec{k}\bullet\vec{R}-\omega t)}{R} \int_{\text{crystal}} \boxed{n(\vec{r})}\,\underline{\exp(-i\overrightarrow{\Delta k}\bullet\vec{r})}dV$$

$$\Downarrow$$

$$E_s = E_i * F$$

scattering amplitude $F = \int dV\, n(\vec{r}) \exp[i(\vec{k}-\vec{k}')\bullet\vec{r}]$

periodic function $n(\vec{r}) = \sum_G n_G \exp(i\vec{G}\bullet\vec{r})$

$$\begin{aligned} \rightarrow F &= \sum_G n_G \int dV \exp\{i[\vec{G}-(\vec{k}'-\vec{k})]\bullet\vec{r}\} \\ &= \sum_G n_G \int dV \exp\{i[\vec{G}-\overrightarrow{\Delta k}]\bullet\vec{r}\} \end{aligned}$$

where scattering vector $\overrightarrow{\Delta k} \equiv \vec{k}-\vec{k}'$ is the change in wavevector

Therefore, $F = \begin{cases} Vn_G & \text{when } \boxed{\Delta\vec{k} = \vec{G}} \\ 0 & \text{when } \Delta\vec{k} \neq \vec{G} \end{cases}$

In the elastic scattering $|\vec{k}| = |\vec{k}'|$

$$k^2 = (\vec{k} + \vec{G})^2$$

$$2\vec{k} \bullet \vec{G} + G^2 = 0$$

For reciprocal lattice G, $-\vec{G}$ is also reciprocal lattice

$2\vec{k} \bullet \vec{G} = G^2$ **Diffraction condition**

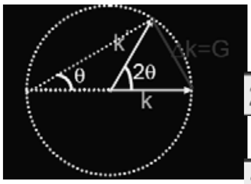
$2d \sin\theta = n\lambda$ **Bragg law**

We prove this in three steps

(1) Show that the reciprocal lattice vector $\vec{G} = h\vec{b}_1 + k\vec{b}_2 + \ell\vec{b}_3$ is orthogonal to the plane represented by Miller indices (*h*,*k*,*l*).

(2) Now we prove that the distance between two adjacent parallel planes of the direct lattice is $d_{hkl} = 2\pi / |G_{hkl}|$.

(3) Show that the diffraction condition is equivalent to the Bragg law



$2\vec{k} \bullet \vec{G} = G^2$

$2\,(2\pi/\lambda)\sin\theta = 2\pi/d_{hk\ell}$

$2\,d\sin\theta = n\lambda$

Bragg law

$\vec{G} = h\vec{b}_1 + k\vec{b}_2 + \ell\vec{b}_3$ **nG** **G**

Diffraction condition $\Delta\vec{k} = \vec{G}$

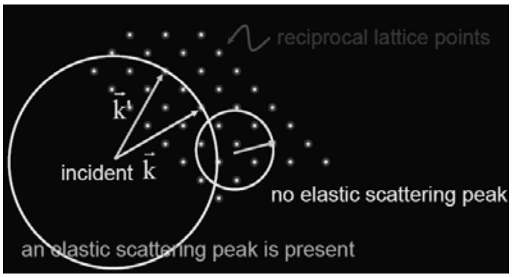
Reciprocal lattice vector

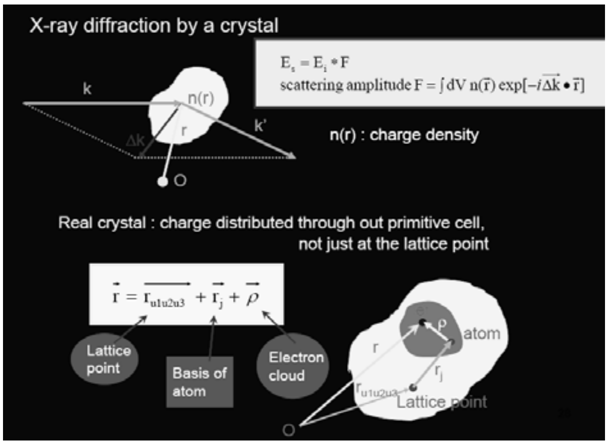
$\vec{G} = v_1\vec{b}_1 + v_2\vec{b}_2 + v_3\vec{b}_3$ and $\vec{b}_i \bullet \vec{a}_j = 2\pi\,\delta_{ij}$

$\vec{a}_1 \bullet \overrightarrow{\Delta k} = 2\pi\, v_1$; $\vec{a}_2 \bullet \overrightarrow{\Delta k} = 2\pi\, v_2$; $\vec{a}_3 \bullet \overrightarrow{\Delta k} = 2\pi\, v_3$

$\Delta\vec{K}$ must lie at the intersection of cones (cos θ fixed) around each lattice vector.

1913 Ewald An Ewaldconstruction





X-ray diffraction by a crystal

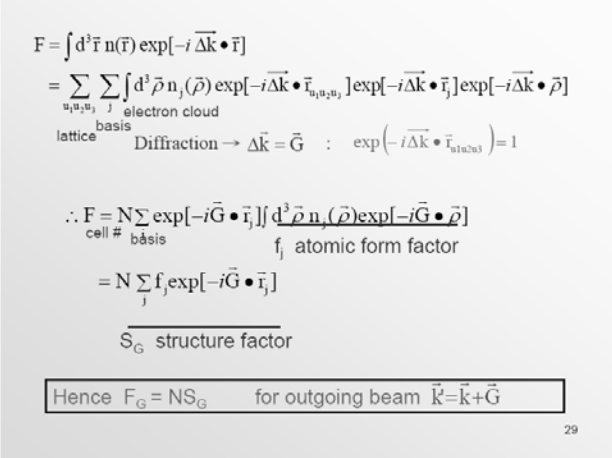
$E_s = E_i * F$

scattering amplitude $F = \int dV\, n(\vec{r}) \exp[-i\overrightarrow{\Delta k} \bullet \vec{r}]$

n(r) : charge density

Real crystal : charge distributed through out primitive cell, not just at the lattice point

$\vec{r} = \overrightarrow{r_{u1u2u3}} + \vec{r}_j + \vec{\rho}$



$$F = \int d^3\vec{r}\, n(\vec{r}) \exp[-i\,\overrightarrow{\Delta k} \bullet \vec{r}]$$

$$= \underbrace{\sum_{u_1u_2u_3}}_{\text{lattice}} \underbrace{\sum_{j}}_{\text{basis}} \underbrace{\int d^3\vec{\rho}\, n_j(\vec{\rho})}_{\text{electron cloud}} \exp[-i\overrightarrow{\Delta k} \bullet \vec{r}_{u_1u_2u_3}] \exp[-i\overrightarrow{\Delta k} \bullet \vec{r}_j] \exp[-i\overrightarrow{\Delta k} \bullet \vec{\rho}]$$

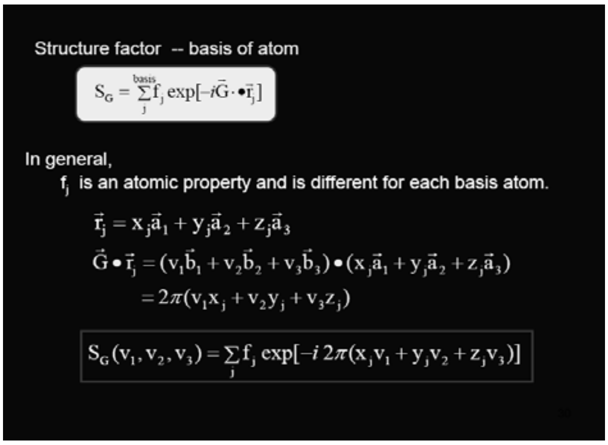
Diffraction → $\Delta\vec{k} = \vec{G}$: $\exp\left(-i\overrightarrow{\Delta k} \bullet \vec{r}_{u1u2u3}\right) = 1$

$$\therefore F = \underset{\text{cell \#}}{N} \sum_{\text{basis}} \exp[-i\vec{G} \bullet \vec{r}_j] \underbrace{\int d^3\vec{\rho}\, n_j(\vec{\rho}) \exp[-i\vec{G} \bullet \vec{\rho}]}_{f_j \text{ atomic form factor}}$$

$$= N \overline{\sum_j f_j \exp[-i\vec{G} \bullet \vec{r}_j]}$$

S_G structure factor

Hence $F_G = NS_G$ for outgoing beam $\vec{k}' = \vec{k} + \vec{G}$



Structure factor -- basis of atom

$$\boxed{S_G = \sum_{j}^{\text{basis}} f_j \exp[-i\vec{G} \cdot \bullet \vec{r}_j]}$$

In general,

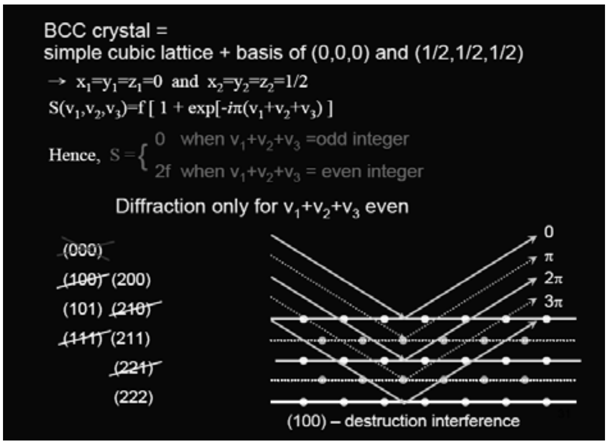
f_j is an atomic property and is different for each basis atom.

$$\vec{r}_j = x_j\vec{a}_1 + y_j\vec{a}_2 + z_j\vec{a}_3$$

$$\vec{G} \bullet \vec{r}_j = (v_1\vec{b}_1 + v_2\vec{b}_2 + v_3\vec{b}_3) \bullet (x_j\vec{a}_1 + y_j\vec{a}_2 + z_j\vec{a}_3)$$

$$= 2\pi(v_1x_j + v_2y_j + v_3z_j)$$

$$\boxed{S_G(v_1, v_2, v_3) = \sum_j f_j \exp[-i\,2\pi(x_jv_1 + y_jv_2 + z_jv_3)]}$$



BCC crystal =
simple cubic lattice + basis of (0,0,0) and (1/2,1/2,1/2)

→ $x_1=y_1=z_1=0$ and $x_2=y_2=z_2=1/2$

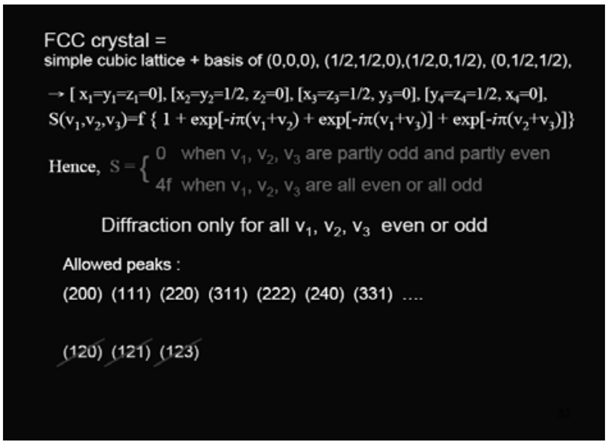
$S(v_1,v_2,v_3)=f\,[\,1 + \exp[-i\pi(v_1+v_2+v_3)\,]$

Hence, $S = \begin{cases} 0 & \text{when } v_1+v_2+v_3 = \text{odd integer} \\ 2f & \text{when } v_1+v_2+v_3 = \text{even integer} \end{cases}$

Diffraction only for $v_1+v_2+v_3$ even

~~(000)~~
~~(100)~~ (200)
(101) ~~(210)~~
~~(111)~~ (211)
~~(221)~~
(222)

(100) – destruction interference



FCC crystal =
simple cubic lattice + basis of (0,0,0), (1/2,1/2,0),(1/2,0,1/2), (0,1/2,1/2),

→ $[\,x_1=y_1=z_1=0]$, $[x_2=y_2=1/2,\ z_2=0]$, $[x_3=z_3=1/2,\ y_3=0]$, $[y_4=z_4=1/2,\ x_4=0]$,

$S(v_1,v_2,v_3)=f\,\{\,1 + \exp[-i\pi(v_1+v_2) + \exp[-i\pi(v_1+v_3)] + \exp[-i\pi(v_2+v_3)]\}$

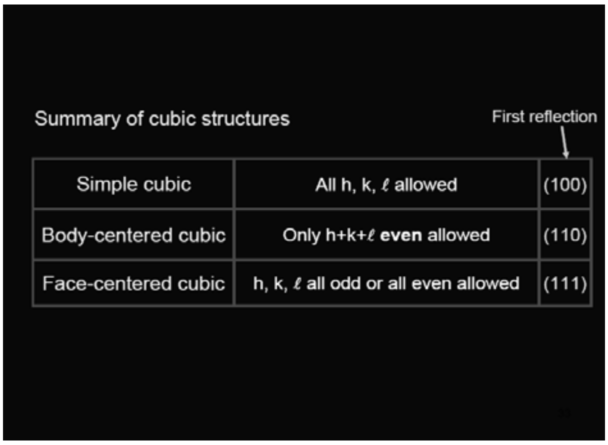
Hence, $S = \begin{cases} 0 & \text{when } v_1, v_2, v_3 \text{ are partly odd and partly even} \\ 4f & \text{when } v_1, v_2, v_3 \text{ are all even or all odd} \end{cases}$

Diffraction only for all v_1, v_2, v_3 even or odd

Allowed peaks :

(200) (111) (220) (311) (222) (240) (331) ….

~~(120)~~ ~~(121)~~ ~~(123)~~



Summary of cubic structures

First reflection

Simple cubic	All h, k, ℓ allowed	(100)
Body-centered cubic	Only h+k+ℓ **even** allowed	(110)
Face-centered cubic	h, k, ℓ all odd or all even allowed	(111)

Homework

- Please calculate primitive translate vectors of crystal lattice and reciprocal lattice to BCC and FCC.

P51 2.1 &2.2

Topic:

How do we determine the structure of crystal experimentally by X-ray diffraction?

Email to ndgong@imu.edu.cn

Chapter Three Crystal Binding

What kind of force holds the atoms together in a solid?

Contents:

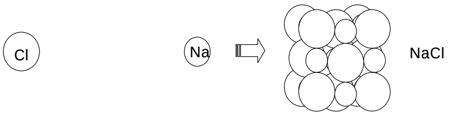
- ☻Types and strengths of binding forces
- ☻Reason for crystal structure formation
- ☻Mechanical properties of crystals

Why do atoms form crystals or solids?

Answer : Interatomic forces that bind atoms.

Atoms bind due to the Coulomb attractive forces between electrons and neighboring atomic ions.

Energies of Interactions Between Atoms



- The energy of the crystal is lower than that of the free atoms by an amount equal to the energy required to pull the crystal apart into a set of free atoms.

Cohesive (binding) energy U

≡ the energy that must be added to the crystal to separate its components into neutral free atoms at rest

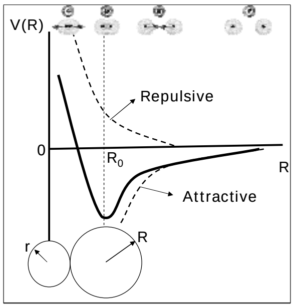
≡ Energy of free atoms - Crystal energy

Hence, U>0 to form a stable solid

- NaCl is more stable than a collection of free Na and Cl.
- Ge crystal is more stable than a collection of free Ge.

- **Magnitude ~ 1-10eV except for the inert gas crystals (0.02-0.2eV)**
- **$U \leq E_{ion}$(Ionization energy = Binding energy of valence electrons)**
- **U controls the melting temperature and bulk modulus**

- This typical curve has a minimum at equilibrium distance R_0
- $R > R_0$;
  - ⇨the potential increases gradually, approaching 0 as $R \rightarrow \infty$
  - ⇨the force is attractive
- $R < R_0$;
  - ⇨the potential increases very rapidly, approaching ∞ at small separation.
  - ⇨the force is repulsive



- Force between the atoms is the negative of the slope of this curve. At equlibrium, repulsive force becomes equals to the attractive part.

- The potential energy of either atom will be given by:

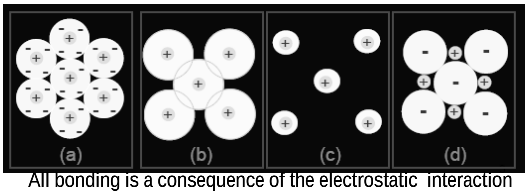
V= decrease in potential energy+increase in potential energy
(due to attraction) (due to repulsion)

or simply: $V(r) = \frac{-a}{r^m} + \frac{b}{r^n}$

V(r): the net potential energy of interaction as function of r.
r : he distance between atoms, ions, or molecules.
a,b: proportionality constant of attraction and repulsion, respectively.
m, n: constant characteristics of each type of bond and type of structure.

Types of bonds

(a) Van der Waals (Molecular)	Electrons localized among atoms
(b) Covalent	Electrons shared by the neighboring atoms
(c) Metallic	Electrons free to move through sample
(d) Ionic	Electrons transferred to adjacent atoms



All bonding is a consequence of the electrostatic interaction between nuclei and electrons obeying Schrödinger's equation.

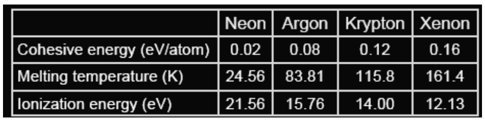
(a) Molecular bonding

Inert gas crystals : He, Ne, Ar, Kr, Xe, Rn

- Transparent Insulators –completely filled outer electron shells
- Weakly bonding –van der Waals bonding
- FCC structures except for He3and He4

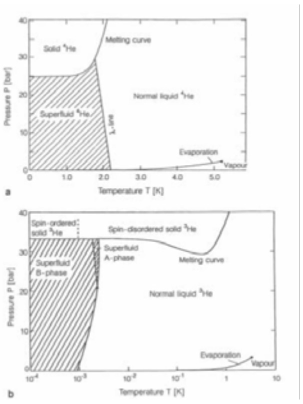
high ionization energies

low melting temperatures



	Neon	Argon	Krypton	Xenon
Cohesive energy (eV/atom)	0.02	0.08	0.12	0.16
Melting temperature (K)	24.56	83.81	115.8	161.4
Ionization energy (eV)	21.56	15.76	14.00	12.13

Phase diagrams of (a) 4He and (b) 3He.



Van der Waals –London Interaction

Consider two identical intert gas atoms

Neutral: positive nucleus + spherically symmetric distribution of electron charge

No interaction between atoms -> No cohesion(No solid) ?

Fluctuating dipole –dipole interaction

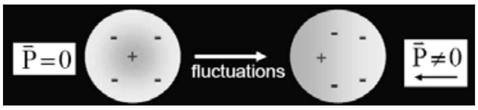
Attractive interaction between the atoms

Inert gas solids

•On average spherically symmetric distribution of electron charge with the positive nucleus in the center. $\langle \vec{P} \rangle = 0$

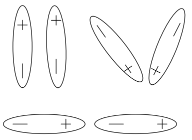
•But thermal fluctuations (finite T) cause instantaneous electric dipole moment

$$\vec{P}(t) \neq 0 \rightarrow \langle P^2 \rangle \neq 0$$

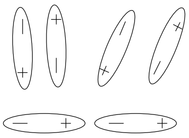


ps. The bigger a molecule is, the easier it is to polarise (to form a dipole), and so the van der Waal's forces get stronger, so bigger molecules exist as liquids or solids rather than gases.

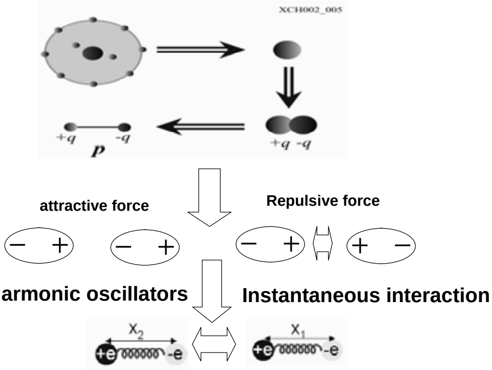
- ☻On adjacent atoms if the dipoles are random there could be no net force (time average)
- ☻But dipole induces a dipole in neighboring atoms that always gives an attractive force



No attraction is produced



Display a marked attractive forces



attractive force

Repulsive force

linear harmonic oscillators

Instantaneous interaction

Model for inert gas solid –two identical linear harmonic oscillators

$p_1$and $p_2$are the momenta of these two oscillators

C is the force constant

Hamiltonian for the unperturbed system

$$\boxed{H_0 = \frac{p_1^2}{2m} + \frac{1}{2}Cx_1^2 + \frac{p_2^2}{2m} + \frac{1}{2}Cx_2^2}$$

–no Coulomb interaction

Hamiltonian for Coulomb interaction energy of the system

$$H_1 = \frac{e^2}{R} + \frac{e^2}{R + x_1 - x_2} - \frac{e^2}{R + x_1} - \frac{e^2}{R + x_2}$$

$$\xrightarrow[|x_1|,|x_2|<<R]{} \qquad \Downarrow$$

$$H_1 \cong -\frac{2e^2 x_1 x_2}{R_3}$$

Normal mode transformation --symmetric (s) and anti-symmetric (a)

$$x_s \equiv \frac{x_1 + x_2}{\sqrt{2}}; x_a \equiv \frac{x_1 - x_2}{\sqrt{2}}$$

$$p_s \equiv \frac{p_1 + p_2}{\sqrt{2}}; p_a \equiv \frac{p_1 - p_2}{\sqrt{2}}$$

diabonalization

Total Hamiltonian after the transformation

$$H = \left[\frac{p_s^2}{2m} + \frac{1}{2}\left(C - \frac{2e^2}{R^3}\right)x_s^2\right] + \left[\frac{p_a^2}{2m} + \frac{1}{2}\left(C + \frac{2e^2}{R^3}\right)x_a^2\right]$$

$$H_0 = \frac{p_1^2}{2m} + \frac{1}{2}Cx_1^2 + \frac{p_2^2}{2m} + \frac{1}{2}Cx_2^2 \quad \Rightarrow \quad H_0, \omega_0 = \sqrt{\frac{C}{m}}$$

$$H = \left[\frac{p_s^2}{2m} + \frac{1}{2}\left(C - \frac{2e^2}{R^3}\right)x_s^2\right] + \left[\frac{p_a^2}{2m} + \frac{1}{2}\left(C + \frac{2e^2}{R^3}\right)x_a^2\right]$$

$$\Downarrow$$

Two frequencies of the coupled oscillators symmetric (s) and anti-symmetric (a)

$$\boxed{\begin{aligned} H, \omega_s &= \sqrt{\frac{C_s}{m}} = \sqrt{\frac{C - 2e^2/R^3}{m}} \\ \omega_a &= \sqrt{\frac{C_a}{m}} = \sqrt{\frac{C + 2e^2/R^3}{m}} \end{aligned}}$$

The zero point energy

The uncoupled oscillators $\frac{1}{2}\hbar\omega_0 + \frac{1}{2}\hbar\omega_0$

The coupled oscillators $\frac{1}{2}\hbar\omega_s + \frac{1}{2}\hbar\omega_a$

$$\omega_s = \sqrt{\frac{C - 2e^2/R^3}{m}} = \sqrt{\frac{C}{m}}\left(1 - \frac{2e^2}{CR^3}\right)^{1/} = \omega_0\left(1 - \frac{1}{2}\left(\frac{2e^2}{CR^3}\right) + \frac{\frac{1}{2}\left(-\frac{1}{2}\right)}{1\times 2}\left(\frac{2e^2}{CR^3}\right)^2 + \dots\right)$$

$$\omega_a = \sqrt{\frac{C + 2e^2/R^3}{m}} = \sqrt{\frac{C}{m}}\left(1 + \frac{2e^2}{CR^3}\right)^{1/} = \omega_0\left(1 + \frac{1}{2}\left(\frac{2e^2}{CR^3}\right) + \frac{\frac{1}{2}\left(-\frac{1}{2}\right)}{1\times 2}\left(\frac{2e^2}{CR^3}\right)^2 + \dots\right)$$

Therefore,
the zero point energy of the coupled oscillators is lowered from the uncoupled oscillators by

$$\boxed{\Delta U = \frac{1}{2}\hbar\omega_0\left[-\frac{1}{8}\left(\frac{2e^2}{CR^3}\right)\times 2\right] = -\frac{A}{R^6}}$$

Attractive interaction

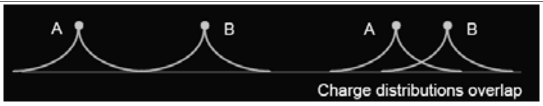
The van der Waals interaction, the London interaction,
the induced dipole-dipole interaction

$$\Delta U = -\frac{A}{R^6} \qquad A = \hbar\omega_0\frac{e^4}{2C^2} \equiv \hbar\omega_0\alpha^2$$

electronic polarizability

What limits attraction ? --Repulsive force (Pauli exclusion principle)

Two electrons can not have all their quantum number s the same.



- When charge distributions of two atoms overlap, there is a tendency for electrons from atom B to occupy in part states of atom A occupied by electrons of atom A, and vice versus.
- Pauli exclusion principle prevents multiple occupancy, and electron distribution of atoms with closed shells can overlap only if accompanies by the partial promotion of electrons to unoccupied high energy state of the atom.

The electron overlap increases the total energy of the system and gives a repulsive contribution to the interaction.

Empirical formula for such repulsive potential

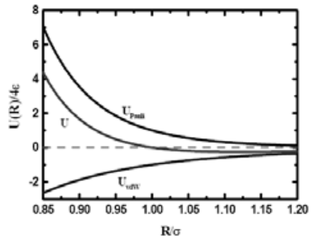
The total potential for inert gas system

$U(r) = U_{Pauli} + U_{vdW}$

$$u(r) = \frac{B}{r^{12}} - \frac{A}{r^6}$$

$$= 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]$$

the Lennard-Jones potential



Potential where empirical parameters $A=4\varepsilon\sigma^6$ and $B= 4\varepsilon\sigma^{12}$ are determined from independent measurements made in the gas phase.

N atoms in the crystal

$$U_{Total} = \frac{1}{2}N(4\varepsilon)\sum_{i\neq j}\left[\left(\frac{\sigma}{P_{ij}R_{nn}}\right)^{12} - \left(\frac{\sigma}{P_{ij}R_{nn}}\right)^6\right]$$

where R_{nn} is nearest neighbor distance and $p_{ij}R_{nn}$ is the distance between atom i and atom j

$$\boxed{U_{Total} = \frac{1}{2}N(4\varepsilon)\left[\left(\underbrace{\sum_{i\neq j}\frac{1}{P_{ij}^{12}}}\right)\left(\frac{\sigma}{R_{nn}}\right)^{12} - \left(\underbrace{\sum_{i\neq j}\frac{1}{P_{ij}^{6}}}\right)\left(\frac{\sigma}{P_{ij}R_{nn}}\right)^6\right]}$$

Dimensionless

Both lattice sums can be done for any structure.

Sum of $1/p^n$ converges rapidly for large n.

More distant neighbors have more influence on the latter term than the former term.

FCC structure $\sum_{i\neq j}\frac{1}{p_{ij}^{12}} = 12.13188$ **and** $\sum_{i\neq j}\frac{1}{p_{ij}^{6}} = 14.45392$

HCP structure, $\sum_{i\neq j}\frac{1}{p_{ij}^{12}} = 12.13229$ **and** $\sum_{i\neq j}\frac{1}{p_{ij}^{6}} = 14.45489$

Both structures have 12 nearest neighbors.

BCC structure, $\sum_{i\neq j}\frac{1}{p_{ij}^{12}} = 9.11418$ **and** $\sum_{i\neq j}\frac{1}{p_{ij}^{6}} = 12.25330$

BCC structure has 8 nearest neighbors.

Cohesive energy of inert gas crystals at 0K

--minimum U_{total}(Equilibrium)

$$\frac{dU_{total}}{dR} = 2N\varepsilon\left[(12.13)(-12)\frac{\sigma^{12}}{R^{13}} - (14.45)(-6)\frac{\sigma^{6}}{R^{7}}\right]$$

$$= 2N\varepsilon(14.45)(6)\frac{\sigma^{12}}{R^{13}}\left[\left(\frac{R}{\sigma}\right)^{6} - \frac{(12.13)(12)}{(14.45)(6)}\right] = 0$$

$$\boxed{\text{at } R_0 = 1.09\sigma,\ U_{tatal} = -(2.15)(4N\varepsilon) \text{ is a minimum}}$$

	Neon	Argon	Krypton	Xenon
R_0(Å)	3.13	3.76	4.01	4.35
σ (Å)	2.74	3.40	3.65	3.98
$R_0/\ \sigma$	1.14	1.11	1.10	1.09

FCC structure

←

Deviation

Quantum corrections

Review

1. Cohesive (binding) energy U

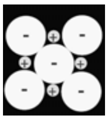
2. Types of bonds

- **(a) Van der Waals (Molecular)**
  Electrons localized among atoms
- **(b) Covalent Electrons shared by the neighboring atoms**
- **(c) Metallic Electrons free to move through sample**
- **(d) Ionic Electrons transferred to adjacent atoms**

3. Molecular bonding

the Lennard-Jones potential $u(r) = \frac{B}{r^{12}} - \frac{A}{r^{6}}$

(d) Ionic bonding



Alkali halides	**Li, Na, K, Rb, Cs** **F, Cl, Br, I**

⌖ Ionic bonding is the electrostatic force of attraction between positively and negatively charged ions (between non-metals and metals).

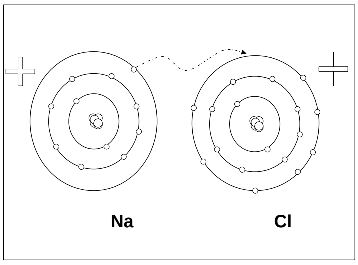
⌖These ions have been produced as a result of a transfer of electrons between two atoms with a large difference in electro-negativities.

⌖All ionic compounds are crystalline solids at room temperature.

Electron configuration : closed electronic shells

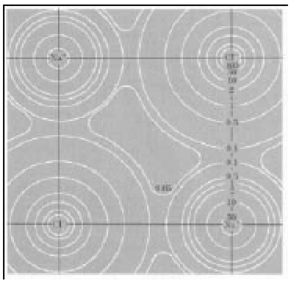
For examples, LiF: Li^{+} ($1S^2$) instead of Li ($1S^22S$)

F^{-} ($1S^22S^22p^6$) instead of F ($1S^22S^22p^5$)



The metallic elements have only up to the valence electrons in their outer shell will lose their electrons and become positive ions, whereas electronegative elements tend to acquire additional electrons to complete their octed and become negative ions, or anions.

Electron density distribution in the base plane of NaCl



Charge distribution is spherically symmetric.

Like inert gas atoms

but

some distortion of charge distribution near the region of contact with neighboring atom

Ionization energies and electron affinities of atoms

Ionization energy

energy that must be supplied in order to remove an electron from a neutral atom

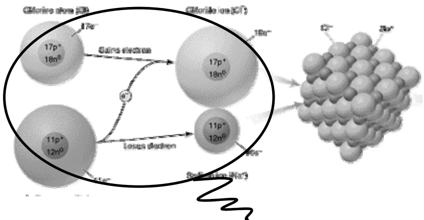
Electron affinity

energy that is gained when an additional electron is added to a neutral atom

> Ionic bonding is produced whenever
> an element w/. a relatively low ionization energy is combined with an element w/. a high electron affinity.

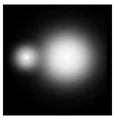
For example : NaCl

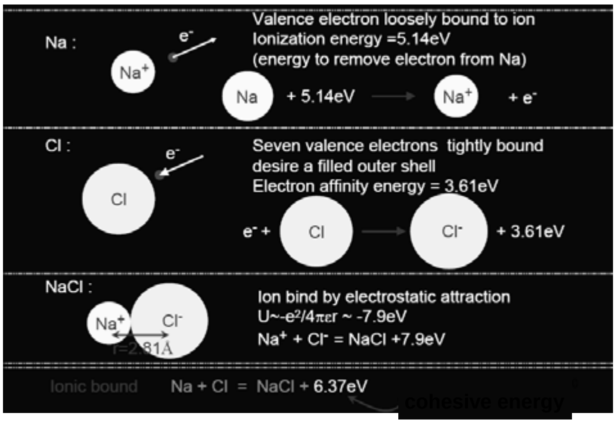
when sodium loses its one valence electron it gets smaller in size, while chlorine grows larger when it gains an additional valance electron.



cohesive energy

ionic bond





Valence electron loosely bound to ion
Ionization energy =5.14eV
(energy to remove electron from Na)

$Na + 5.14eV \rightarrow Na^+ + e^-$

Seven valence electrons tightly bound
desire a filled outer shell
Electron affinity energy = 3.61eV

$e^- + Cl \rightarrow Cl^- + 3.61eV$

Ion bind by electrostatic attraction
$U \sim -e^2/4\pi\varepsilon r \sim -7.9eV$
$Na^+ + Cl^- = NaCl + 7.9eV$

Ionic bound $Na + Cl = NaCl + 6.37eV$

cohesive energy

- When the Na+ and Cl- ions approach each other closely enough so that the orbits of the electron in the ions begin the overlap each other, then the electron begins to repel each other by virtue of the repulsive electrostatic coulomb force.

- Pauli exclusion principle has an important role in repulsive force. To prevent a violation of the exclusion principle, the potential energy of the system increases very rapidly.

N molecular s in the crystal
U_{ij} is the interaction energy between ions i and j (i ≠ j)

$$U_{ij} = \lambda \exp\left(-\frac{r_{ij}}{\rho}\right) + \frac{q_i q_j}{r_{ij}} \qquad \text{CGS}$$

short range Pauli repulsive **(why?)** long range electrostatic

$$U_{ij} = \lambda \exp\left(-\frac{R}{\rho}\right) + \frac{q_i q_j}{p_{ij} R}$$ where R = nearest neighbor distance

$$U_{\text{tot}} = \sum_{i \neq j} U_{ij} = Nz\lambda \exp\left(-\frac{R}{\rho}\right) + \sum_{i \neq j} \frac{q_i q_j}{p_{ij} R} = N\left(z\lambda \exp\left(-\frac{R}{\rho}\right) - \frac{\alpha q^2}{R}\right)$$

where *z* = number of nearest neighbors of any ion

$$\alpha \equiv \sum_j {}' \frac{\pm}{p_{ij}}$$

Madelungconstant

minimum U_{total} (Equilibrium)

$$\frac{dU_{tot}}{dR} = -\frac{Nz\lambda}{\rho}\exp\left(-\frac{R}{\rho}\right) + \frac{N\alpha q^2}{R^2} = 0$$

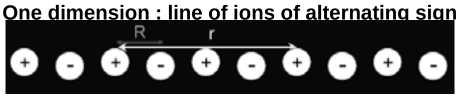
At equilibrium R_o, $R_o^2 \exp\left(-\frac{R_o}{\rho}\right) = \frac{\rho\alpha q^2}{z\lambda}$

$$\Rightarrow U_{tot} = -\underbrace{\frac{N\alpha q^2}{R_o}}_{\text{Madelung energy}}\left(1 - \overset{\text{Short range repulsive } \rho = 0.1R_o}{\frac{\rho}{R_o}}\right)$$

Madelung constant α : geometric sum
depends on relative distance, number, and sign of neighboring atoms
----- crystal structures and basis

Calculation of Madelung constant

One dimension : line of ions of alternating signs



$$\alpha = \sum_{ij}{}' \frac{\pm}{p_{ij}} \qquad \frac{\alpha}{R} = \sum_{ij}{}' \frac{\pm}{r_{ij}} = 2\left(\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} - \frac{1}{4R} + \cdots\right)$$

$$\Rightarrow \alpha = 2\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots\right)$$

$$\text{and } \ell n(1+x) = \left(x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots\right)$$

⇨ $\alpha = 2\,\ell n(2) = 1.386$ **for one dimensional chain**

In three dimensions
it is more complicated to calculate α.

- very long range electrostatic forces
- very slowly convergent

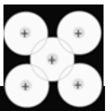
Special mathematical tricks are used to calculate Madelung constant.

structure	Coordinate No	α
NaCl (FCC)	6	1.7476
CsCl (BCC)	8	1.7627
GaAs (Zinc blende)	4	1.6381
ZnS (Wurtzite)	4	1.641

Higher coordination number gives larger Madelung constant.

It depends on the structure of the crystal but not unit cell dimensions.

(b) Covalent bonding

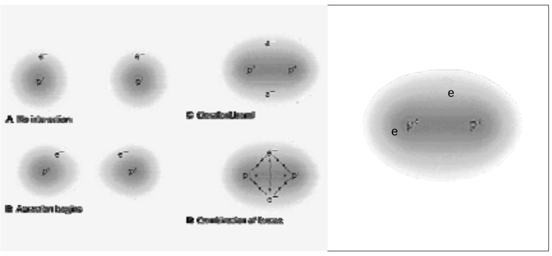


Tetrahedral bond		
C — C	Organic chemistry / diamond	7.3eV/atom
Si — Si	Semiconductor	4.6eV/atom
Ge — Ge		3.9eV/atom

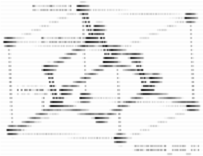
⌖ Covalent bonding takes place between atoms with small differences in electronegativity which are close to each other in periodic table (*between non-metals and non-metals*).

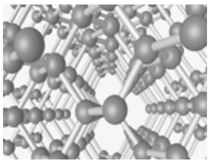
⌖The covalent bonding is formed by sharing of outer shell electrons (i.e., s and p electrons) between atoms rather than by electron transfer.

⌖ Each electron in a shared pair is attracted to both nuclei involved in the bond. The approach, electron overlap, and attraction can be visualized as shown in the following figure representing the nuclei and electrons in a hydrogen molecule.

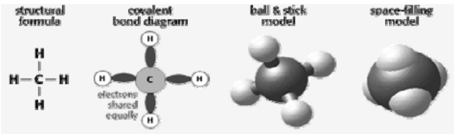


4 atoms in the valence band bond to 4 neighboring

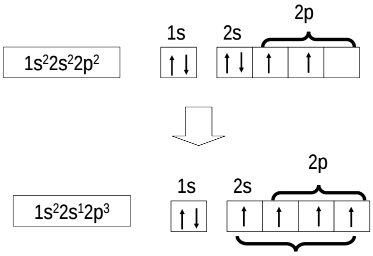




Tetrahedral bonding



Diamond

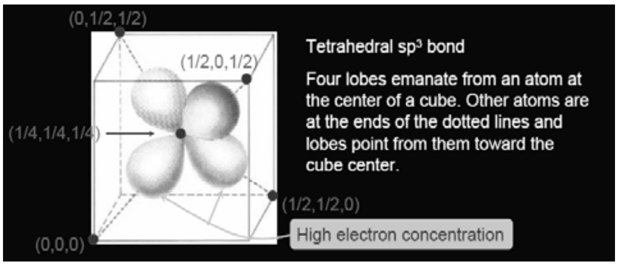


$$\varphi_{h_1} = \frac{1}{2}(\phi_{2s} + \phi_{2p_x} + \phi_{2p_y} + \phi_{2p_z})$$

$$\varphi_{h_2} = \frac{1}{2}(\phi_{2s} + \phi_{2p_x} - \phi_{2p_y} - \phi_{2p_z})$$

$$\varphi_{h_3} = \frac{1}{2}(\phi_{2s} - \phi_{2p_x} + \phi_{2p_y} - \phi_{2p_z})$$

$$\varphi_{h_4} = \frac{1}{2}(\phi_{2s} - \phi_{2p_x} - \phi_{2p_y} + \phi_{2p_z})$$



Tetrahedral sp³ bond

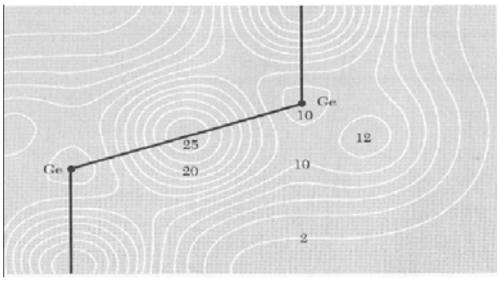
Four lobes emanate from an atom at the center of a cube. Other atoms are at the ends of the dotted lines and lobes point from them toward the cube center.

■ The bond is usually formed from two electrons, one from each atom participating in the bond.

■ Electron forming the bond tend to be partially localized in the region between two atoms joined by the bond.

■ The spins of two electrons in the bond are antiparallel.

Calculated valence electron concentration in Ge.

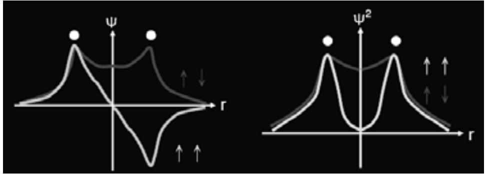


Consider simple covalent bond : H -H

Both hydrogen atoms would like to form a filled outer shell--share electrons

Two cases : ↑ ↑ (same spins on electrons)

↑ ↓ (opposite spins on electrons)



Pauli exclusion principle forbids two electrons with the same states.

↑ ↑ same spins: electrons must stay apart

↑ ↓ opposite spins: electrons can occupy the same place

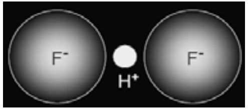
Neutral H has only one electron

⟹ covalent bonding with one other atom

In the extreme ionic form of the hydrogen bond, the hydrogen atom loses its electron to another atom in the molecule;

the bare proton forms the hydrogen bond.

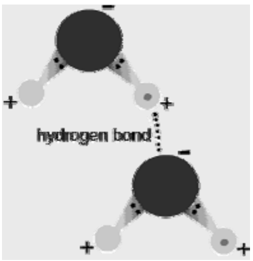
The hydrogen bond connects only two atoms.



HF_2^- is stabilized by a hydrogen bond.

a hydrogen bond between them under certain conditions

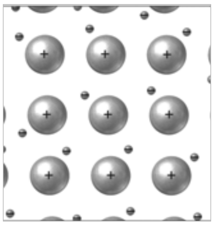
0.1eV



being formed only between the most electronegative atoms, such as F, O, and N.

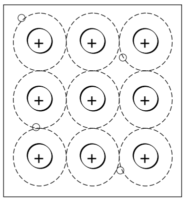
(c) metallic bonding

- Metallic bonding is the type of bonding found in metal elements. This is the electrostatic force of attraction between positively charged ions and delocalized outer electrons.
- The metallic bond is weaker than the ionic and the covalent bonds.



❖ **A metallic bond result from the sharing of a variable number of electrons by a variable number of atoms.**

Outer electrons of atoms that form metals are loosely bound.



High electrical conductivity : a large number of electrons in a metal are free to move

conduction electrons

---

1. The potential energy barrier between atoms is reduced, the electron energy may be well above the potential energy maximum and their wave functions are then nearly plane waves in regions between atoms.

2. Weak binding, 1~5eV/atom enlargement of the internuclear spacing.

3. Metals tend to crystallize in relatively closed packed structures : hcp, fcc, bcc, …

Homework

P93
3.1, 3.2, 3.3, 3.5a, 3.6

Review

Types of Bonding

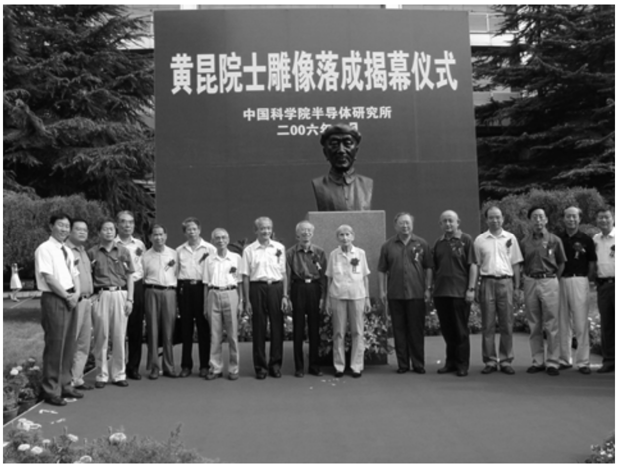
Ionic Bonding	Van Der Waals Bonding	Metallic Bonding	Covalent Bonding	Hydrogen Bonding
High Melting Point	Low Melting Points	Variable Melting Point	Very High Melting Point	Low Melting Points
Hard and Brittle	Soft and Brittle	Variable Hardness	Very Hard	Soft and Brittle
Non conducting solid	Non-Conducting	Conducting	Usually not Conducting	Usually Non-Conducting
NaCl, CsCl, ZnS	Ne, Ar, Kr and Xe	Fe, Cu, Ag	Diamond, Graphite	Ice, organic solids

Chapter Four Phonons I.

Crystal vibrations

1. Vibrations of crystal with monatomic basis
2. Two atoms per primitive basis
3. Quantization of elastic waves (phonon)
4. Phonon momentum
5. Inelastic scattering by phonons

Prof. HUANG Kun

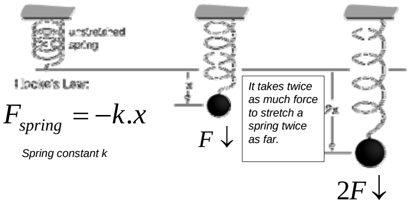


Crystal Dynamics

- Concern with the spectrum of characteristics vibrations of a crystalline solid.
- Leads to;
  - consideration of the conditions for wave propagation in a periodic lattice,
  - the energy content,
  - the specific heat of lattice waves,
  - the particle aspects of quantized lattice vibrations (phonons)
  - consequences of an harmonic coupling between atoms.

Hooke's Law

- One of the properties of elasticity is that it takes about twice as much force to stretch a spring twice as far. That linear dependence of displacement upon stretching force is called Hooke's law.



$$F_{spring} = -k.x$$

Spring constant k

It takes twice as much force to stretch a spring twice as far.

SOUND WAVES

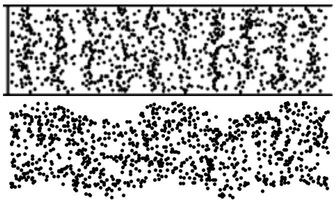
- Mechanical waves are waves which propagate through a material medium (solid, liquid, or gas) at a wave speed which depends on the elastic and inertial properties of that medium. There are two basic types of wave motion for mechanical waves: longitudinal waves and transverse waves.

- **Sound waves are atomic vibrations with a long wavelength.**
- **Presence of atoms has no significance in this wavelength limit, since λ>>a, so there will be no scattering due to the presence of atoms.**

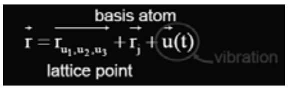
- A solid is composed of discrete atoms, however when the wavelength is very long, one may disregard the atomic nature and treat the solid as a continuous medium. Such vibrations are referred to as elastic waves.

Longitudinal Waves

Transverse Waves

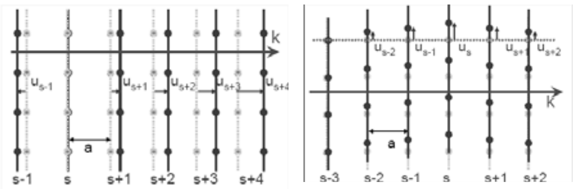


Lattice is not rigid. Atoms can move from equilibrium.



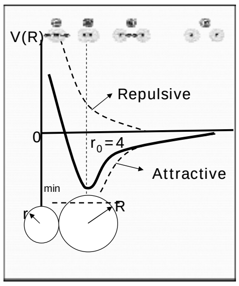
$$\vec{r} = \overrightarrow{r_{u_1,u_2,u_3}} + \vec{r}_j + \vec{u}(t)$$

When wave propagates in the solid, there are
one longitudinal and two transverse polarizations



Lattice vibrations of 1D crystal
Chain of identical atoms

- **Atoms interact with a potential V(r) which can be written in Taylor's series.**



$$V(r) = V(a) + \frac{(r-a)^2}{2}\left(\frac{d^2V}{dr^2}\right)_{r=a} + \ldots\ldots\ldots\ldots$$

This equation looks like as the potential energy associated of a spring with a spring constant :

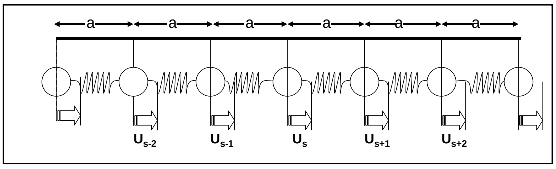
We should relate K with elastic modulus C:

$$\boxed{Force\ = C \times \frac{(r-a)}{a}} \qquad \boxed{Force = K(r-a)}$$

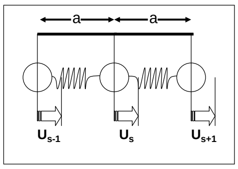
$$\boxed{C\ =\ Ka}$$

Monoatomic Chain

- **The simplest crystal is the one dimensional chain of identical atoms.**
- **Chain consists of a very large number of identical atoms with identical masses.**
- **Atoms are separated by a distance of "a".**
- **Atoms move only in a direction parallel to the chain.**
- **Only nearest neighbours interact (short-range forces).**



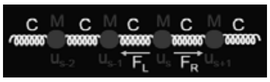
- **Start with the simplest case of monoatomic linear chain with only nearest neighbour interaction**



The force on the sth atom;

The force to the right $C(u_{s+1}-u_s)$

The force to the left; $C(u_{s-1}-u_s)$



$$F_s = F_R + F_L = C(u_{s+1}-u_s) + C(u_{s-1}-u_s)$$

$$\Longrightarrow \qquad M\frac{d^2u_s}{dt^2} = C(u_{s+1}+u_{s-1}-2u_s)$$

☻ Set of coupled, linear, second order differential equations.

☻ Hard to solve in general if M's and C's are different.

☻ Method : a trial solution (good guess)

- **All atoms oscillate with a same amplitude A and frequency ω. Then we can offer a solution;**

$$u_s(t) = A\exp[i(kx_s - \omega t)] \quad \text{where } x_s = sa$$

$$M(-\omega^2)Ae^{iksa}e^{-i\omega t} = C(Ae^{ik(s+1)a} + Ae^{ik(s-1)a} - 2Ae^{iksa})e^{-i\omega t}$$

$$-M\omega^2 = C(e^{ika} + e^{-ika} - 2)$$

$$= C2(\cos(ka) - 1)$$

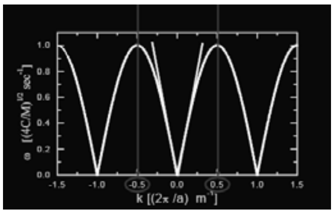
$$\Rightarrow \quad \omega^2 = \frac{2C}{M}(1-\cos(ka)) = \frac{2C}{M}\left(2\sin^2\left(\frac{ka}{2}\right)\right)$$

Dispersion relation

When $k = \pm\frac{\pi}{a}$

$\omega = \sqrt{\frac{4C}{M}}$: maximum

set the boundary of first BZ



Brillouin zone

The dispersion relation is periodic with a period of 2 π /a

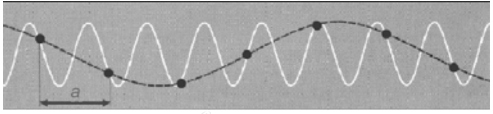
For a small k (ka<<1)   Long wavelength limit

Continuum elastic wave limit

Dispersion : $\omega \neq vk$

What is the wave velocity?

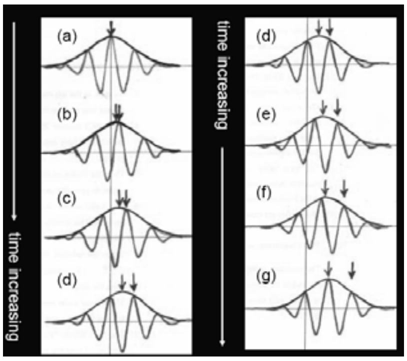
$$\begin{cases} \text{phase velocity } v_p \\ \text{group velocity } v_g \end{cases}$$



phase velocity $v_p = \frac{\omega}{k}$

group velocity $v_g \equiv \frac{d\omega}{dk} = \nabla_k \omega(k)$

the velocity of energy propagation in the medium



group velocity

$$v_g \equiv \frac{d\omega}{dk} = \nabla_k \omega(k)$$

phase velocity

$$v_p = \frac{\omega}{k}$$

phase velocity

$$v_p \equiv \frac{\omega}{k} = \frac{\sqrt{4C/M}\,|\sin(ka/2)|}{k} = \frac{a}{2}\sqrt{\frac{4C}{M}}\,\frac{|\sin(ka/2)|}{ka/2}$$

$$\boxed{v_p = v_s \frac{|\sin(ka/2)|}{ka/2}}$$

group velocity

$$v_g \equiv \frac{d\omega}{dk} = \sqrt{4C/M}\,\frac{d|\sin(ka/2)|}{dk} = \frac{a}{2}\sqrt{\frac{4C}{M}}\left|\cos\left(\frac{ka}{2}\right)\right|$$

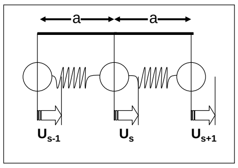
$$\boxed{v_g = v_s|\cos(ka/2)|}$$

When $k = \pm\frac{\pi}{a}$, $v_g = 0$ group velocity vanishes!

$v_p = (2/\pi)v_s$ (k lies on the boundary of first BZ)

Review

Monoatomic Chain

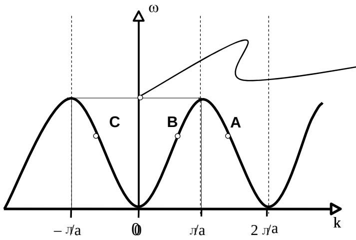


$$M\frac{d^2u_s}{dt^2}=C(u_{s+1}+u_{s-1}-2u_s)$$

$$u_s(t)=A\exp\left[i(kx_s-\omega t)\right]\quad\text{where }\ \mathrm{x_s}=sa$$

Dispersion relation

ω versus k relation;



$$\omega_{\max}=2\sqrt{\frac{C}{m}}$$

$$V_s=\omega/\mathrm{k}$$

Note that:

- In above equation s is cancelled out, this means that the eqn. of motion of all atoms leads to the same algebraic eqn. This shows that our trial function U_s is indeed a solution of the eqn. of motion of s-th atom.
- We started from the eqn. of motion of N coupled harmonic oscillators.. If one atom starts vibrating, it does not continue with constant amplitude, but transfer energy to the others in a complicated way; the vibrations of individual atoms are not simple harmonic because of this exchange energy among them.
- Our wavelike solutions on the other hand are *uncoupled* oscillations called *normal modes;* each k has a definite w given by above eqn. and oscillates independently of the other modes.
- So the number of modes is expected to be the same as the number of equations N. Let's see whether this is the case;

How about the motion of atoms?

The relative displacement between two adjacent atoms

For a fixed k, $\frac{\mathrm{u_{s+1}}}{\mathrm{u_s}}=e^{\mathrm{ika}}$

same

For the other fixed $k'=k+n\frac{2\pi}{a}=k+G$

$$\frac{U_{s+1}}{U_s}=e^{i(k+n2\pi/a)a}=e^{ika}e^{in2\pi}=e^{ika}$$

The displacement can always be described by a wave vector **within the first BZ**

$$\text{At k=q,}\quad \mathrm{u_s(t)=A\exp}\left[i(\mathrm{qsa}-\omega\,\mathrm{t})\right]$$

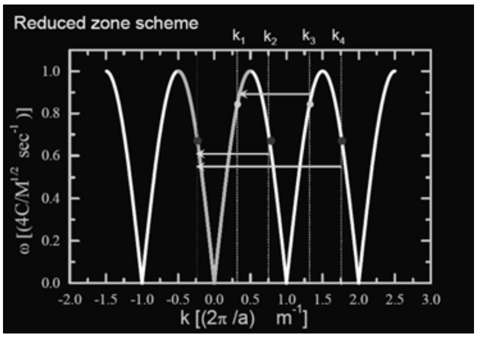
$$\text{same as}\ \ \mathrm{k}=\frac{2\pi}{\mathrm{a}}+\mathrm{q}$$

$$\text{At k=}\frac{2\pi}{\mathrm{a}}-\mathrm{q}\,,\ \mathrm{u_s(t)=A\exp}\left[i\left((\frac{2\pi}{\mathrm{a}}-\mathrm{q})\mathrm{sa}-\omega\,\mathrm{t}\right)\right]$$

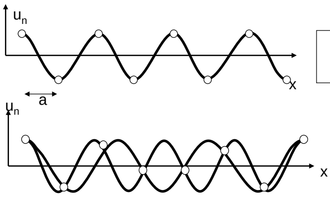
$$=A\exp[i(2\pi s-qsa-\omega t)]=A\exp[i(-qsa-\omega t)]$$

same as k = -q

The displacement can always be described by a wave vector within the first BZ.



What is the physical significance of wave numbers outside the range of $2\pi/a$?

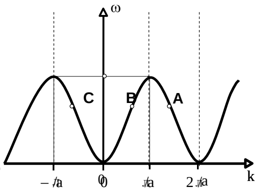


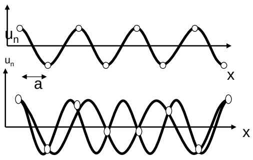
White line :

Green line :

$$3\lambda=7a\Rightarrow\lambda=\frac{7a}{3}\Rightarrow k=\frac{2\pi}{7a/3}=\frac{6\pi}{7a}=0.85\frac{\pi}{a}$$

- **The points A and C both have same frequency and same atomic displacements**
- **They are waves moving to the left.**
- **The green line corresponds to the point B in dispersion diagram.**
- **The point B has the same frequency and displacement with that of the points A and C with a difference.**
- **The point B represents a wave moving to the right since its group velocity (d ω /dk)>0.**





- **The points A and C are exactly equivalent; adding any multiple of 2 π /a to k does not change the frequency and its group velocity, so point A has no physical significance.**

Consider that k's range over all reciprocal space,

All the information is in the first Brillouin zone :
the rest is repeated with periodicity 2 π /a –that is, the frequencies are the same for ω(k) and ω(k+G) where G is any reciprocal lattice vector $= n\times\frac{2\pi}{a}$

In fact, the motions of atoms with wavevector $\vec{k}$ is identical to the motion with wavevector $\vec{k}+\vec{G}$.

All independent vibrations are described by $\vec{k}$'s inside BZ.

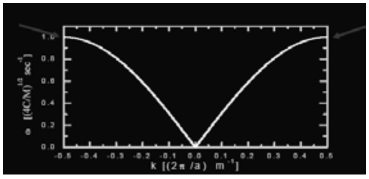
Group velocity of vibration wave

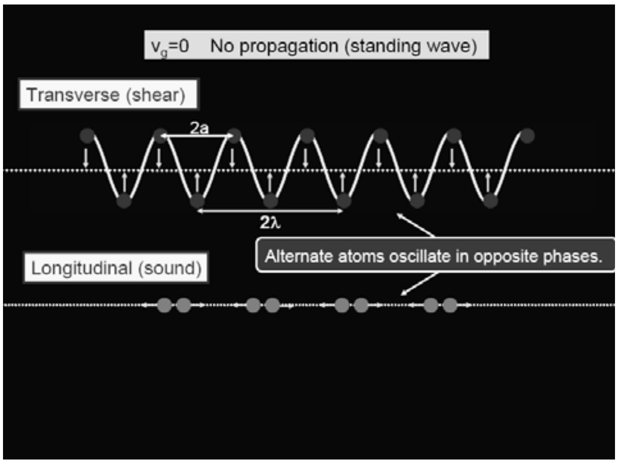
$$v_g = v\,|\cos(ka/2)|$$

At the BZ boundary, $k=\pm\frac{\pi}{a}$ and $\lambda=2a$

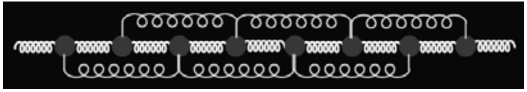
$v_g=0$ **Zero group velocity**

- fundamentally different from elastic wave in a continuum
- any wave (vibration or others) is diffracted if k is on the zone boundary
- leads to standing wave with zero group velocity

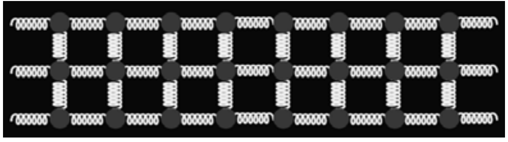




More complicated lattices



1st and 2nd nearest neighboring couplings in 1D monatomic chain

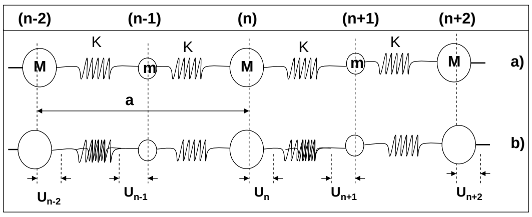


Two dimensional monatomic rectangular lattice

How about two atoms per primitive basis in one dimension?

Chain of two types of atom

- Two different types of atoms of masses M and m are connected by identical springs of spring constant C;



- This is the simplest possible model of an ionic crystal.
- Since a is the repeat distance, the nearest neighbors separations is a/2

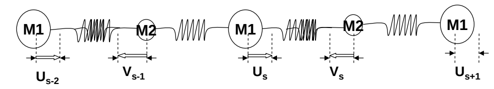
- We will consider only the first neighbour interaction although it is a poor approximation in ionic crystals because there is a long range interaction between the ions.
- The model is complicated due to the presence of two different types of atoms which move in opposite directions.

Our aim is to obtain ω-k relation for diatomic lattice

Two equations of motion must be written;

One for mass M1, and
One for mass M2.

1D diatomic lattice



Equation of motion for mass M1 (s^{th}):

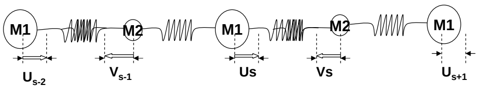
mass x acceleration = restoring force

Equation of motion for mass M2 (s^{th}):

$$M_1(-\omega^2)u\, e^{iksa}e^{-i\omega t} = \left(C(v\, e^{iksa} + v\, e^{ik(s-1)a}) - 2Cue^{-iksa}\right)e^{-i\omega t}$$

$$-M_1\omega^2 u = Cv\left(1+e^{-ika}\right) - 2Cu$$

$$\boxed{\left(2C - M_1\omega^2\right)u - C\left(1+e^{-ika}\right)v = 0}$$



Offer a solution for the mass M1

For the mass M2

$$M_2(-\omega^2)v\, e^{iksa}e^{-i\omega t} = \left(C(u\, e^{ik(s+1)a} + u\, e^{iksa}) - 2Cve^{-iksa}\right)e^{-i\omega t}$$

$$-M_2\omega^2 v = Cu\left(e^{ika}+1\right) - 2Cv$$

$$\boxed{-C\left(1+e^{ika}\right)u + \left(2C - M_2\omega^2\right)v = 0}$$

$$(2C-M_1\omega^2)u-C(1+e^{-ika})v=0$$

$$-C(1+e^{ika})u+(2C-M_2\omega^2)v=0$$

$$(2C-M_1\omega^2)(2C-M_2\omega^2)-C(1+e^{-ika})C(1+e^{ika})=0$$

$$M_1M_2\omega^4-2C(M_1+M_2)\omega^2+C^2(4-(2+2\cos(ka)))=0$$

$$\omega^4-\frac{2C(M_1+M_2)}{M_1M_2}\omega^2+2C^2\,\frac{2\sin^2(ka/2)}{M_1M_2}=0$$

$$\omega^4-2C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\omega^2+\frac{4C^2}{M_1M_2}\sin^2(ka/2)=0$$

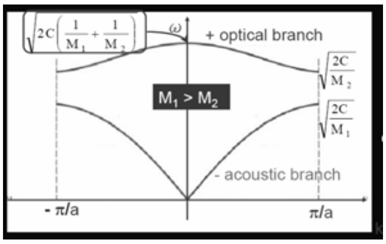
The two roots are;

$$\omega^2=C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\pm C\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2-\frac{4}{M_1M_2}\sin^2(\frac{ka}{2})}$$

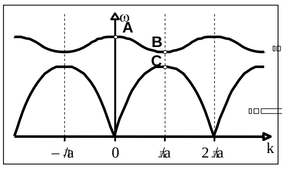
$$\omega^2=C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\left(1\pm\sqrt{1-\frac{4M_1M_2}{(M_1+M_2)^2}\sin^2(\frac{ka}{2})}\right)$$

Dispersion relation

$$\omega^2=C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\left(1\pm\sqrt{1-\frac{4M_1M_2}{(M_1+M_2)^2}\sin^2(\frac{ka}{2})}\right)$$



Two branches correspond to ± signs of dispersion relation



Optical Branch

Upper branch is due to the +ve sign of the root.

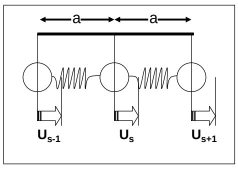
Acoustical Branch

Lower branch is due to the -ve sign of the root.

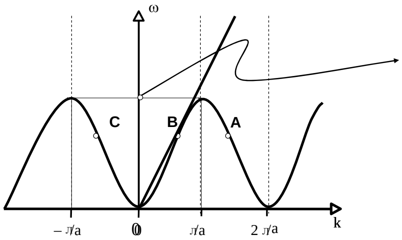
- **As there are two values of ω for each value of k, the dispersion relation is said to have two branches;**
- **The dispersion relation is periodic in k with a period 2 π /a = 2 π /(unit cell length).**
- **This result remains valid for a chain of containing an arbitrary number of atoms per unit cell.**

Review

1D Monoatomic chain



$$u_s(t) = A\exp\left[i(kx_s - \omega t)\right] \quad \text{where } x_s = sa$$

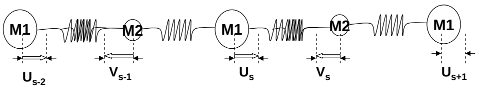


$$\omega_{\max} = 2\sqrt{\frac{C}{m}}$$

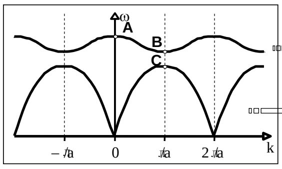
$$V_s = \omega/\mathrm{k}$$

Long wavelength limit

1D diatomic lattice



$$\omega^2 = C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\left(1 \pm \sqrt{1-\frac{4M_1M_2}{(M_1+M_2)^2}\sin^2(\frac{ka}{2})}\right)$$



Optical Branch

Upper branch is due to the +ve sign of the root.

Acoustical Branch

Lower branch is due to the -ve sign of the root.

1. For a small k (ka<<1) long wavelength limit (λ >>a)

$$\omega^2 = C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\left(1 \pm \sqrt{1-\frac{4M_1M_2}{(M_1+M_2)^2}\sin^2(\frac{ka}{2})}\right)$$

sin (ka/2) ~ ka/2

$$\omega = \left(C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\right)^{1/2}\sqrt{1 \pm \left[1-\frac{4M_1M_2}{(M_1+M_2)^2}\left(\frac{ka}{2}\right)^2\right]^{1/2}}$$

$$= \sqrt{C\left(\frac{M_1+M_2}{M_1M_2}\right)\left\{1 \pm \left[1-\frac{M_1M_2}{(M_1+M_2)^2}(ka)^2\right]^{1/2}\right\}}^{1/2}$$

$$\sqrt{C\left(\frac{M_1+M_2}{M_1M_2}\right)\left\{1 \pm \left[1-\frac{M_1M_2}{(M_1+M_2)^2}(ka)^2\right]^{1/2}\right\}}^{1/2}$$

$$\cong \sqrt{C\left(\frac{M_1+M_2}{M_1M_2}\right)\left(1 \pm \left[1-\frac{M_1M_2}{2(M_1+M_2)^2}(ka)^2+\ldots\right]\right)}^{1/2}$$

acoustic branch $\omega_- \approx \sqrt{\frac{C}{2(M_1+M_2)}}(ka)$ $\omega \propto k$

as k→0

optical branch $\omega_+ \approx \sqrt{2C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)}$ ω is finite

2. At BZ boundary k=± π /a: sin (ka/2) ~ ±1

$$\omega^2 = C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\left(1\pm\sqrt{1-\frac{4M_1M_2}{(M_1+M_2)^2}\sin^2(\frac{ka}{2})}\right)$$

$$\omega^2 = C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\left(1\pm\sqrt{1-\frac{4M_1M_2}{(M_1+M_2)^2}}\right)$$

$$\Downarrow$$

$$\omega=\sqrt{C\left(\frac{M_1+M_2}{M_1M_2}\right)}\sqrt{\left(1\pm\frac{|M_1-M_2|}{M_1+M_2}\right)}$$

$$\Downarrow$$

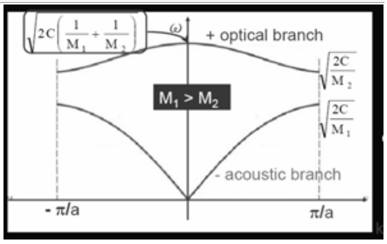
$$=\sqrt{C}\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\pm\left|\frac{1}{M_1}-\frac{1}{M_2}\right|}$$

$M_1>M_2$

acoustic branch $\omega_- = \sqrt{C}\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)-\left(\frac{1}{M_2}-\frac{1}{M_1}\right)}=\sqrt{\frac{2C}{M_1}}$

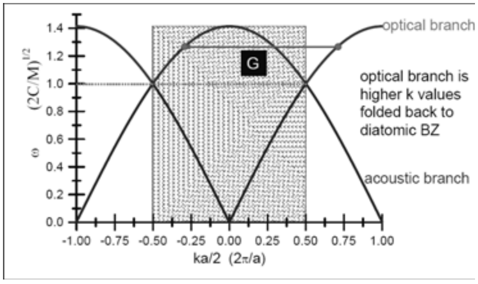
Gap

optical branch $\omega_+ = \sqrt{C}\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)+\left(\frac{1}{M_2}-\frac{1}{M_1}\right)}=\sqrt{\frac{2C}{M_2}}$



3. How about M1=M2

$$\omega=\sqrt{\frac{2C}{M}}\sqrt{1\pm\sqrt{1-\sin^2(\frac{ka}{2})}}=\sqrt{\frac{2C}{M}}\sqrt{1\pm\left|\cos(\frac{ka}{2})\right|} \Longleftrightarrow \omega=\sqrt{\frac{2C}{M}}\sqrt{1-\cos(ka)}$$



4. Amplitude of adjacent atoms

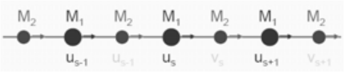
$$\left(2C-M_1\omega^2\right)u-C\left(1+e^{-ika}\right)v=0$$

$$-C\left(1+e^{ika}\right)u+\left(2C-M_2\omega^2\right)v=0$$

1) k=0

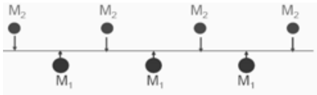
Acousitic branch $\omega=0$

$\frac{u}{v}=1$



optical branch $\omega=\sqrt{2C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)}$

$\frac{u}{v}=-\frac{M_2}{M_1}$



2) k= π /a

Acousitic branch $\omega=\sqrt{\frac{2C}{M_1}}$

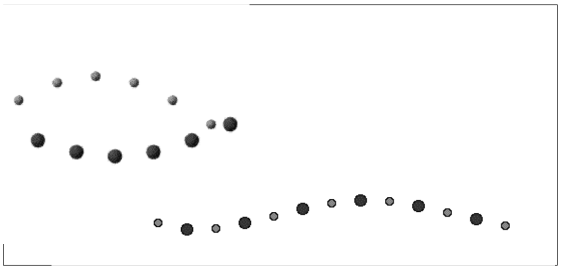
$v=0$

optical branch $\omega=\sqrt{\frac{2C}{M_2}}$

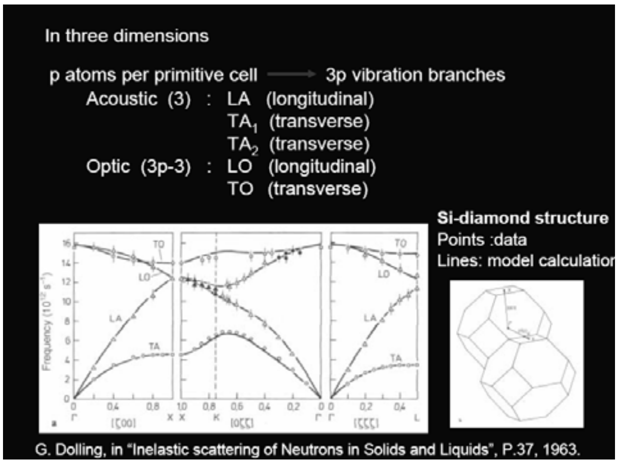
$u=0$

Transverse optical mode for diatomic chain

Transverse acoustical mode for diatomic chain



Amplitude of vibration is strongly exaggerated!



In three dimensions

p atoms per primitive cell ⟶ 3p vibration branches

Acoustic (3) : LA (longitudinal)
TA_1 (transverse)
TA_2 (transverse)
Optic (3p-3) : LO (longitudinal)
TO (transverse)

Si-diamond structure
Points :data
Lines: model calculatio

G. Dolling, in "Inelastic scattering of Neutrons in Solids and Liquids", P.37, 1963.

Periodic boundary conditions (Born-Karman)

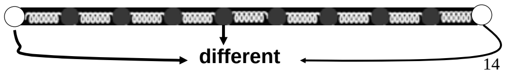
So far, ω and k are continuous except that,

- k is restricted in the first BZ (discrete of lattice spacing)
- ω is forbidden in some gaps (splitting of acoustic and optical modes)

Additional quantization effects:

- **k** is quantized by finite crystal size.
- Energy of vibration mode is quantized by quantum effect.

Real crystal size ⇨ **Finite crystal size**



different

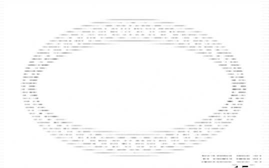
Born-Karman:

There are infinite crystals out of finite crystal, and the motion of atoms are identical inside each crystal.

For example:

☒ **N atom form a cirque, which make all atoms to be equivalent.**

☒ **The motion of atom can be seen as linearity, due to numbers of atoms are large.**



Eg. 1D monatomic chain

1 atoms ⟺ N+1 atoms

$u_s(k,t)=A\exp[i(kx_s-\omega t)]$ where x_s=sa

$u_{N+n}=u_n \rightarrow Ae^{i[(N+n)ak-\omega t]}=Ae^{i[nak-\omega t]}$

$e^{iNak}=1 \quad Nak=2\pi h$

$$\boxed{k=h\left(\frac{2\pi}{Na}\right) \quad \text{discrete !}}$$

$-\frac{\pi}{a}<k\le\frac{\pi}{a}$

$h=-\frac{N}{2}+1,\ -\frac{N}{2}+2,\ -\frac{N}{2}+3,\ \cdots 0,\cdots \frac{N}{2}-2,\ \frac{N}{2}-1,\ \frac{N}{2}$

N=20, k=h(2π/20a)=(h/10)(π /a) **only 20 modes are allowed.**

quantized energy of vibration mode

Each k has a corresponding ω,

what is the energy associated w/. This mode?

Some quantum systems:

photons: $k=2\pi/\lambda$ **photon energy** $E=h\omega$

$\omega=ck$ **mode energy** $E_{k,\omega}=n_k(h\omega)$

A particle in a box: **Number of photon at (k,ω)**

$\lambda_n=\frac{2\ell}{n}$ $k_n=\frac{2\pi}{\lambda_n}=n\left(\frac{\pi}{\ell}\right)$ $E_n=\frac{(\hbar k_n)^2}{2m}=n^2\frac{\hbar^2\pi^2}{2m\ell^2}$

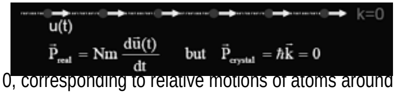
Phonon: particle-like properties

number n_i
Energy $\hbar\omega_i$
wavevector $\vec{k}_i$
crsytal momentum $\vec{P}_i=\hbar\vec{k}_i$

Not a real momentum !

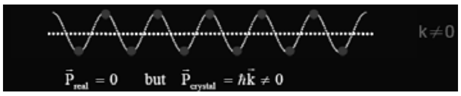
What is the real momentum? **Physical momentum**

eg. k=0, corresponding to translation of the whole crystal



$\vec{P}_{real}=Nm\frac{d\vec{u}(t)}{dt}$ but $\vec{P}_{crystal}=\hbar\vec{k}=0$

eg. k≠0, corresponding to relative motions of atoms around the equilibrium



$\vec{P}_{real}=0$ but $\vec{P}_{crystal}=\hbar\vec{k}\neq 0$

$$\vec{P}_{real} = M\sum_i \frac{d\vec{u}_i(t)}{dt}$$

$$u_s(t) = u(t)\exp[iksa] \longrightarrow \vec{P}_{real} = M\frac{du(t)}{dt}\sum_s \exp[iksa]$$

$$= M\frac{du(t)}{dt}\left(\frac{1-\exp[ikNa]}{1-\exp[ika]}\right)$$

$$\because \text{ discrete } k = \pm\frac{2\pi n}{Na} \quad \therefore \exp[ikNa] = \exp[\pm i2\pi n] = 1$$

$$\Longrightarrow \boxed{\vec{P}_{real} = 0}$$

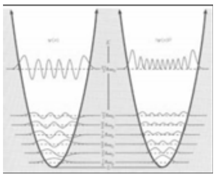
Lattice vibrations

Specifying the vibrational states of the crystal by specifying number of phonon in each state k_i

($k_{i,\omega}$) is determined by structure and binding

n_i is determined by excitation (thermal, acoustic, etc..)

Simple harmonic oscillator:



$$U(x) = \frac{1}{2}cx^2$$

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega \text{ where } \omega = \sqrt{\frac{c}{m}}$$

Zero point energy

PHONONS: quantized lattice vibrations

Lattice vibrations:

wavevector $\vec{k}$

frequency $\omega = f(\vec{k})$ Dispersion relation

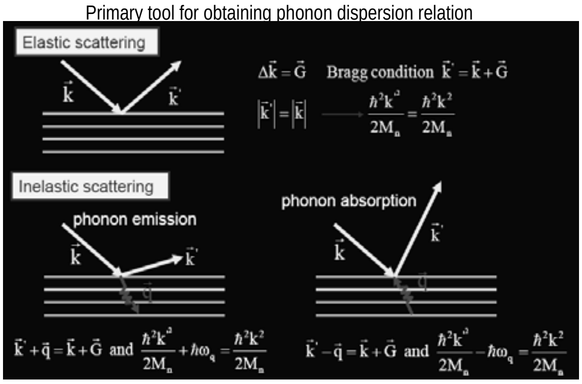
energy $E_n = \left(n+\frac{1}{2}\right)\hbar\omega$ SHO

Phonons: can be thought as particles interact with other electrons, phonons, etc...

Determination of phonon structure :

Neutron scattering –neutrons only scatter off atoms, not electrons

Primary tool for obtaining phonon dispersion relation



Elastic scattering

$$\Delta\vec{k} = \vec{G} \quad \text{Bragg condition } \vec{k}' = \vec{k} + \vec{G}$$

$$|\vec{k}'| = |\vec{k}| \longrightarrow \frac{\hbar^2 k'^2}{2M_n} = \frac{\hbar^2 k^2}{2M_n}$$

Inelastic scattering

phonon emission

$$\vec{k}' + \vec{q} = \vec{k} + \vec{G} \text{ and } \frac{\hbar^2 k'^2}{2M_n} + \hbar\omega_q = \frac{\hbar^2 k^2}{2M_n}$$

phonon absorption

$$\vec{k}' - \vec{q} = \vec{k} + \vec{G} \text{ and } \frac{\hbar^2 k'^2}{2M_n} - \hbar\omega_q = \frac{\hbar^2 k^2}{2M_n}$$

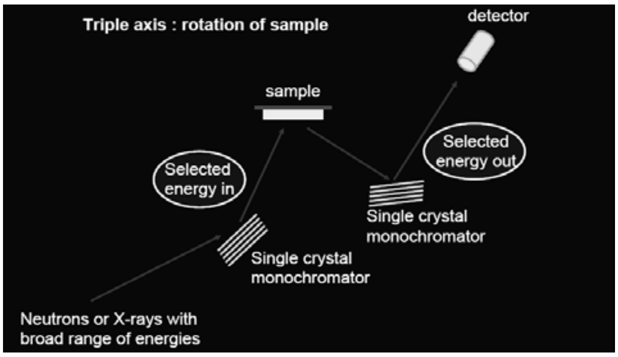
Experimental measurements of dispersion curves

- Dispersion curves ω as a function are measured by inelastic diffraction
- If the atoms are vibrating then diffraction can occur with energy loss or gain by scattering particles
- In principle, can use any particle –neutrons from a reactor, X-rays from a synchrotron, He atoms which scatter from surfaces, …

Neutrons are most useful for vibrations

For λ ~ atomic size, energies ~ vibration energies

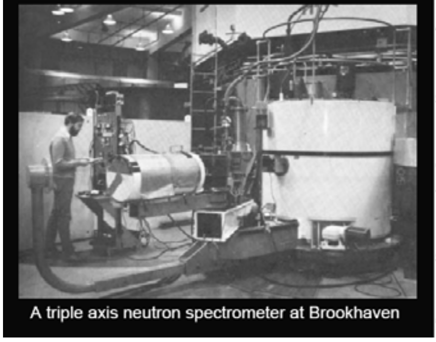
Experimental setup



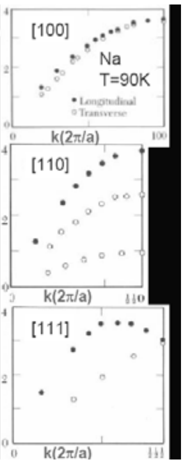
Triple axis : rotation of sample

Measure $\boxed{\vec{k}, \vec{k}', \text{ and } \Delta E}$

$\Longrightarrow \boxed{\vec{q} \text{ and } \hbar\omega_q}$ for phonons



A triple axis neutron spectrometer at Brookhaven



Homework

4-1 Monatomic line lattice.

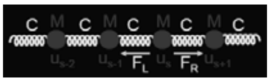
4-3 Basis of two unlike atoms.

4-5 Diatoms chain

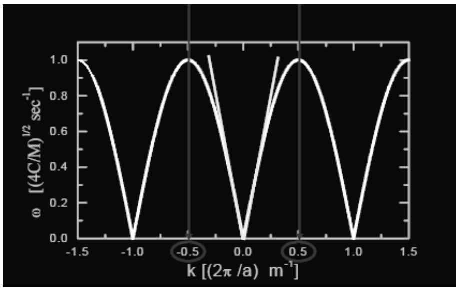
4-6 Atomic vibrations in metal.

Review

1. Vibrations of crystal with monatomic basis

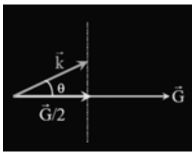


Dispersion relation



2. Brillouin zone

Diffraction condition



Start at reciprocal lattice

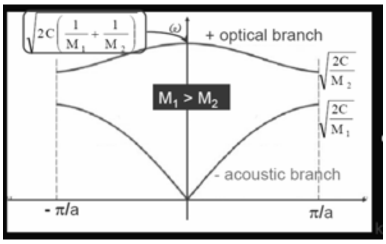
Bisect all G vectors with planes

Enclosed volume is Brillouin zone

Brillouim zone surface describes all k vectors that are constructively diffracted by the crystal.

3. 1D diatom lattices

$$\omega^2 = C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\left(1 \pm \sqrt{1-\frac{4M_1M_2}{(M_1+M_2)^2}\sin^2(\frac{ka}{2})}\right)$$



4. In three dimensions

p atoms per primitive cell ⇨ 3p vibration branches

Acoustic (3) : LA (longitudinal)
TA1(transverse)
TA2(transverse)

Optic (3p-3) : LO (longitudinal)
TO(transverse)

N primitive cell ⇨ 3pN vibration branches

Acoustic (3N) : LA (longitudinal)
TA1(transverse)
TA2(transverse)

Optic ((3p-3)N): LO (longitudinal)
TO(transverse)

5. phonon

PHONONS	**PHOTONS**
• Quanta of lattice vibrations • Energies of phonons are quantized	• Quanta of electromagnetic radiation • Energies of photons are quantized as well

$$E_{phonon} = \frac{h\nu_s}{\lambda}$$

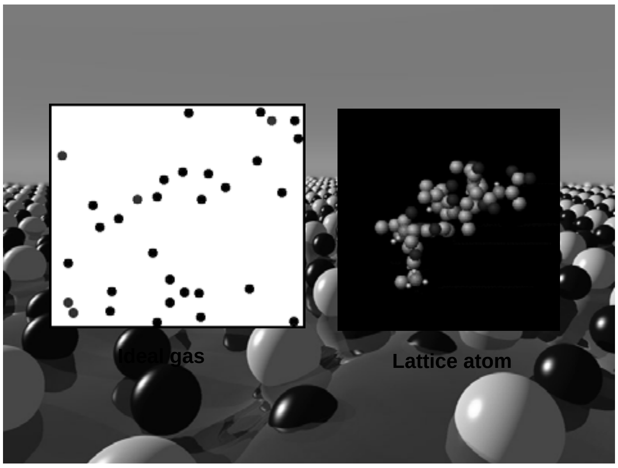
~a_0=10^{-10}m

$$p_{phonon} = \frac{h}{\lambda}$$

$$E_{photon} = \frac{hc}{\lambda}$$

~10^{-6}m

$$p_{photon} = \frac{h}{\lambda}$$



•Atoms vibrate about their equilibrium position.

•They produce vibrational waves.

•This motion is increased as the temperature is raised.

In a solid, the energy associated with this vibration and perhaps also with the rotation of atoms and molecules is called as *thermal energy.*

Note: In a gas, the translational motion of atoms and molecules contribute to this energy.

Therefore, the concept of thermal energy is fundamental to an understanding many of the basic properties of solids. We would like to know:

•What is the value of this thermal energy?

•How much is available to scatter a conduction electron in a metal; since this scattering gives rise to electrical resistance.

•The energy can be used to activate a crystallographic or a magnetic transition.

•How the vibrational energy changes with temperature since this gives a measure of the heat energy which is necessary to raise the temperature of the material.

Chapter Five
Phonons II. Thermal Properties

- **Phonon heat capacity**
- **Anharmonic crystal interactions**
- **Thermal conductivity**

Heat capacity from Lattice vibrations

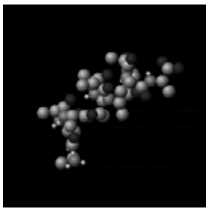
***The* energy given to lattice vibrations is the dominant contribution to the heat capacity in most solids. In non-magnetic insulators, it is the only contribution.**

Other contributions;

•In metals→ from the conduction electrons.

•n magnetic materials→ from magneting ordering.

Phonon heat capacity



Phonons:

dominate thermal properties of materials and affect the electrical transports of conductors by scatterings of electrons

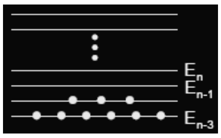
Phonon generations:

How are phonons created or excited in a crystal?

- **External perturbations–vibrations or sound transducer**
- **Scattering of particles–energy transferred into lattice vibrations**
- **Thermal (K_BT)–excited at any finite temperature ($T \neq 0K$)**

Thermal phonons :

consider a system with energy level E_n



Probability of occupancy

$$P(E_n) \propto \exp\left(-\frac{E_n}{k_BT}\right)$$

at temperature T

"Boltzmann factor"

Mode *k*, ω

Excitation level amplitude (n) w/. Energy $\left(n+\frac{1}{2}\right)\hbar\omega$

Average of phonons

$$= \frac{\sum_s s \exp\left(-\frac{(s+1/2)\hbar\omega}{k_BT}\right)}{\sum_s \exp\left(-\frac{(s+1/2)\hbar\omega}{k_BT}\right)}$$

$$\langle n\rangle = \frac{-\frac{d}{dx}\boxed{\sum_s \exp(-sx)}}{\sum_s \exp(-sx)}$$

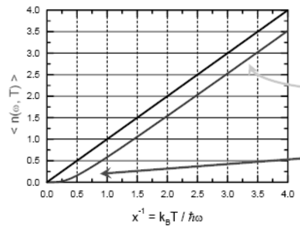
Where

$$\frac{1}{1-e^{-x}}$$

Planck distribution of $\langle n(\omega,T)\rangle$

average # of phonons excited per mode at ω

$$\boxed{\langle n(\omega,T)\rangle = \frac{1}{\exp\left[\frac{\hbar\omega}{k_BT}\right]-1}}$$



High T

$$\langle n(\omega,T)\rangle >\sim \frac{k_BT}{\hbar\omega}$$

Low T

$$\langle n(\omega,T)\rangle >\sim \exp\left(-\frac{k_BT}{\hbar\omega}\right)$$

Thermal energy

$$\langle U\rangle = \sum_i^{\text{mode}} \langle n_i\rangle \hbar\omega_i$$

$$= \int d\omega D(\omega)\langle n(\omega)\rangle \hbar\omega$$

density of modes

$$= \int d\omega \boxed{D(\omega)} \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_BT}\right)-1}$$

?

thermal equilibrium

Density of states (modes) : uniform in k-space

1D D(k)≡density of states = number of states per unit k at k

D(k)dk number of states from k to k+dk

A linear chain of length L carries N+1 particles with separation a.

1. Boundary condition : $u_0(t)=0$ and $u_N(t)=0$ fixed points

$\boxed{s=0}$ $\boxed{s=N}$

$\mathbf{u_s(t)=u\exp[-i\omega_{k,p}t]\sin(ska)}$

where

Why is there no N π /L for allowed k?

$$u_s(t)\propto\sin\left(\frac{sN\pi a}{L}\right)=\sin(s\pi)=0$$ No motion at all.

One mode for each interval $\Delta k=\frac{\pi}{L}$

The number of modes per unit range of k

$$\boxed{D(k)=\begin{cases}\frac{L}{\pi} & for \quad k\le\frac{\pi}{a}\\ 0 & for \quad k>\frac{\pi}{a}\end{cases}}$$

2. Unbounded medium but w/. periodic solution over the distance L

Periodic boundary conditions u(sa)=u(sa+L) for a large system

$\mathbf{u_s(t)=u\exp[\,i(ska-\omega_{k,p}t)\,]}$ where $k=0,\pm\frac{2\pi}{L},\pm\frac{4\pi}{L},\pm\frac{6\pi}{L},....$

One mode for each interval

$$\Delta k=\frac{2\pi}{L}$$

The number of modes per unit range of k

$$D(k)=\frac{L}{2\pi}\quad \text{for}\quad -\frac{\pi}{a}\le k\le\frac{\pi}{a}$$
$$=0\quad \text{otherwise}$$

$$D(k)dk=\frac{L}{2\pi}dk\qquad \text{and}\,2\quad \text{for}\pm\text{of}\quad k$$

$$D(\omega)d\omega=2D(k)dk=2D(k)\frac{dk}{d\omega}d\omega$$

The number of modes per unit frequency range

$$D(\omega)=2D(k)\frac{dk}{d\omega}=\frac{2D(k)}{d\omega/dk}=\frac{2D(k)}{v_g}$$

Dispersion relation

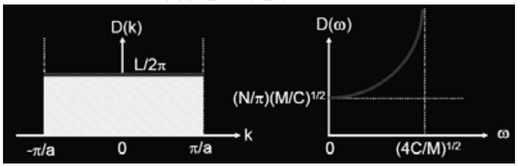
Singularity at $v_g=0$, determined by ω(k)

Van Hove Singularity

One dimensional monatomic lattice

$$\omega=\sqrt{\frac{4C}{M}}\left|\sin\left(\frac{ka}{2}\right)\right|$$

$$D(\omega)=\frac{2D(k)}{d\omega/dk}=\frac{2(Na/2\pi)}{\sqrt{\frac{4C}{M}}\frac{a}{2}\cos\left(\frac{ka}{2}\right)}=\frac{N}{\pi}\sqrt{\frac{M}{C}}\sqrt{\frac{\omega_{\max}^2}{\omega_{\max}^2-\omega^2}}$$



Total number of modes

$$N=\int_{-\pi/a}^{\pi/a}D(k)dk=\frac{L}{2\pi}\frac{2\pi}{a}=N=\int_0^{\omega_{\max}}D(\omega)d\omega=\int_0^{\sqrt{\frac{4C}{M}}}D(\omega)d\omega$$

Planck distribution of $\langle n(\omega,T)\rangle$

average # of phonons excited per mode at ω

$$\langle n(\omega,T)\rangle = \frac{1}{\exp\left[\frac{\hbar\omega}{k_B T}\right]-1}$$

Thermal energy

$$\langle U\rangle = \sum_K \sum_p \langle n_{K,p}\rangle \hbar\omega_{K,p} = \sum_i^{\text{mode}} \langle n_i\rangle \hbar\omega_i$$

$$= \int d\omega D(\omega)\langle n(\omega)\rangle \hbar\omega$$

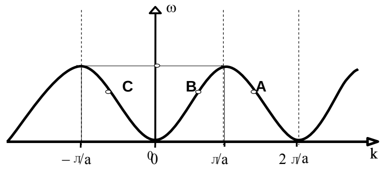
$D(\omega)$ **Density of states (modes)**

$\Downarrow$

$D(K)$

D(k)≡density of states = number of states per unit k at k

1D



Density of States

D(k)≡density of states = number of states per unit k at k

There are two sets of waves for solution;
Running waves
Standing waves

<u>Standing waves:</u>

Boundary condition : $u_0(t)=0$ and $u_N(t)=0$ fixed points

s=0 **s=N**

$u_s(t)=u \exp[-i\omega_{k,p}t] \sin(ska)$

$\Downarrow$

Nka=n π ⇒ **k=n π /L**

One mode for each interval $\Delta k = \frac{\pi}{L}$

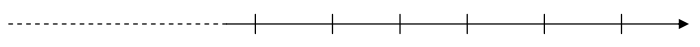
The number of modes per unit range of k

$$D(k) = \begin{cases} \frac{L}{\pi} & \text{for} \quad k \le \frac{\pi}{a} \\ 0 & \text{for} \quad k > \frac{\pi}{a} \end{cases}$$

<u>Running waves:</u>

Periodic boundary conditions u(sa)=u(sa+L)

$u_s(t)=u \exp[\, i(ska-\omega_{k,p}t)\,]$



$$k = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \pm\frac{6\pi}{L}, \ldots\ldots$$

One mode for each interval $\Delta k = \frac{2\pi}{L}$

The number of modes per unit range of k

$$D(k) = \frac{L}{2\pi} \quad \text{for} \quad -\frac{\pi}{a} \le k \le \frac{\pi}{a}$$

$$= 0 \quad \text{otherwise}$$

These allowed k's are uniformly distributed between k and k+dk

$$D_s(k)dk = \frac{L}{\pi}dk$$ DOS of standing wave

$$D_s(k)dk = \frac{L}{2\pi}dk$$ DOS of running wave

•The *density of standing wave states is twice that of the running waves*.

•However in the case of standing waves only positive values are allowed

•Then the total number of states for both running and standing waves will be the same in a range dk of the magnitude k

•The standing waves have the same dispersion relation as running waves, and for a chain containing N atoms there are exactly N distinct states with k values in the range 0 to π/a .

The density of states per unit frequency range g(ω):

- The number of modes with frequencies ω and ω+dω will be g(ω)dω.
- g(ω) can be written in terms of D(*k*).

$$D(k)dk = \frac{L}{2\pi}dk \quad \text{and } 2 \quad \text{for} \pm \text{of} \quad k$$

$$D(\omega)d\omega = 2D(k)dk = 2D(k)\frac{dk}{d\omega}d\omega$$

The number of modes per unit frequency range

$$D(\omega) = 2D(k)\frac{dk}{d\omega} = \frac{2D(k)}{d\omega/dk} = \frac{2D(k)}{v_g}$$

Dispersion relation

Singularity at v_g=0, determined by ω(k)

Van Hove Singularity

Let's remember dispertion relation for 1D monoatomic lattice

$$D(\omega) = 2D(k)\frac{dk}{d\omega}$$

Let's remember dispertion relation for 1D monoatomic lattice

$$\omega^2 = \frac{4K}{m}\sin^2\frac{ka}{2} \Longrightarrow \omega = 2\sqrt{\frac{K}{m}}\left|\sin\frac{ka}{2}\right|$$

$$\frac{d\omega}{dk} = a\sqrt{\frac{K}{m}}\cos\frac{ka}{2} \Longrightarrow D(\omega) = 2D(k)\frac{1}{a\sqrt{\frac{K}{m}}\cos\left(\frac{ka}{2}\right)}$$

$$D(\omega) = 2D(k)\frac{1}{a}\sqrt{\frac{m}{K}}\frac{1}{\cos(ka/2)}$$

$$\sin^2 x + \cos^2 x = 1 \Rightarrow \cos x = \sqrt{1-\sin^2 x} \Longrightarrow \cos\left(\frac{ka}{2}\right) = \sqrt{1-\sin^2\left(\frac{ka}{2}\right)}$$

$$D(\omega) = 2D(k)\frac{1}{a}\sqrt{\frac{m}{K}}\frac{1}{\sqrt{1-\sin^2\left(\frac{ka}{2}\right)}}\frac{\sqrt{4}}{\sqrt{4}}$$

Multibly and divide

$$D(\omega) = 2D(k)\frac{1}{a}\frac{2}{\sqrt{\frac{4K}{m}-\frac{4K}{m}\sin^2\left(\frac{ka}{2}\right)}}$$

$$\mathbf{D(\omega)} = \frac{2N}{\pi}\left(\omega_{\max}^2 - \omega^2\right)^{-1/2}$$

True density of states

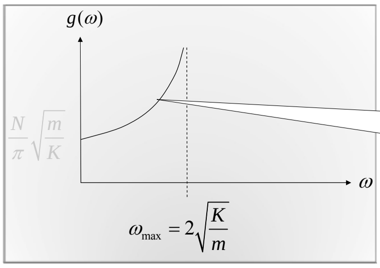
Let's remember:

$$D(k)dk = \frac{L}{2\pi}dk$$

$$L = Na$$

$$\omega^2 = \frac{4K}{m}\sin^2\left(\frac{ka}{2}\right)$$

$$\omega_{\max}^2 = \frac{4K}{m}$$



$$g(\omega) = \frac{2N}{\pi}\left(\omega_{\max}^2 - \omega^2\right)^{-1/2}$$

True density of states by means of above equation

True DOS(density of states) tends to infinity at ,

Total number of modes

since the $N = \int_{-\pi/a}^{\pi/a} D(k)dk = \frac{L}{2\pi}\frac{2\pi}{a} = N = \int_0^{\omega_{\max}} D(\omega)d\omega = \int_0^{\sqrt{\frac{4C}{M}}} D(\omega)d\omega$.

In two dimensions :

periodic boundary condition, N^2 primitive cells within a square of side L

exp[i(k_xx+k_yy)] = exp[i(k_x(x+L) + k_y(y+L))]

whence

One mode for each interval

The number of modes in k-space

Number of modes with wave vector from k to k+dk in k-space

$$D(k)dk = \frac{1}{\Delta k_x \Delta k_y} dk_x dk_y = \frac{L^2}{4\pi^2} 2\pi k dk$$

The number of modes per unit frequency range

$$\boxed{D(\omega) = \frac{D(k)}{d\omega / dk} = \frac{A}{4\pi^2} 2\pi k \frac{1}{v_g}}$$

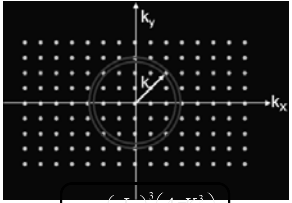
In three dimensions :

$$\boxed{D(\omega) = \frac{D(k)}{d\omega / dk} = \frac{V}{8\pi^3} 4\pi k^2 \frac{1}{v_g}}$$

complicated ! --must map out dispersion relation and count all k-values with each frequency

Continuum waves :

ω= v_gk depending only on amplitude of k



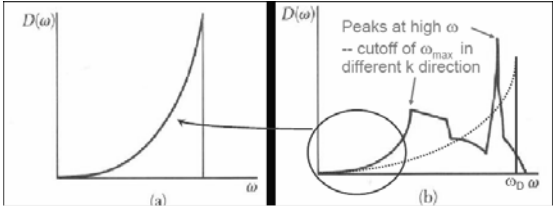
$$N = \left(\frac{L}{2\pi}\right)^3 \left(\frac{4\pi K^3}{3}\right)$$

The number of modes per unit frequency range for each polarization

$$\boxed{D(\omega) = \frac{V}{2\pi^2} \frac{\omega^2}{v_g^3}}$$

a quadratic dependence !

Quadratic at low ω



N primitive cells in the crystal,

A total number of acoustic phonon mode is N for each polarization.

Cutoff frequency

$$\omega_D = \left(\frac{6\pi^2 v_g^3 N}{V}\right)^{1/3}$$

Cutoff wave vector

$$k_D = \frac{\omega_D}{v_g} = \left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

Thermal energy

each polarization

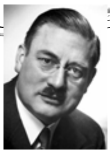
There are three polarizations : 2 transverse + 1 longitudinal

$$U = \frac{3V\hbar}{2\pi^2 v_g^3} \int_0^{\omega_D} d\omega \left(\frac{\omega^3}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \right) \quad \Leftarrow \quad x = \frac{\hbar\omega}{k_B T}$$

$$= \frac{3V\hbar}{2\pi^2 v_g^3} \left(\frac{k_B T}{\hbar}\right)^4 \int_0^{x_D} dx \left(\frac{x^3}{\exp(x) - 1} \right)$$

Defining the Debye temperature Θ $_D$

$$\Theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar}{k_B}\left(\frac{6\pi^2 v_g^3 N}{V}\right)^{1/3} = \frac{\hbar v_g}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$$



Peter Debye, 1884-1966 1936 Nobel prize winner in chemistry

Therefore x_D= hω $_D$/k_BT= Θ $_D$/TThe

$$\boxed{U = 9Nk_B T \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} dx \left(\frac{x^3}{\exp(x) - 1}\right)}$$

The total phonon energy

In classical model : equipartition theorem (0.5k_BT for each excitation mode)

3 translational + 3 vibrational modes : six degrees of freedom

U= N 6 (0.5kBT) = 3Nk_BT for N atoms in the crystal

C_V= 3Nk_B Dulong and Petit Law

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = \left(\frac{3V\hbar}{2\pi^2 v_g^3}\right)\frac{\partial}{\partial T}\left[\int_0^{\omega_D} d\omega \frac{\omega^3}{\exp(\hbar\omega/k_BT)-1}\right]$$

$$= \left(\frac{3V\hbar}{2\pi^2 v_g^3}\right)\left(-\frac{\hbar}{k_B}\right)\left(-\frac{1}{T^2}\right)\int_0^{\omega_D} d\omega \frac{\omega^4\exp(\hbar\omega/k_BT)}{(\exp(\hbar\omega/k_BT)-1)^2}$$

$$= 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x-1)^2}$$

$$\boxed{\begin{aligned} &\int_0^{x_D} dx\left(\frac{x^3}{e^x-1}\right) \to \frac{1}{3}(x_D)^3 = \frac{1}{3}\left(\frac{\Theta_D}{T}\right)^3 \\ &\int_0^{x_D} dx \frac{x^4e^x}{(e^x-1)^2} \to \frac{1}{3}(x_D)^3 = \frac{1}{3}\left(\frac{\Theta_D}{T}\right)^3 \end{aligned}}$$

At $T >> \Theta_D$, $\boxed{\begin{aligned} U &\longrightarrow 3Nk_BT \\ C_V &\longrightarrow 3Nk_B \end{aligned}}$

Einstein model(1907) : N identical oscillators of frequency ω

$$\langle U\rangle = \sum_K \sum_p \langle n_{K,p}\rangle \hbar\omega_{K,p} = \sum_i^{\text{mode}} \langle n_i\rangle \hbar\omega_i$$

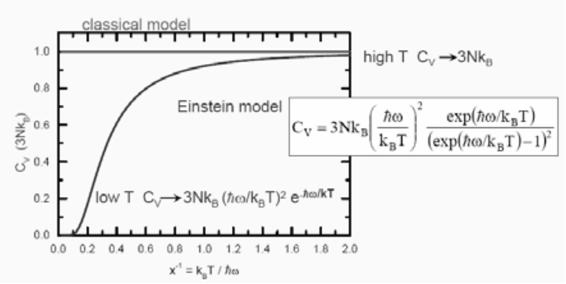
Einstein model

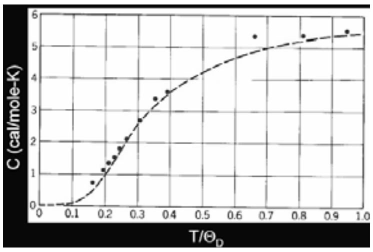
$$U = 3N\langle n\rangle\hbar\omega = \frac{3N\hbar\omega}{\exp(\hbar\omega/k_BT)-1}$$

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = 3Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{\exp(\hbar\omega/k_BT)}{(\exp(\hbar\omega/k_BT)-1)^2}$$

At high T, $C_V \to 3Nk_B$ same as the Dulongand Petitvalue

At Low T, $C_V \to 3Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2 \exp\left(-\frac{\hbar\omega}{k_BT}\right)$





Diamond,

Experimental data –red points

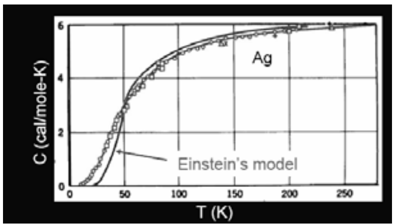
Einstein's model –blue curvew/.

Θ_D=1320K

Ann. Physik 22, 180 (1907)

Einstein theory shows correct trends with temperature.

For simple harmonic oscillator of spring constant C and mass M, $\omega = \sqrt{\frac{C}{M}}$



By Walther Nernst

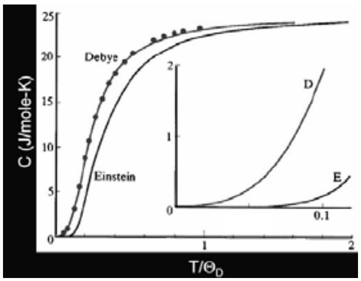
At low T, there are systematic deviations between data and Einstein model.
Einstein realized that the oscillations of a solid where complex,
far from single frequency.

Key point is that however low the temperature, there are always some modes with low enough frequencies to be excited.

Einstein model : At low T, $C_V \to 3Nk_B (\hbar\omega/k_BT)2\exp(-\hbar\omega/k_BT)$

Experimental data show T^3 dependence of C_V instead

Debye and Einstein models



Red points : Experimental data of Ag

Θ_D=225K

In the Einstein model, C decreases too rapidly at low temperatures.

Debye model gives correct T^3 dependence of C at low T.

Review

$C_V \Rightarrow U$

$$\langle U\rangle = \sum_i^{\text{mode}} \langle n_i\rangle \hbar\omega_i \Rightarrow = \int d\omega D(\omega) \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right)-1}$$

In three dimensions :

$$D(\omega) = \frac{D(k)}{d\omega/dk} = \frac{V}{8\pi^3} 4\pi k^2 \frac{1}{v_g}$$

N primitive cells in the crystal,

A total number of acoustic phonon mode is N for each polarization.

$$\int_0^\infty D(\omega)d\omega = \int_0^\infty \frac{V}{2\pi^2}\frac{\omega^2}{v_g^3} d\omega = N$$

$$\omega_D$$

Cutoff frequency $\omega_D = \left(\frac{6\pi^2 v_g^3 N}{V}\right)^{1/3}$

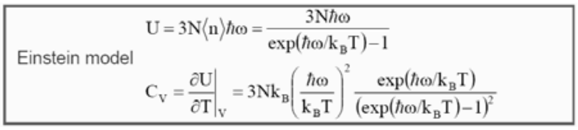
Cutoff wave vector $k_D = \frac{\omega_D}{v_g} = \left(\frac{6\pi^2 N}{V}\right)^{1/3}$

U $\Rightarrow$ **$3Nk_BT$**

C_V $\Rightarrow$ **$3Nk_B$**

Einstein model(1907) : N identical oscillators of frequency ω

$$\langle U\rangle = \sum_K \sum_p \langle n_{K,p}\rangle \hbar\omega_{K,p} = \sum_i^{\text{mode}} \langle n_i\rangle \hbar\omega_i$$



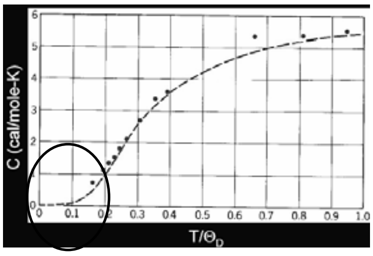
Einstein model

$$U = 3N\langle n\rangle\hbar\omega = \frac{3N\hbar\omega}{\exp(\hbar\omega/k_BT)-1}$$

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = 3Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{\exp(\hbar\omega/k_BT)}{(\exp(\hbar\omega/k_BT)-1)^2}$$

At high T, $C_V \to 3Nk_B$ same as the Dulongand Petitvalue

At Low T, $C_V \to$ $3Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2 \exp\left(-\frac{\hbar\omega}{k_BT}\right)$



Θ_D=1320K
Ann. Physik 22, 180 (1907)

Diamond,

Experimental data –red points

Einstein's model –blue curve

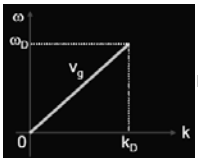
The Discrepancy of Einstein model

- **Einstein model also gave correctly a specific heat tending to zero at absolute zero, but the temperature dependence near T=0 did not agree with experiment.**
- **Taking into account the actual distribution of vibration frequencies in a solid this discrepancy can be accounted using one dimensional model of monoatomic lattice**

DebyeT^3model

Assume *continuum elastic phonon mode* only up to some cutoff ω_D

Number of phonon mode for each polarization is equal to N



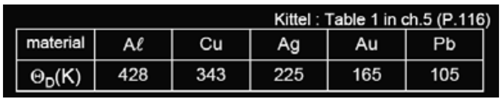
Debye frequency $\omega_D = \left(\frac{6\pi^2 v_g^3 N}{V}\right)^{1/3}$

Debye wave vector $k_D = \frac{\omega_D}{v_g} = \left(\frac{6\pi^2 N}{V}\right)^{1/3}$

Debye temperature $\Theta_D = \frac{\hbar\omega_D}{k_B}$

ω_D, Θ_D depend on v_g, n, ~ v_gn1/3

High for stiff, light materials


Kittel : Table 1 in ch.5 (P.116)

material	Aℓ	Cu	Ag	Au	Pb
Θ_D(K)	428	343	225	165	105

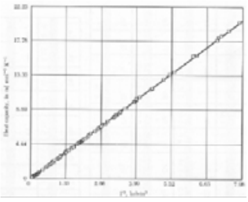
$$U = \frac{3V\hbar}{2\pi^2 v_g^3}\left(\frac{k_B T}{\hbar}\right)^4 \int_0^{x_D} dx \left(\frac{x^3}{e^x - 1}\right)$$

$$C_V = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{\left(e^x - 1\right)^2}$$

At very low temperature, T<<Θ_D, x_D= Θ_D/T →∞

$U \cong \frac{3\pi^4 N k_B T^4}{5\Theta_D^3}$ **and** $C_V \cong \frac{12\pi^4 N k_B T^3}{5\Theta_D^3} \cong 234 N k_B \left(\frac{T}{\Theta_D}\right)^3$

DebyeT^3approximation



T^3 observed in most insulators for T<0.1 Θ_D

solid Ar w/. Θ_D=92K

Why T^3 at low temperatures ?

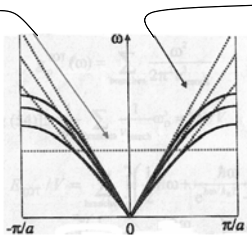
- *Only long wave length acoustic modes are thermally excited.*
- *These modes can be treated as an elastic continuum.*
- *The energy of short wave length modes is too high for them to be populated significantly at low temperatures.*

The Debye approximation has two main steps:

1. **Approximate the dispersion relation of any branch by a linear extrapolation of the small *k* behaviour:**

Einstein approximation to the dispersion

Debye approximation to the dispersion



2. Ensure the correct number of modes by imposing a cut-off frequency ω_D , above which there are no modes. The cut-off freqency is chosen to make the total number of lattice modes correct.

$$N = \int_0^{\omega_D} d\omega D(\omega) = \int_0^{\omega_D} d\omega \frac{V\omega^2}{2\pi^2 v_g^3}$$

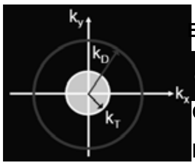
$$\omega_D = \left(\frac{6\pi^2 v_g^3 N}{V}\right)^{1/3}$$

$$k_D = \frac{\omega_D}{v_g} = \left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

$$\Theta_D = \frac{\hbar\omega_D}{k_B}$$

Other simple idea to understand T^3dependence :

Total phonon mode : $\omega \le \omega_D$ (or $k \le k_D = \frac{k_B}{\hbar v_g}\Theta_D$)



Excited phonon mode Thermal wavevector

$\omega \le k_B T/\hbar$ (or $k \le \omega/v_g = \frac{k_B}{\hbar v_g} T = k_T$)

Others are frozen out

Fraction excited at T : $\left(\frac{k_T}{k_D}\right)^3 = \left(\frac{T}{\Theta_D}\right)^3$

of the total volume in k-space

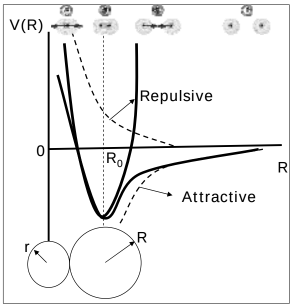
Each mode has energy *k_BT*

$U \sim 3N\left(\frac{T}{\Theta_D}\right)^3 k_B T$ $C_V \sim 12Nk_B\left(\frac{T}{\Theta_D}\right)^3$ **~ T^3**

too small but correct T^3 dependence

1. Any real crystal resists compression to a smaller volume than its equilibrium value more strongly than expansion due to a larger volume.

2. This is a departure from Hooke's law, since harmonic application does not produce this property.



The harmonic theory

$$V(r) = V(a) + \frac{(r-a)^2}{2}\left(\frac{d^2V}{dr^2}\right)_{r=a} + \ldots\ldots\ldots\ldots\ldots\ldots$$

1. In harmonic approximation phonons do not interact with each other, in the absence of boundaries, lattice defects and impurities (which also scatter the phonons), the thermal conductivity is infinite.

2. No thermal expansion

3. The heat capacity becomes constant at high temperatures

The anharmonic effects

Transport properties (non-equilibrium)

Conduction of sound and heat through the crystal

vibration	energy
Ultrasonic attenuation	Thermal conduction
excite single phonon mode measure decay of amplitude	apply temperature gradient measure heat current by phonons

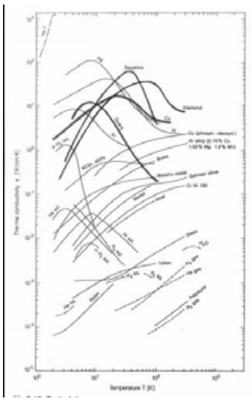
Phonon thermal conductivity

Apply temperature gradient ∇T →determine heat current density j_U

The flux of the thermal energy $\vec{j}_U = -\kappa \frac{dT}{dx}$

the energy transmitted across unit area per unit time

κ : thermal conductivity coefficient



In solids, heat is transported by phonon and free electrons.

For metals, it is electronic contribution that dominates the thermal conductivity.

This does not mean that insulators are necessarily poor thermal conductors.

Propagations of phonons ?

Ballistic   No interaction/scattering

In harmonic approximation in perfect, infinite crystal,

Expect no scattering → phonon modes are uncoupled,
independent plane waves and
standing waves

$$v = v_g = \frac{d\omega}{dk}$$

Diffusion **Phonons scatter, random walk through crystal**

Phonons scatter in real crystals.

Scattering processes :
- ✓ **boundary scattering**
- ✓ **defect scattering**
- ✓ **phonon-phonon scattering**

$$v << v_g = \frac{d\omega}{dk}$$

The flux of thermal energy is based on that
the process of thermal energy transfer is a random process.

ie. the energy diffuses through the crystal, suffering frequent collisions.

Ballistic : $\vec{J}_U \propto \Delta T$ **across the whole sample**

Diffusive : $\vec{J}_U \propto \nabla T = \frac{dT}{dx}$ **local**

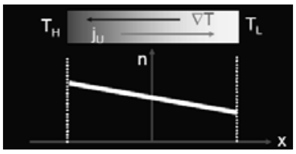
For diffusion, thermal conductivity is defined by

⇐
phonon properties
Scattering
crystal quality (size, defect)
temperature

j_U[Watt/m^2], κ [(Watt/m^2)/(K/m)] = [Watt/m/K]

κ ← **Kinetic theory of gases**

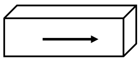
consider phonons as gases contained in a crystal volume
calculate diffusion in the presence of temperature gradient



Fick's law

$$\frac{dn}{dx} = \frac{dn}{dT}\frac{dT}{dx}$$

n : concentration of molecules
C : heat capacity per unit volume = nc
v_g: phonon velocity
l : phonon mean free path $= v_g\,\tau$



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thermal energy per unit volume across unit area

$$j_U = -(C\Delta T)\langle v_x\rangle \cdot t(=1) \quad \Leftarrow \quad \Delta T = \frac{dT}{dx} l_x$$

Average value

$$\langle v_x^2 \rangle = \frac{1}{3}\langle v_g^2 \rangle$$

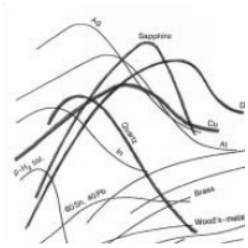
$$j_U = -n\langle v_x^2\rangle c\tau\frac{dT}{dx} = -\frac{1}{3}C\langle v_g^2\rangle\tau\frac{dT}{dx}$$

$$\Rightarrow \quad j_U = -\frac{1}{3}Cv_g l\frac{dT}{dx}$$

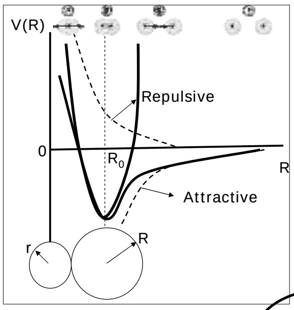
$$j_U = -\frac{1}{3}Cv_g l\frac{dT}{dx} \quad \Rightarrow$$

thermal conductivity

$$\kappa = \frac{1}{3}Cv_g l \qquad \kappa \propto l$$



Review



Problem:

thermal conductivity

thermal expansion

$$U(x)=U(x_0)+\frac{\partial U}{\partial x}\Big|_{x_0}(x-x_0)+\frac{1}{2}\frac{\partial^2 U}{\partial x^2}\Big|_{x_0}(x-x_0)^2+\frac{1}{6}\frac{\partial^3 U}{\partial x^3}\Big|_{x_0}(x-x_0)^3+\ldots$$

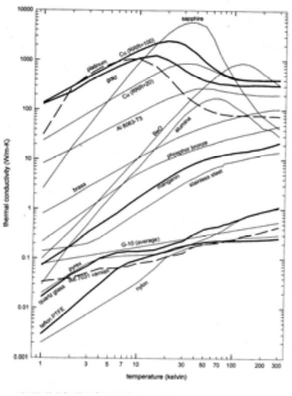
Phonon thermal conductivity

The flux of the thermal energy $\vec{j}_U=-\kappa\frac{dT}{dx}$

Propagations of phonons ? Diffusion

Scattering processes :
- ✓ **boundary scattering**
- ✓ **defect scattering**
- ✓ **phonon-phonon scattering**

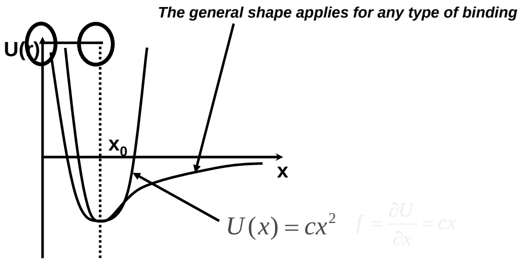
thermal conductivity $\boxed{\kappa=\frac{1}{3}Cv_g l}$



$$\boxed{\kappa=\frac{1}{3}Cv_g l}$$

Thermal expansion

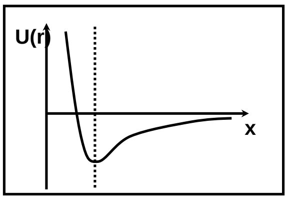
From anharmonic terms in binding potential



$U(x)=cx^2$ $f=\frac{\partial U}{\partial x}=cx$

$$U(x)=U(x_0)+\frac{\partial U}{\partial x}\Big|_{x_0}(x-x_0)+\frac{1}{2}\frac{\partial^2 U}{\partial x^2}\Big|_{x_0}(x-x_0)^2+\frac{1}{6}\frac{\partial^3 U}{\partial x^3}\Big|_{x_0}(x-x_0)^3+\ldots$$

$$\Delta U(x)=U(x)-U(x_0)=\frac{1}{2}\frac{\partial^2 U}{\partial x^2}\Big|_{x_0}(x-x_0)^2+\frac{1}{6}\frac{\partial^3 U}{\partial x^3}\Big|_{x_0}(x-x_0)^3+\ldots$$



Reset the equilibrium,
let displacement x-x$_o$→x

$$U(x)=\underset{\text{harmonic term}}{cx^2}\underset{\text{anharmonic term}}{\boxed{-gx^3-fx^4\ldots}}$$

anharmonic term gives the net change of <x>

$$\boxed{\langle x\rangle=\frac{\int_{-\infty}^{\infty}dx\,x\exp\left[-\frac{U(x)}{k_BT}\right]}{\int_{-\infty}^{\infty}dx\exp\left[-\frac{U(x)}{k_BT}\right]}\cong\frac{\int_{-\infty}^{\infty}dx\,x\exp\left[-\frac{cx^2-gx^3-fx^4}{k_BT}\right]}{\int_{-\infty}^{+\infty}dx\exp\left[-\frac{cx^2-gx^3-fx^4}{k_BT}\right]}}$$

thermal energy causes fluctuation of x from x$_o$

--Thermal expansion

$$\boxed{\exp\left(-\frac{cx^2-gx^3-fx^4}{k_BT}\right)=\exp\left(-\frac{cx^2}{k_BT}\right)\exp\left(\frac{gx^3}{k_BT}+\frac{fx^4}{k_BT}\right)}$$

$$\cong\exp\left(-\frac{cx^2}{k_BT}\right)\left(1+\frac{gx^3}{k_BT}+\frac{fx^4}{k_BT}\right)$$

Using $e^x=1+x+\frac{x^2}{2!}+\frac{x^3}{3!}+...$

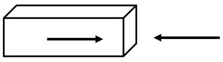
$$\langle x\rangle=\frac{3g}{4C^2}k_BT$$

linear dependence of T

high T limit

Coefficient of linear expansion

Phonon thermal conductivity



$\Delta T=-\frac{dT}{dx}l_x$ ⟹

$$j_U=-\frac{1}{3}Cv_gl\frac{dT}{dx}$$

thermal conductivity $\kappa=\frac{1}{3}Cv_gl$

The mean free path l

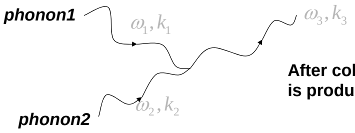
✓defect scattering

✓ phonon-phonon scattering

Phonon-phonon scattering

phonon displaces atom
which changes the force constant C (anharmonic terms)

⟹ **scatter other phonons** **three phonon process**



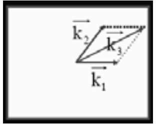
After collision another phonon is produced

$\hbar\omega_3=\hbar\omega_1+\hbar\omega_2$ ⟹ **conservation of energy**

$\hbar k_3=?\hbar k_1+\hbar k_2$ **conservation of momentum ?**

Normal processes : all k_3 are in BZ

1st BZ in k-space

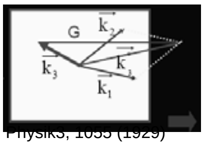


$\vec{k}_1+\vec{k}_2=\vec{k}_3$

crystal momentum is conserved

Umklapp processes : k_3 is outside BZ

1st BZ in k-space



$\vec{k}_1+\vec{k}_2=\vec{k}_3^*$ outside BZ

$\vec{k}_3+\vec{G}=\vec{k}_3^*$

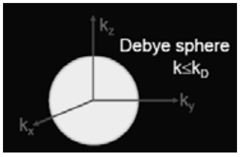
$\vec{k}_1+\vec{k}_2=\vec{k}_3+\vec{G}$

R. Peierls, Ann. Physik3, 1055 (1929)

crystal momentum is not conserved

U-processes occur at high temperatures : require large k (ie. large ω)

How large ?



$$\langle n(\omega,T)\rangle=\frac{1}{\exp\left[\frac{\hbar\omega}{k_BT}\right]-1}$$

$$\langle k\rangle\sim\frac{1}{2}k_D$$

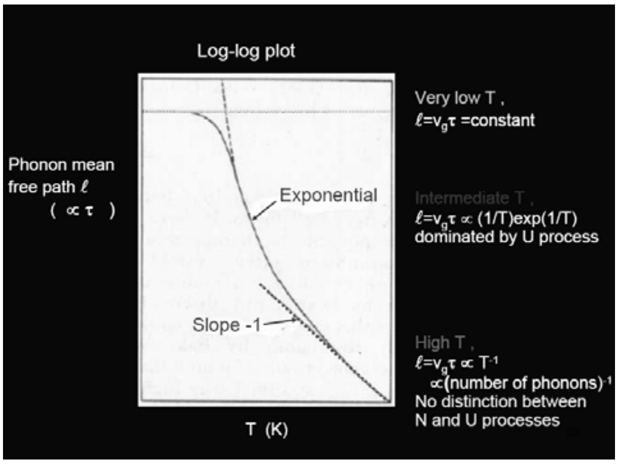
$$\langle\omega\rangle\sim\frac{1}{2}\omega_D$$

$$\langle E\rangle\sim\frac{1}{2}\hbar\omega_D\sim\frac{1}{2}k_B\Theta_D$$

Phonon-phonon scattering: rate $\ell^{-1}\propto$ # of phonons involved

U-process : $\ell^{1}\propto N_U$ ~ exp(-Θ_D/2T)(phonons w/. large k only)at intermediate temperatures

At very low temperatures, phonons are populated at low k mode U process can not occur

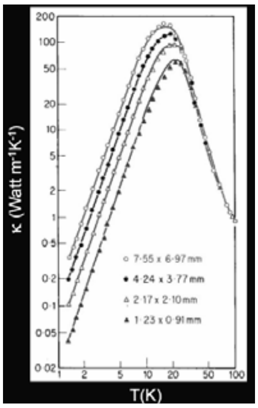


Very low T , $\ell=v_g\tau$ =constant

Intermediate T , $\ell=v_g\tau\propto$ (1/T)exp(1/T) dominated by U process

High T , $\ell=v_g\tau\propto T^{-1}$ $\propto$(number of phonons)$^{-1}$ No distinction between N and U processes

Thermal conductivity of LiF crystal bar w/. different cross sectional areas



Data show

1. **Below 10K, $\kappa \propto T^3$**
2. **As temperature increases, κ increases and reaches a maximum around 18K.**
3. **Above 18K, κ decreases w/. increasing temperature and follows that exp(1/T).**
4. **Cross sectional area influences κ below 20K. Bigger area crystal has, larger κ it has.**

Summary of part (I)

- **Solids are defined by their capacity to be solid**
  - **–to resist shear stress**
- **A crystal is truly solid (as opposed to a glass which is just a "slow liquid")**
- **Crystalline order is defined by the regular positions of the nuclei**
  - **crystal structure = lattice + basis**
- **Lattice and reciprocal lattice**
  - **Diffraction and experimental studies**
  - **Brillouin zone**
- **Crystal binding**
  - **Type of binding**

Summary of part (I)

- **Vibrations of atoms**
  - **Harmonic approximation**
- **Quantization of vibrations**
  - **phonons act like particles**
  - **--can be created or destroyed by inelastic scatterings**
- **Thermal properties**
  - **Fundamental law of probabilities**
  - **Planck distribution for phonons**

Heat capacity : C

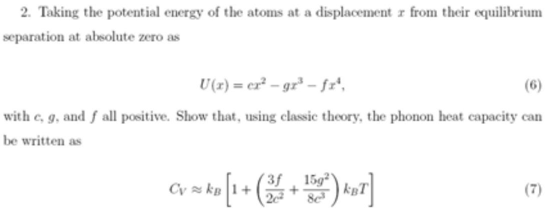
Low T, C $\propto$T3 and High T, C ~ constant

Thermal conductivity : κ

maximum as function of T

Homework

5.1

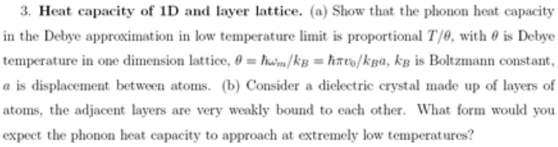


2. Taking the potential energy of the atoms at a displacement x from their equilibrium separation at absolute zero as

$$U(x) = cx^2 - gx^3 - fx^4, \tag{6}$$

with c, g, and f all positive. Show that, using classic theory, the phonon heat capacity can be written as

$$C_V \approx k_B\left[1 + \left(\frac{3f}{2c^2} + \frac{15g^2}{8c^3}\right)k_BT\right] \tag{7}$$



3. **Heat capacity of 1D and layer lattice.** (a) Show that the phonon heat capacity in the Debye approximation in low temperature limit is proportional T/θ, with θ is Debye temperature in one dimension lattice, $\theta = \hbar\omega_m/k_B = \hbar\pi v_0/k_Ba$, k_B is Boltzmann constant, a is displacement between atoms. (b) Consider a dielectric crystal made up of layers of atoms, the adjacent layers are very weakly bound to each other. What form would you expect the phonon heat capacity to approach at extremely low temperatures?

History of solid electron theory

In 1897, J. J. Thomson

Discovered electron

In 1900, P. Drude

Classic free electron gas

In 1925, E. Fermi and W. Pauli

Pauli exclusion principle

Fermi Dirac statistics

History of solid electron theory

In 1928, A. Sommerfel

Quantum free electron gas

Debby, Heisenberg, Pauli, Bethe

In 1928, F. Bloch

Bloch theory energy band

In 1963, W. Kohn

Density functional theory

Chapter Six
Free Electron Fermi Gas

- **Energy levels in one dimension**
- **Free electron gas in three dimension**
- **Effect of temperature on the Fermi-Dirac distribution**
- **Heat capacity of the electron gas**
- **Electron conductivity and Ohm's law**
- **Motion in magnetic field**
- **Thermal conductivity of metal**

Hendrik A. Lorentz

The Nobel Prize in Physics 1902

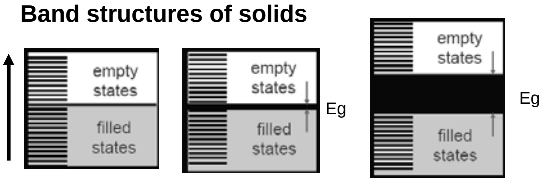
In a theory which has given results like these, there must certainly be a great deal of true.

---H.A. Lorentz

What determines if the crystal will be a metal, an insulator, or a semiconductor ?

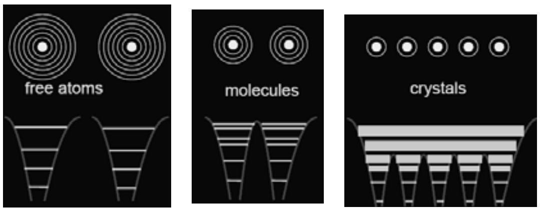
Band structures of solids

Band structures of solids

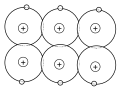


Conduction band partially filled	Valence band filled /Conduction band empty $E_g<k_BT$	$E_g>>k_BT$
Metal	semiconductor	Insulator
Conduction electrons are available	Conduction electrons are available at high T or by doping	No conduction electrons

Basic idea : pushing atoms together to form a crystal



discrete energy levels splitting of levels band of states



crystal

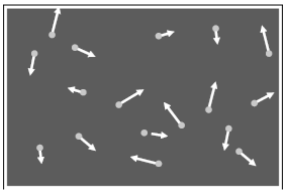
- **Low energy levels remain discrete and localized on atoms.**
  Core states
- **High energy levels split to form bands of closely energy levels that can extend through the crystal**
  valence and conduction bands
- **This mobile electron becomes a conduction electron in a solid.**
- **The charge density associated the positive ion cores is spread uniformly throughout the metal so that the electrons move in a constant electrostatic potential. All the details of the crystal structure is lost when this assunption is made.**
- **this potential is taken as zero and the repulsive force between conduction electrons are also ignored.**

Free electron model
–treat conduction electrons as free particles

- Continuum states–density of states
- Fermi statistics–occupancy of states
- Thermal properties–Thermal energy, heat capacity, …
- Electrical and thermal transports–scatterings of conduction electron
- Magnetic field effect

The models of Drude and Sommerfeld free electron gas

Free conduction electrons in the box



Not interacting electrons(except w/. walls of the box)

$$\varepsilon = K.E. = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m} = \frac{3}{2}k_B T$$

In reality, interactions of electrons :

Ions – steady Coulomb interaction (electron binding)
But
- Screening by core electrons weakens the attraction at large distance
- Pauli exclusion principle requires that conduction electrons stay away from core electrons localized at the atoms.

Electrons – strong Coulomb repulsion
But
- Coulomb repulsion
- Pauli exclusion principle

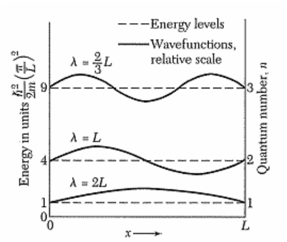
⟹ Electrons tend to stay apart

In one dimension

Schrödinger equation

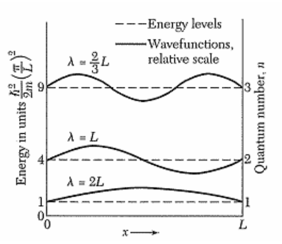
$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi + U(x)\Psi = \varepsilon\Psi$$

Boundary condition



$\varphi_n = A\sin(k_n x)$ W\. $k_n = \frac{n\pi}{L}$ **and** $\varepsilon = \frac{(\hbar k_n)^2}{2m} = \frac{\hbar^2(n\pi)^2}{2mL^2}$

How to accommodate N electrons on the line ?



Pauli exclusion principle+ spin degeneracy

(two spins ↑ ↓ per level)

Start to fill the levels from the bottom (n=1) and continue to fill higher levels with electrons until all N electrons are accommodated.

1,..., n_F, where n_F is the value of n for the uppermost filled level.

In general cases, such as periodic chain

Boundary condition $\varphi_n(x) = \varphi_n(x+L)$ $k_n = \pm\frac{n2\pi}{L}$

One state every k-interval $\Delta k = 2\pi/L$

Density of states $D(k) = \frac{1}{\Delta k_n} = \frac{1}{(2\pi/L)} = \frac{L}{2\pi}$

$$2D(k)dk = D(\varepsilon)d\varepsilon$$

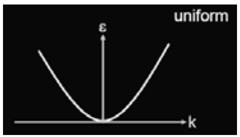
$$D(\varepsilon) = \frac{2D(k)dk}{d\varepsilon} = \frac{2(L/2\pi)}{d\varepsilon/dk}$$

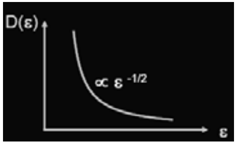
and $\varepsilon = \hbar^2 k^2/2m$

$$D(\varepsilon) = \frac{2(L/2\pi)}{\hbar^2 k/m} = \frac{\sqrt{m}L}{\sqrt{2}\pi\hbar}\sqrt{\frac{2m}{(\hbar k)^2}}$$

$$= \frac{\sqrt{m}L}{\sqrt{2}\pi\hbar}\frac{1}{\sqrt{\varepsilon}}$$

singly spin density of states in one dimension





In three dimensions

Schrödinger equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi + U(x,y,z)\Psi = \varepsilon\Psi$$

0

Boundary condition : Ψ is periodic in *x*, *y*, and *z* with period L

$$k_x = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \ldots \quad ; k_y = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \ldots \quad ; k_z = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \ldots$$

One state every k-volume interval $\Delta k_x \Delta k_y \Delta k_z = (2\pi/L)3$

$$D(k) = \frac{1}{\Delta k_x \Delta k_y \Delta k_z} = \frac{1}{(2\pi/L)^3} = \left(\frac{L}{2\pi}\right)^3 = \frac{V}{(2\pi)^3}$$

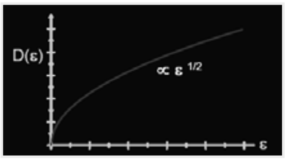
$$D(\varepsilon)d\varepsilon = D(k)4\pi k^2 dk = \frac{V}{(2\pi)^3}4\pi k^2\frac{1}{d\varepsilon/dk}d\varepsilon$$

$$= \frac{4\pi k^2 V}{(2\pi)^3}\frac{m}{\hbar^2 k}d\varepsilon = \frac{V}{4\pi^2}\frac{\sqrt{(2m)^3\varepsilon}}{\hbar^3}d\varepsilon$$

$$D(\varepsilon) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}$$

singly spin density of states in three dimensions

x 2 for spin degeneracy



Conduction electrons : free to move through the crystal

Density of conduction electrons n = N/V

typically n ~ 10^{22} ~ 10^{23}cm^{-3}

mostly “s”orbital electrons but also “p”and “d”

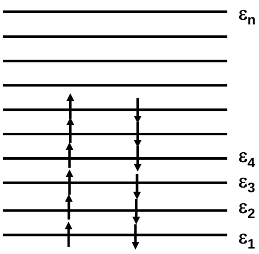
Difference between electrons and phonons

	Electron	Phonons
Number	N=nV fixed	N ~ k_BT varies w/. T
Degeneracy	Fermions (Fermi-Dirac statistics) two per orbital state ↑ ↓	Bosons (Planck distribution) n per mode excited
Dispersion	$\varepsilon \propto k^2$	$\omega \propto k$
Density of states	$D(\varepsilon) \propto \varepsilon^{1/2}$	$D(\omega) \propto \omega^2$

up to ω_D Debye

How do we determine ground states ?

Ground states T=0, Fill energy level from bottom : 2 per level ↑ ↓

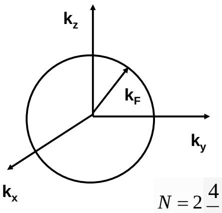


ε_F ←

highest level occupied w/. ε_F

Fermi energy

Energy Maximum energy : $\varepsilon_F = \hbar^2 k_F^2/2m$



States w/. $k \leqslant k_F$ are occupied

Fermi sphere–volume in k-space occupied by electrons in the ground states

Fermi surface–k_F states w/. $\varepsilon = \varepsilon_F$

$$N = 2\,\frac{4}{3}\pi k_F^3\,\frac{V}{(2\pi)^3} = \#\,of\ electrons$$

spin

volume of Fermi sphere

D(k)

$$\Rightarrow\quad k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3} \quad \text{and} \quad \varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

typically, ~ 10^{-8}cm^{-1} ~ 1 –10 eV

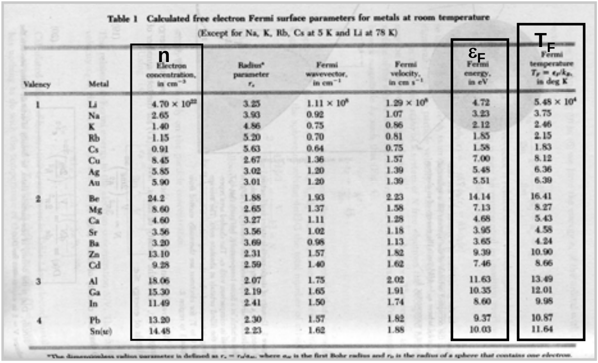
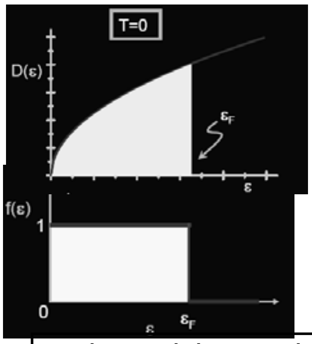


Table 1 Calculated free electron Fermi surface parameters for metals at room temperature
(Except for Na, K, Rb, Cs at 5 K and Li at 78 K)

Valency	Metal	n Electron concentration, in cm^{-3}	Radius* parameter r_s	Fermi wavevector, in cm^{-1}	Fermi velocity, in cm s^{-1}	ε_F Fermi energy, in eV	T_F Fermi temperature $T_F = \varepsilon_F/k_B$, in deg K
1	Li	4.70×10^{22}	3.25	1.11×10^8	1.29×10^8	4.72	5.48×10^4
	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	Be	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
	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
	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
	Sn(w)	14.48	2.23	1.62	1.88	10.03	11.64

*The 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.

Fermi-Dirac distribution



$$N = \int_0^\infty D(\varepsilon) f(\varepsilon)\,d\varepsilon$$

$$= \int_0^{\varepsilon_F} D(\varepsilon)\,d\varepsilon$$

f(ε) is the probability that a state of energy ε is occupied

$$f(\varepsilon) = \begin{cases} 1, & \varepsilon \le \varepsilon_F \\ 0, & \varepsilon > \varepsilon_F \end{cases}$$

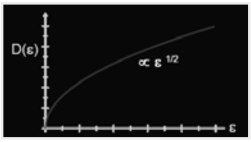
Fermi energy is important because electronic properties are dominated by states near ε_F only.

Review

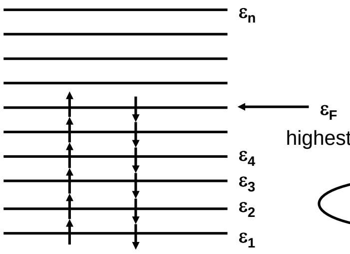
- Free electron mode
  treat conduction electrons as free particles
- The potential well

In one dimensions $D(\varepsilon)=\frac{\sqrt{m}L}{\sqrt{2}\pi\hbar}\frac{1}{\sqrt{\varepsilon}}$

In three dimensions $D(\varepsilon)=\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}$



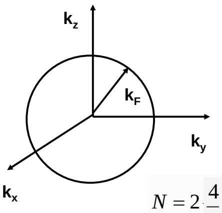
- Ground states T=0, Fill energy level from bottom



highest level occupied w/. ε_F

Fermi energy

Energy Maximum energy : $\varepsilon_F = \hbar^2 k_F^2/2m$

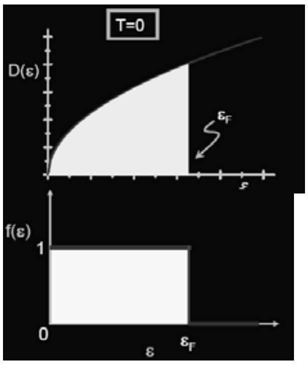


Fermi sphere

Fermi surface–$k_F$states w/. $\varepsilon = \varepsilon_F$

$$N = 2\,\frac{4}{3}\pi k_F^3\,\frac{V}{(2\pi)^3} = \#\text{of electrons}$$

$k_F=\left(\frac{3\pi^2 N}{V}\right)^{1/3}$ **and** $\varepsilon_F=\frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$



$$N=\int_0^\infty D(\varepsilon)f(\varepsilon)d\varepsilon = \int_0^{\varepsilon_F} D(\varepsilon)d\varepsilon$$

f(ε) is the probability that a state of energy ε is occupied

$$f(\varepsilon)=\begin{cases}1, & \varepsilon\le\varepsilon_F\\ 0, & \varepsilon>\varepsilon\end{cases}$$

Finite temperatures

What is the probability of occupancy of an electron state?

What is free electrons contribution to heat capacity?

$C_V \propto T^3$ or Constant

Finite temperatures

Kinetic energy of electron increases due to the increase of thermal energy

occupy higher energy levels

What is the probability of occupancy of an electron state w/. energy ε at T ?

Boltzmann factor exp(-ε/k_BT) ? For phonons (Bosons)

Electrons are Fermions
-------quantum effects such as Pauli exclusion principle

Standard problem in statistics

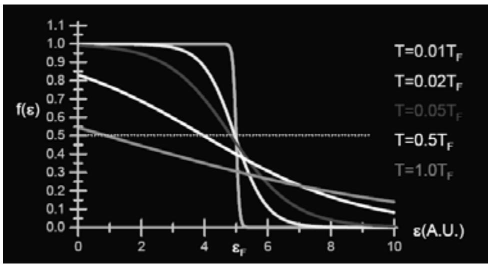
Fermi-Dirac distribution

$$f(\varepsilon) = \frac{1}{\exp[(\varepsilon - \mu)/k_B T] + 1}$$

where μ is the chemical potential to conserve electron number.

- At T=0 $\mu = \varepsilon_F$, when $\varepsilon = \mu = \varepsilon_F$, f($\varepsilon$) changes discontinuously
- At finite T, when $\varepsilon = \mu$, f(ε)=1/2
- When (ε-μ) >> k_BT, f(ε) Boltzmann distribution

(1) 0 ≤f(ε,T) ≤1



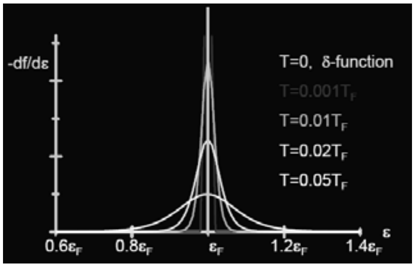
(2) when T<0.1T_F, $\mu \approx \varepsilon_F$, and f(ε,T)=1/2 when ε =E_F

when ε <μ, f(ε,T)>1/2

when ε>μ, f(ε,T)<1/2

(3) Electrons excited from below ε_F to above ε_F as T is increased

Δ ε ~ k_BT



Spread energy region increases with increasing temperature.

(4) μ= μ(T) decreases as T increased

why ?

What does determine μ? Total number of electrons is conserved

$$\Rightarrow N = \int_0^\infty d\varepsilon \frac{V}{4\pi^2} \frac{\sqrt{(2m)^3 \varepsilon}}{\hbar^3} \frac{1}{\exp((\varepsilon - \mu)/k_B T) + 1}$$

Hence, $\mu(T) = \varepsilon_F \left(1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F}\right)^2\right)$

Homework :Calculate the μ(T) when temperature is finite.

(5) Useful expression for D(ε)

$$D(\varepsilon) = \frac{dn_{state}}{d\varepsilon} = \frac{V}{4\pi^2} \frac{\sqrt{(2m)^3}}{\hbar^3} \sqrt{\varepsilon} = c\sqrt{\varepsilon}$$

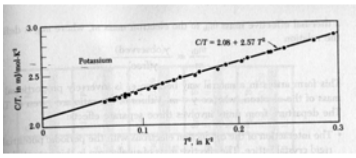
$$\boxed{\begin{aligned} N &= \int_0^\infty d\varepsilon D(\varepsilon) f(\varepsilon) \\ &= \int_0^{\varepsilon_F} d\varepsilon c\sqrt{\varepsilon} = \frac{2c}{3}\sqrt{\varepsilon_F^3} \end{aligned}}$$

T=0

where $c = \frac{3N}{2\sqrt{\varepsilon_F^3}}, D(\varepsilon) = \frac{3N\sqrt{\varepsilon}}{2\sqrt{\varepsilon_F^3}}$ and $D(\varepsilon_F) = \frac{3N}{2\varepsilon_F}$

Total thermal energy and heat capacity of electrons at T

Classical point of view, U = $N_e(3k_BT/2)$ and $C_V = N_e(3k_B/2)$

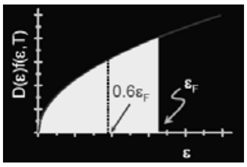


In reality, much smaller at room T

Not every electrons gains energy $3k_BT/2$

$$U = \int_0^{\infty} d\varepsilon D(\varepsilon) f(\varepsilon, T)\varepsilon$$

At ground state, T=0

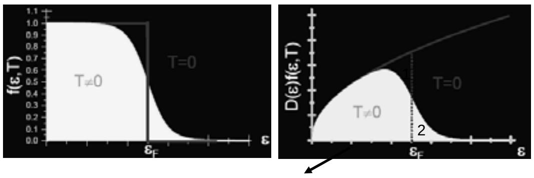


$$U = \int_0^{\varepsilon_F} d\varepsilon \frac{3N}{2\sqrt{\varepsilon_F^3}}\sqrt{\varepsilon}\varepsilon = \frac{3N}{2\sqrt{\varepsilon_F^3}}\frac{2}{5}\sqrt{\varepsilon_F^5}$$

$$= \frac{3N}{5}\varepsilon_F$$

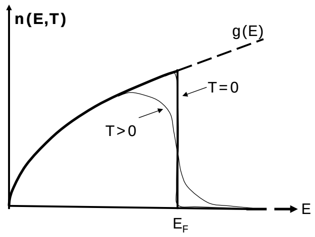
Average energy of each electron < ε > = 0.6ε_F

At finite temperature (T≠0), electrons are excited to higher energy states and U(T) increases.



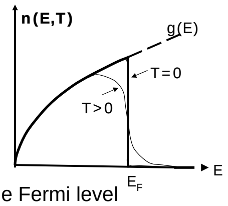
The filled orbital at finite temperature

- Fermi-Dirac distribution function is a symmetric function; at finite temperatures, the same number of levels below E_F is emptied and same number of levels above E_F are filled by electrons.



Qualitative arguments

When we heat the specimen from absolute zero not every electron gains an energy ~*k*k_BT as expected classically.



energy range k_BT of the Fermi level

number of electrons excited	Nk_BT/E_F
thermal energy of each electron	$3/2k_BT$
total electronic thermal kinetic energy	$U\sim(Nk_BT/E_F)k_BT$
electronic heat capacity	$C_{el}=dU/dT\sim3/2Nk_B(k_BT/E_F)$

Total energy

$$U(T) = \int_0^{\infty} d\varepsilon D(\varepsilon) f(\varepsilon, T)\varepsilon = U(0K) + \Delta U(T)$$

$$\Downarrow$$

$$\Delta U(T) = \int_0^{\infty} d\varepsilon D(\varepsilon) f(\varepsilon, T)\varepsilon - \int_0^{\varepsilon_F} d\varepsilon D(\varepsilon)\varepsilon$$

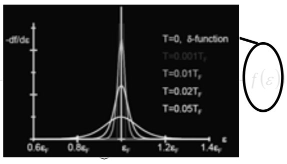
$$N = \int_0^{\infty} d\varepsilon\, D(\varepsilon)\, f(\varepsilon) = \int_0^{\varepsilon_F} d\varepsilon\, D(\varepsilon)$$

$$\boxed{\int_0^{\varepsilon_F} + \int_{\varepsilon_F}^{\infty}} d\varepsilon\ \varepsilon_F D(\varepsilon)\, f(\varepsilon) = \boxed{\int_0^{\varepsilon_F} d\varepsilon\, \varepsilon_F D(\varepsilon)}$$

$$\Delta U = \int_{\varepsilon_F}^{\infty} d\varepsilon(\varepsilon - \varepsilon_F) D(\varepsilon) f(\varepsilon) + \int_0^{\varepsilon_F} d\varepsilon(\varepsilon_F - \varepsilon) D(\varepsilon)(1 - f(\varepsilon))$$

First integral gives energy needed to take electrons from ε_F to the orbitals of energy ε> ε_F	Scend integral gives energy needed to bring electrons to ε_F from the orbitals of below ε_F

Heat Capicity



$$\Delta U = \int_{\varepsilon_F}^{\infty} d\varepsilon(\varepsilon - \quad f(\varepsilon))$$

$$C_e = \frac{dU}{dT} = \int_0^{\infty} d\varepsilon(\varepsilon - \varepsilon_F) D(\varepsilon) \frac{\partial f(\varepsilon, T)}{\partial T}$$

In general, $T/T_F<0.01$, df/dT has non-zero value within couples of k_BT
D(ε) is about D(ε_F) in the energy regime $\varepsilon_F \pm k_BT$

$$C_e = D(\varepsilon_F)\int_0^{\infty} d\varepsilon(\varepsilon - \varepsilon_F) \frac{\partial f(\varepsilon, T)}{\partial T}$$

$$C_e = D(\varepsilon_F)\int_0^\infty d\varepsilon(\varepsilon-\varepsilon_F)\frac{\partial f(\varepsilon,T)}{\partial T}$$

$$\left.\frac{\partial f(\varepsilon,T)}{\partial T}\right|_\varepsilon = \frac{d}{dT}\left[\frac{1}{\exp((\varepsilon-\varepsilon_F)/(k_BT))+1}\right]$$

$$= \frac{(\varepsilon-\varepsilon_F)}{k_BT^2}\left[\frac{\exp((\varepsilon-\varepsilon_F)/(k_BT))}{(\exp((\varepsilon-\varepsilon_F)/(k_BT))+1)^2}\right]$$

$$= \frac{x}{T}\frac{e^x}{(e^x+1)^2} \qquad \text{where } x = \frac{\varepsilon-\varepsilon_F}{k_BT}$$

Ignore the variation of the chemical potential with temperature

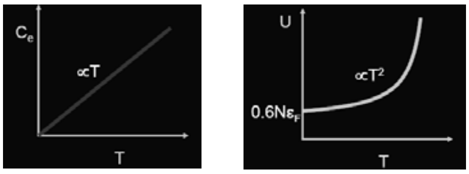
$$C_e = D(\varepsilon_F)k_B^2T\int_{-\varepsilon_F/k_BT}^{\infty} dx\,x^2\frac{e^x}{(e^x+1)^2}$$

$$\int_{-\infty}^{\infty} dx\,x^2\frac{e^x}{(e^x+1)^2} = \frac{\pi^2}{3}$$

$$C_e = D(\varepsilon_F)k_B^2T\frac{\pi^2}{3} = \frac{\pi^2}{3}\frac{3N}{2k_BT_F}k_B^2T$$

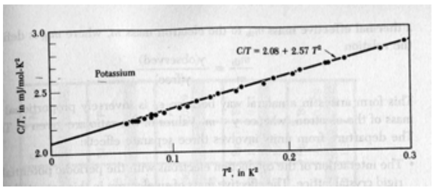
$$= \boxed{\frac{1}{2}\pi^2Nk_B\frac{T}{T_F}} \quad \propto T$$

Free electrons contribution to heat capacity



In general, when $T \ll \Theta_D$ and $T \ll T_F = \varepsilon_F/k_B$

$C = \gamma T + AT^3$ sum of electron and phonon contributions



$$\gamma = \frac{\pi^2}{2}\frac{Nk_B}{T_F}$$ $\propto T_F^{-1} \propto$ m (mass of electron)

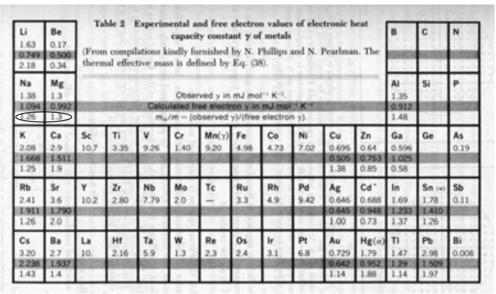


Table 2 Experimental and free electron values of electronic heat capacity constant γ of metals

(From compilations kindly furnished by N. Phillips and N. Pearlman. The thermal effective mass is defined by Eq. (38).

Observed γ in mJ mol⁻¹ K⁻².
Calculated free electron γ in mJ mol⁻¹ K⁻²
m_{th}/m = (observed γ)/(free electron γ).

Li 1.63 0.749 2.18	Be 0.17 0.500 0.34											B	C	N
Na 1.38 1.094 1.26	Mg 1.3 0.992 1.3											Al 1.35 0.912 1.48	Si	P
K 2.08 1.668 1.25	Ca 2.9 1.511 1.9	Sc 10.7	Ti 3.35	V 9.26	Cr 1.40	Mn(γ) 9.20	Fe 4.98	Co 4.73	Ni 7.02	Cu 0.695 0.505 1.38	Zn 0.64 0.753 0.85	Ga 0.596 1.025 0.58	Ge	As 0.19
Rb 2.41 1.911 1.26	Sr 3.6 1.790 2.0	Y 10.2	Zr 2.80	Nb 7.79	Mo 2.0	Tc —	Ru 3.3	Rh 4.9	Pd 9.42	Ag 0.646 0.645 1.00	Cd* 0.688 0.948 0.73	In 1.69 1.233 1.37	Sn (w) 1.78 1.410 1.26	Sb 0.11
Cs 3.20 2.238 1.43	Ba 2.7 1.937 1.4	La 10.	Hf 2.16	Ta 5.9	W 1.3	Re 2.3	Os 2.4	Ir 3.1	Pt 6.8	Au 0.729 0.642 1.14	Hg(α) 1.79 0.952 1.88	Tl 1.47 1.29 1.14	Pb 2.98 1.509 1.97	Bi 0.008

Thermal effective mass $\frac{m_{th}}{m} = \frac{\gamma(observed)}{\gamma(free)}$

m_{th}, obtained from measured γ observed, is different from m_e.

Three separate effect

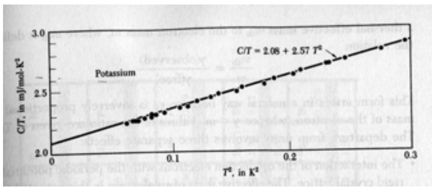
- Interaction between conduction electrons with periodic potential of the crystal lattice.
  ------Band effective mass
- Interaction between conduction electrons with phonons.
  moving electrons drag nearby ions along
- Interaction between conduction electrons with themselves.
  A moving electron causes an inertial reaction in the surrounding electron gas.

For some materials, m_{th}can be 1000me. Heavy Fermions

such as $CeAl_3$, $CeCu_2Si_2$,…and other exotic superconductors.

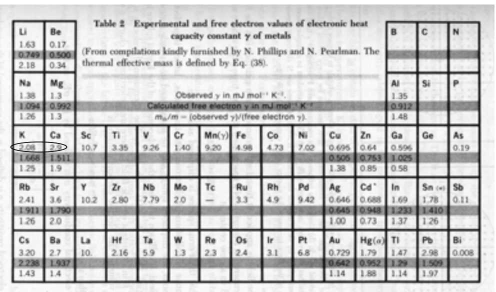
In general, when T<<Θ_D and T<<$T_F=\varepsilon_F/k_B$

C = $\underline{\gamma T}$ + $\underline{AT^3}$ sum of electron and phonon contributions



$$C_e=\frac{1}{2}\pi^2Nk_B\frac{T}{T_F}\qquad \gamma=\frac{\pi^2}{2}\frac{Nk_B}{T_F}$$

$\propto T_F^{-1} \propto$ m (mass of electron)



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such as $CeAl_3$, $CeCu_2Si_2$,…and other exotic superconductors.

Transport properties

Applying $\vec{E},\vec{\nabla}T \Rightarrow \vec{J},\vec{J}_U$

driving field current density

Electric current density $\vec{J}=\sigma\vec{E}+L_T\left(-\vec{\nabla}T\right)$

Heat current density $\vec{J}_U=\kappa\left(-\vec{\nabla}T\right)+TL_T\vec{E}$

coefficients

σ : electrical conductivity
κ : thermal conductivity
L_T: thermal electric coefficient

coupling both electric and thermal responses

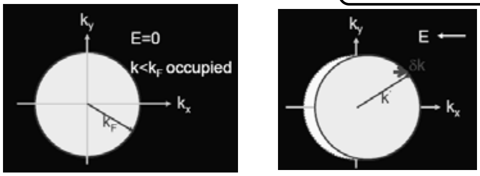
Electrical conductivity and Ohm's law

Applying an electric field

Equation of motion $\vec{F}=(-e)\vec{E}=m\frac{d^2\vec{v}}{dt^2}=\frac{d\vec{P}}{dt}=\hbar\frac{d\vec{k}}{dt}$

At a constant *E*, $\vec{k}(t)-\vec{k}(0)=\frac{-e\vec{E}t}{\hbar}$

Electric field accelerates electrons *k* increases linearly



E shifts Fermi sphere in k-space
Each k increases by

Current density

$$\begin{aligned}\vec{J}&=\sum_k -e\vec{v}_k n_k\\&=\sum_k -e\frac{\hbar\vec{k}}{m}n_k\\&=\sum_{k_0}-e\left(\frac{\hbar\vec{k}_0}{m}+\frac{\hbar\delta\vec{k}}{m}\right)n_k^0\\&=\sum_{k_0}\boxed{-e\frac{\hbar\vec{k}_0}{m}n_k^0}+\sum_{k_0}-e\frac{\hbar\delta\vec{k}}{m}n_k^0\\&=\frac{-e\hbar}{m}\left(\sum_{k_0}n_k^0\right)\delta\vec{k}\\&=-n\frac{e\hbar}{m}\delta\vec{k}\end{aligned}$$

unshifted

What limits δ k ?

scatterings

Electrons can scatter to states of lower energy and reduce current.

Assume collision time is τ

$$\vec{k}(t)-\vec{k}(0)=\frac{-e\vec{E}t}{\hbar} \Rightarrow \delta\vec{k}=\frac{-e\vec{E}}{\hbar}\tau$$

$$\vec{J}=-n\frac{e\hbar}{m}\delta\vec{k}$$

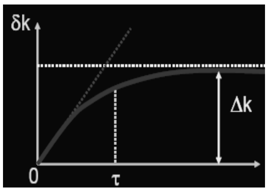
$$\vec{J}=-n\frac{e\hbar}{m}\left(\frac{-e\vec{E}}{\hbar}\right)\tau=\frac{ne^2\tau}{m}\vec{E}$$

And $\vec{J}\equiv\sigma\vec{E}$ Ohmic devices

$$\Rightarrow \boxed{\sigma=\frac{ne^2\tau}{m}}$$

Electric conductivity

Free electron model



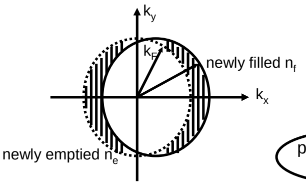
$$\delta\vec{k}=\frac{-e\vec{E}}{\hbar}t$$

Approaches to a "steady state"value
non-equilibrium

@ In classical picture, all e–s carry charge –e at a constant velocity v_d.

$$J=-nev_d=-ne\frac{-eE\tau}{m}=\frac{ne^2\tau}{m}E\equiv\sigma E$$

@ Only electrons near the Fermi surface contribute to current. δ k<<k_F



$$\vec{J}=\sum_k e\vec{v}_k n_k$$

$$=n_f\,ev_F-n_e e(-v_F)$$

$$=\underline{(n_f+n_e)}\,\underline{ev_F}$$

participating states

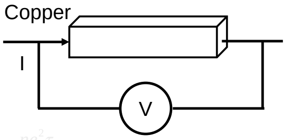
all at v_F

@ Current is carried only by a fraction of electrons traveling at v_F.

Both newly filled and newly emptied states contribute same current.

$n_f \Rightarrow$ electrons

$n_e \Rightarrow$ holes



Cross sectional area
A=wt Length *l*

$\boxed{R=\rho l/A}$

ρ(300K)= 1.7$\mu\Omega$cm
n=8.45 × 10^{28} 1/m^3
v_F= 1.57 × 10^6m/sec

$$\sigma=\frac{ne^2\tau}{m}$$

$$\tau=\frac{m\sigma}{ne^2}=\frac{9.1\times10^{-31}kg}{8.45\times10^{28}m^{-3}\left(1.6\times10^{-19}coulomb\right)^2 1.7\times10^{-8}\Omega m}$$

$$=2.5\times10^{-14}\sec$$

For E = 1 volt/cm $\Rightarrow$ v_d~0.43 m/sec

Fraction of states participating

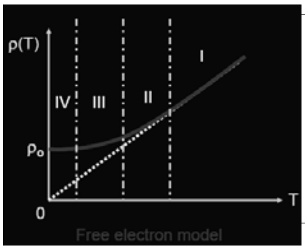
$$\frac{\delta n}{n}\approx\frac{2\delta k}{k_F}\sim\frac{2v_d}{v_F}=10^{-6}$$

Electron scattering processes

Conductivity σ is limited by scatterings (τ , l)

for a perfect crystal, no scattering $\sigma\rightarrow\infty$

Scattering mechanisms



Regime I
Large e-ph scatterings ρ (T) $\propto$T
Regime II
Small e-ph scatterings ρ (T) $\propto T^5$
Regime III e-e scatterings ρ (T) $\propto T^2$
Regime IV impurity scatterings ρ (T) $\propto T^0$~ ρ_0

Two additional rules :

(1) Multiple scattering mechanisms

$$\frac{1}{\tau}=\frac{1}{\tau_{e-ph}}+\frac{1}{\tau_{e-e}}+\frac{1}{\tau_{e-impurity}}+\ldots$$

$$\frac{1}{\sigma}=\frac{1}{\sigma_{e-ph}}+\frac{1}{\sigma_{e-e}}+\frac{1}{\sigma_{e-impurity}}+\ldots$$

$$\rho=\rho_{e-ph}+\rho_{e-e}+\rho_{e-impurity}+\ldots$$

Matthiessen's rule

not exact but pretty good

(2) Residual resistance ratio

$$RRR\equiv\frac{R(300K)}{R(0K)}=\frac{\rho(300K)}{\rho_o}$$

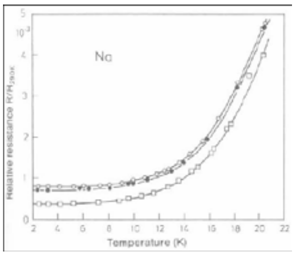
Phonon dominates

Impurity dominates

RRR →∞, perfect crystal

In general, RRR ~ $10^2$to 10^4 (pure metal)

Experimental evidences for Matthiesen’s Rule



Three different samples w/. different defect concentrations.

McDonald and Mendelssohn (1950).

Motion in magnetic fields

Electric field

$$\vec{F} = q\vec{E} = \hbar\frac{d\vec{k}}{dt}$$ change magnitude of

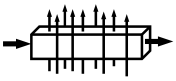
Magnetic field

$$\vec{K}$$

$$\vec{F}_B = q\vec{v}\times\vec{B} = \frac{q\hbar}{m}\vec{k}\times\vec{B} = \hbar\frac{d\vec{k}}{dt}$$ change direction of

Lorentz force ⊥motion direction

Example : $\vec{B} = B\hat{z}$



$\hbar\frac{d\vec{k}}{dt} = q\vec{v}\times\vec{B}$ and $m\vec{v} = \hbar\vec{k}$

$$\frac{dk_x}{dt} = \frac{qB}{m}k_y \qquad \frac{dk_y}{dt} = -\frac{qB}{m}k_x \qquad \frac{dk_z}{dt} = 0$$

$$\rightarrow \boxed{\begin{aligned}\frac{d^2k_x}{dt^2} &= -\left(\frac{qB}{m}\right)^2 k_x\\ \frac{d^2k_y}{dt^2} &= -\left(\frac{qB}{m}\right)^2 k_y\\ \frac{dk_z}{dt} &= 0\end{aligned}} \rightarrow$$

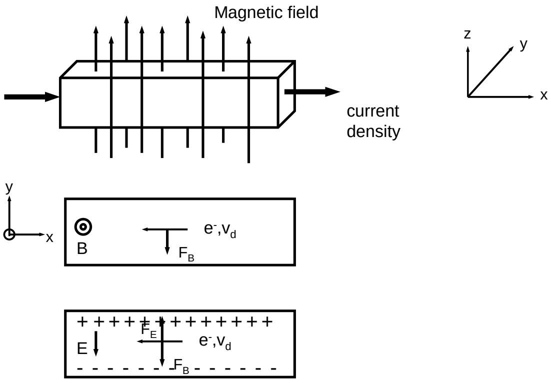
solutions

$$k_x(t) = A\cos(\omega_c t)$$
$$k_y(t) = A\sin(\omega_c t)$$
$$k_z(t) = C$$

Helical circular motion ⊥B

ω_c=qB/m “cyclotron frequency”

Hall Effect



The electric force and Lorentz force on an electron

$$\vec{F} = q\vec{E} + q\vec{v}\times\vec{B} \rightarrow F_y = -eE_y + ev_dB$$

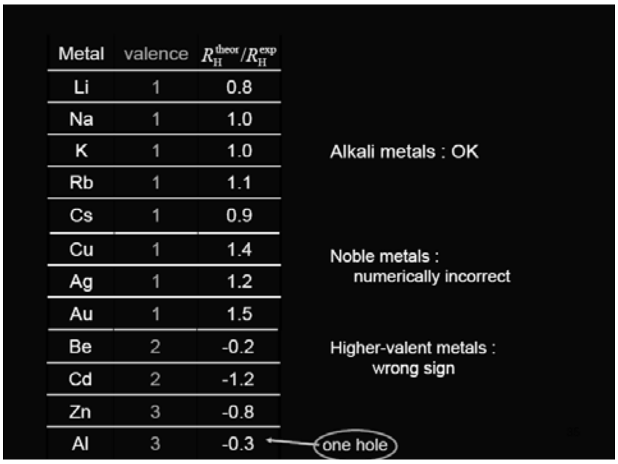
$$E_y = -\frac{j_xB}{ne}$$

In general $R_H \equiv \frac{E_y}{j_xB} = -\frac{1}{ne}$ Hall coefficient

Hall effect reveals density and sign of charge carriers.

Hall resistivity

$$\rho_H = \frac{E_y}{j_x} = BR_H$$



Metal	valence	$R_H^{\text{theor}}/R_H^{\text{exp}}$
Li	1	0.8
Na	1	1.0
K	1	1.0
Rb	1	1.1
Cs	1	0.9
Cu	1	1.4
Ag	1	1.2
Au	1	1.5
Be	2	-0.2
Cd	2	-1.2
Zn	3	-0.8
Al	3	-0.3

Alkali metals : OK

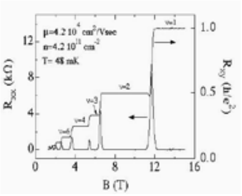
Noble metals :
numerically incorrect

Higher-valent metals :
wrong sign

one hole

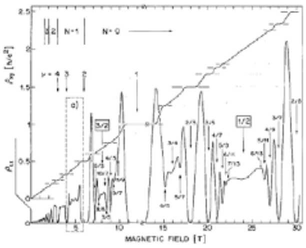
Classical Hall resistance

Quantum Hall resistance (von Klitzing, 1980)



Fractional quantum Hall effect

(Stormer, Tsui, Gossard, 1982)



GaAs/AlGaAs epitaxial heterojunction at 150 mK.

Thermal conductivity

The flux of the thermal energy $\vec{j}_U = -\kappa \frac{dT}{dx}$ the energy transmitted across unit area per unit time

κ : thermal conductivity coefficient

Electric current density $\vec{J} = \sigma\vec{E} + L_T(-\vec{\nabla}T)$

Heat current density $\vec{J}_U = \kappa(-\vec{\nabla}T) + TL_T\vec{E}$

L_T: thermal electric coefficient

Heat current from phonon –previous chapter

$$\kappa = \frac{1}{3}Cv_g l = \frac{1}{3}Cv_g^2\tau$$

Apply to free electrons

$$\boxed{\begin{aligned} C_e &= \frac{1}{2}\pi^2 nk_B\frac{k_BT}{\varepsilon_F} \\ \varepsilon_F &= \frac{1}{2}mv_F^2 \end{aligned}}$$

$$\kappa_e = \frac{1}{3}\pi^2\frac{nk_B^2}{m}T\tau$$

The electron or phonon Carry the greater heat current in the metal?

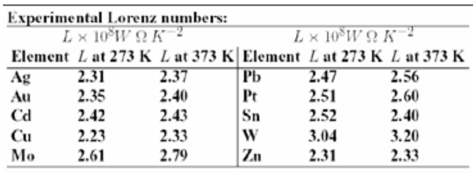
- In pure metal, the electronic contribution is dominant at all Ts.
- In impure metals or disordered materials, τ is reduced by collisions with impurities, and the phonon contribution may be comparable with the electronic contribution.

Ratio of Thermal to Electrical Conductivity

$$\frac{\kappa_e}{\sigma} = \frac{\pi^2 nk_B^2 T\tau/3m}{ne^2\tau/m} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T \equiv LT$$

Lorenz number $\boxed{L = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2}$

Wiedemann-Franz law $L_{th} = 2.45 \times 10^{-8}$ Watt-Ω/K²



Experimental Lorenz numbers:

$L \times 10^8 W\,\Omega\,K^{-2}$			$L \times 10^8 W\,\Omega\,K^{-2}$		
Element	L at 273 K	L at 373 K	Element	L at 273 K	L at 373 K
Ag	2.31	2.37	Pb	2.47	2.56
Au	2.35	2.40	Pt	2.51	2.60
Cd	2.42	2.43	Sn	2.52	2.40
Cu	2.23	2.33	W	3.04	3.20
Mo	2.61	2.79	Zn	2.31	2.33

Quizzes

1. Discussing the relation between thermal conductivity and temperature in the insulator crystal.

2. 1D chain of two unlike atoms (M and m). According the phonon dispersion relation, calculating the heat capacity in the case of M>>m.

Review

- •**Free electron model**

  treat conduction electrons as free particles

- •**The heat capacity of the electron**

  C = γT + AT^3

- •**Electric conductivity**

  $\vec{J} \equiv \sigma\vec{E}$

- •**Hall Effect in magnetic field**

  $R_H \equiv \frac{E_y}{j_x B} = -\frac{1}{ne}$ **Hall coefficient**

  $\rho_H = \frac{E_y}{j_x} = BR_H$ **Hall resistively**

Thermal conductivity

The flux of the thermal energy $\vec{j}_U = -\kappa\frac{dT}{dx}$ the energy transmitted across unit area per unit time

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L$_T$: thermal electric coefficient

Heat current from phonon –previous chapter

$$\boxed{\kappa = \frac{1}{3}Cv_g l = \frac{1}{3}Cv_g^2\tau} \qquad l = v_g\tau$$

Apply to free electrons

$$\boxed{\begin{array}{l} C_e = \frac{1}{2}\pi^2 nk_B\frac{k_BT}{\varepsilon_F} \\ \varepsilon_F = \frac{1}{2}mv_F^2 \end{array}} \qquad \kappa_e = \frac{1}{3}\pi^2\frac{nk_B^2}{m}T\tau$$

The electron or phonon carry the greater heat current in the metal?

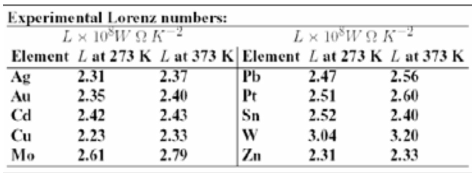
- ● In pure metal, the electronic contribution is dominant at all Ts.
- ● In impure metals or disordered materials, τ is reduced by collisions with impurities, and the phonon contribution may be comparable with the electronic contribution.

Ratio of Thermal to Electrical Conductivity

$$\kappa_e = \frac{1}{3}\pi^2\frac{nk_B^2}{m}T\tau \qquad \sigma = \frac{ne^2\tau}{m} \qquad \frac{\kappa_e}{\sigma} = \frac{\pi^2 nk_B^2 T\tau/3m}{ne^2\tau/m} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T \equiv LT$$

Wiedemann-Franz law

Lorenz number: $\boxed{L = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2}$ L$_{th}$= 2.45 × 10^{-8}WattΩ/K^2



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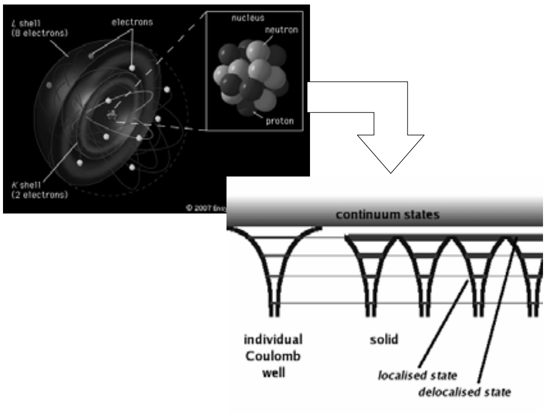
Cu	2.23	2.33	W	3.04	3.20
Mo	2.61	2.79	Zn	2.31	2.33

Homework: 1,2,3,5,6

Note

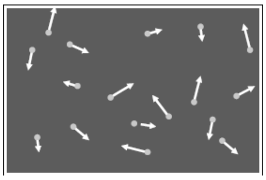
Your homeworks should be submitted by 5:30 pm on next Friday!

Otherwise…



Free electron model

--- neglect the interactions of electrons with ions and other electrons.



treat conduction electrons as free particles
electrons are completely "free of the nuclei"

Success:

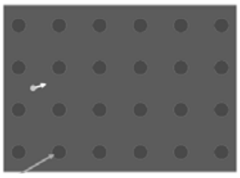
- **The heat capacity in metal. (quantum effect)**
- **Electron conductivity, Ohm's low.**
- **Ratio of thermal to electrical conductivity.**

Failings :

- **The distinction between metals, semiconductors, and insulator.**
- **The positive value of Hall coefficient.**
- **The relation of conductivity electron and free value electron.**

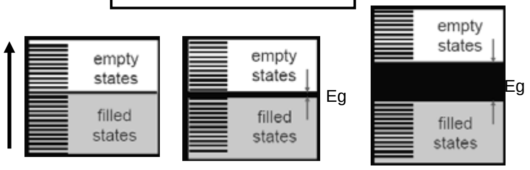
Real crystal–potential variation with the periodicity of the crystal

Attractive potential around each nucleus.



1. What determines if the crystal will be a metal, an insulator, or a semiconductor?

Band structures of solids



Conduction band partially filled	Valence band filled /Conduction band empty	
	$E_g<k_BT$	$E_g>>k_BT$
Metal	semiconductor	Insulator

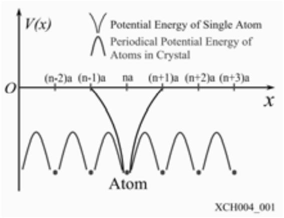
2. What form the energy band of solid?

Chapter Seven
Energy Bands

- Nearly free electron model
- Bloch functions
- Kronig-Penney model
- Wave equation of electron in a periodic potential
- Number of orbitals in a band

Nearly free electron model

--add the periodic potential of the ion cores to free electrons



Supposing: The variation of the periodic potential is small.

Energy Band Theory

Idea of the energy band theory

Ideal crystal

Periodic crystal structure, the potential of ion cores is also periodic.

Electrons in crystal

The electron move in this periodic potential.

The motion equation ⇔ **The Schrodinger equation of single electron**

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V\left(\vec{r}\right)\right]\psi=E\psi$$ **where** $V\left(\vec{r}\right)=V\left(\vec{r}+\vec{R}\right)$

Felix Bloch

The Nobel Prize in Physics 1952

> *When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal.... By straight Fourier analysis I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation.*
>
> *F. Bloch*

1. the quantum mechanics of electrons in crystals and developing the theory of metallic conduction.

2. the production and observation of polarized neutron beams.

3. Present new method of nuclear induction, a purely electromagnetic procedure for the study of nuclear moments in solids, liquids, or gases.

http://nobelprize.org/nobel_prizes/physics/laureates/1952/bloch-bio.html

Bloch's theorem

--- solution to Schrödinger equation is of the form

$$\boxed{\Psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})\,\underline{\exp(i\mathbf{k}\bullet\mathbf{r})}}$$

plane wave function

periodic function due to periodic potential

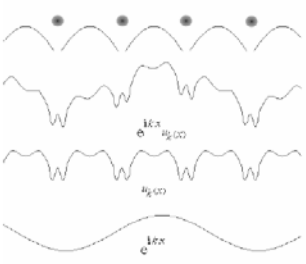
$$u_k(\vec{r}) = u_k(\vec{r}+\vec{R}) = u_k(\vec{r}+n_1\vec{a}_1+n_2\vec{a}_2+n_3\vec{a}_3)$$

Lattice vector in real space

Mixing free and bound characters

Free : extend through the whole crystal

Bound : modulated by ion core interaction



The electron wave function in the crystal

Plane wave factor: free electron motion in the crystal.
Periodic function: electron motion in the primitive cell

The expresses of Bloch theorem

$$\boxed{\Psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})\exp(i\mathbf{k}\bullet\mathbf{r})} \qquad u_k(\vec{r}) = u_k(\vec{r}+\vec{R})$$

The eigen functions of the wave equation for a periodic potential are the product of a plane wave exp(ik•r) time a function $u_k(r)$ with the periodicity of the crystal lattice.

……

The alternative form of Bloch theorem

$$\boxed{\Psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = \exp(i\mathbf{k}\bullet\mathbf{R})\Psi(\mathbf{r})}$$

The function waves are the product of the Bloch function time the phase factor exp(ik•R)

The strict proof of Bloch theorem

(1) The first step:equivalence

Bloch function: $\Psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})\exp(i\mathbf{k}\bullet\mathbf{r})$

Under a crystal lattice translation r —> r+R

$$\Psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{\mathbf{k}}(\mathbf{r}+\mathbf{R})e^{i\mathbf{k}\bullet\mathbf{R}}e^{i\mathbf{k}\bullet\mathbf{r}}$$

$$\Downarrow$$

$$\Psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\bullet\mathbf{R}}e^{i\mathbf{k}\bullet\mathbf{r}}$$

$$\Downarrow$$

$$\Psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = \Psi_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\bullet\mathbf{R}}$$

(2) The second step

For each lattice vector R we define a translation operator T_R

$$T_R f(\mathbf{r}) = f(\mathbf{r}+\mathbf{R})$$

The Hamitonian is periodic $T_{\mathbf{R}}H = HT_{\mathbf{R}}$

T_R is commuting operator $T_{\mathbf{R}}T_{\mathbf{R}'} = T_{\mathbf{R}'}T_{\mathbf{R}} = T_{\mathbf{R}+\mathbf{R}'}$

The eigenstate of *H* can therefore be chosen to be simultaneous eigenstates of all the $T_{\mathbf{R}}$

$$H\Psi = \epsilon\Psi$$

$$T_{\mathbf{R}}\Psi = c(\mathbf{R})\Psi$$

One dimension

$$T_a\Psi = c(a)\Psi \quad \Rightarrow \quad T_{na}\Psi = c(a)^n\Psi$$

Periodic boundary condition

$$\Psi(x+Na) = \Psi(x)$$

$$T_{Na}\Psi(x) = \Psi(x+Na) = c(a)^N\Psi(x)$$

$$\Rightarrow$$

$c(a) = e^{ika}$ **where** $\boxed{k = l\frac{2\pi}{Na}}$

Three dimension

$$T_{\mathbf{R}}\Psi = c(a_1)^{n_1}c(a_2)^{n_2}c(a_3)^{n_3}\Psi$$

$$c(\mathbf{R}) = e^{ik_1n_1a_1}e^{ik_2n_2a_2}e^{ik_3n_3a_3}$$

$$c(\mathbf{R}) = e^{i\mathbf{k}\bullet\mathbf{R}}$$

$\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3$ **$\mathbf{b}_i$ are reciprocal lattice vectors**

Summarizing

$$\boxed{T_{\mathbf{R}}\Psi = \Psi(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{k}\bullet\mathbf{R}}\Psi(\mathbf{r})}$$

The Bloch theorem

Review

- Nearly free electron model

add the periodic potential of the ion cores to free electrons

- Bloch's theorem

$$\boxed{\Psi_k(\mathbf{r}) = u_k(\mathbf{r})\exp(i\mathbf{k}\bullet\mathbf{r})} \quad u_k(\vec{r}) = u_k(\vec{r}+\vec{R})$$

$$\boxed{\Psi_k(\mathbf{r}+\mathbf{R}) = \exp(i\mathbf{k}\bullet\mathbf{R})\Psi(\mathbf{r})}$$

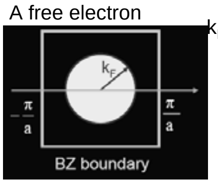
Origin of the energy band and gap

Magnitude of the energy gap

Kronig-Penny Model

Origin of the energy band and gap

A free electron



$k_F << k_{BZ}$ and $\lambda >> a$

Electron wave function samples many atoms

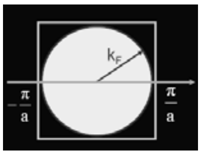
U=constant

"Free Electrons"

Note : $k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3} \approx 3n^{1/3}$ $\quad$ $\frac{3}{a}v^{1/3}$ valence electron #

$k_{BZ} \geq \frac{\pi}{a}$

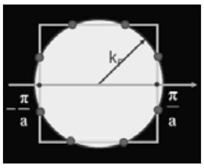
Typical metals v>1and hence, $k_F \sim k_{BZ}$.



$k_F <\sim k_{BZ}$ and $\lambda > \sim a$

k = ± π /a (BZ) ⇔ Bragg reflection

$2a\sin\theta = n\lambda \Rightarrow \lambda = \frac{2a}{n} \Rightarrow k = \frac{n\pi}{a}$



$k_F > k_{BZ}$ and $\lambda \sim a$

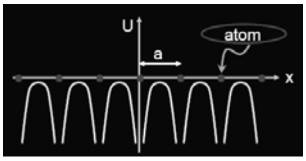
Diffraction of Bloch waves

--Bragg scatterings

"Energy gaps"

1D electron wave function

electron in a linear chain of lattice constant a



k small (λ >>a)

Free electron $\Psi_k \propto e^{i\vec{k}\bullet\vec{r}}$ Plane wave

……

k = ± π /a (BZ)

Bragg reflection $\Psi_k \propto e^{i\vec{k}\bullet\vec{r}} \pm e^{-i\vec{k}\bullet\vec{r}}$ standing waves

$$\Psi_k \propto e^{i\vec{k}\bullet\vec{r}} \pm e^{-i\vec{k}\bullet\vec{r}} \propto \begin{cases} 2\cos\left(\vec{k}\bullet\vec{r}\right) = 2\cos\left(\frac{\pi x}{a}\right) \approx \psi_+ \\ i2\sin\left(\vec{k}\bullet\vec{r}\right) = i2\sin\left(\frac{\pi x}{a}\right) \approx \psi_- \end{cases}$$

Electron probability density $\rho = \psi^* \psi$

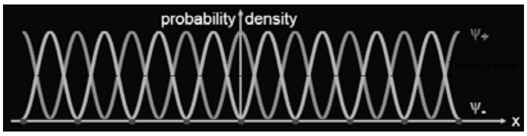
For a pure traveling wave exp(ikx)

$$\rho = \exp(-ikx)\exp(ikx) = 1$$

k = ± π /a (BZ)

High density at atoms

Low density at atoms



The potential energy of an electron in the field of a positive ion is negative

$$E_{total} = T - |V|$$

Energies due to potential energy U(x)

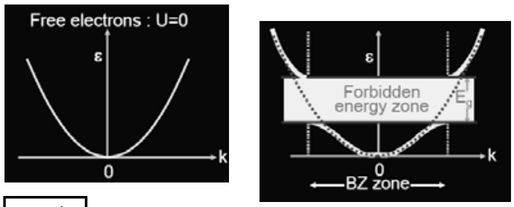
$$U_+ = \int_0^L dx U(x) |\Psi_+|^2 = \frac{2}{L}\int_0^L dx U(x) \cos^2\left(\frac{\pi x}{a}\right)$$

$$U_- = \int_0^L dx U(x) |\Psi_-|^2 = \frac{2}{L}\int_0^L dx U(x) \sin^2\left(\frac{\pi x}{a}\right)$$

Energy difference

$$E_g \equiv U_+ - U_- = \frac{2}{L}\int_0^L dx U(x) \left[\cos^2\left(\frac{\pi x}{a}\right) - \sin^2\left(\frac{\pi x}{a}\right)\right]$$

$$= \frac{2}{L}\int_0^L dx U(x) \cos\left(\frac{2\pi x}{a}\right)$$



Result :

energy band: due to the periodicity of lattice

energy gap:due to Bragg reflection of Bloch waves

- Standing wave at the zone boundary.
- Energy gap–energies at which no wave can travel through crystal

---

Magnitude of the energy gap

expanding potential U(x) in Fourier series : U(x)=U(x+a)

$$U(x) = \sum_G U_G e^{iGx} = \sum_{G>0} U_G \left(e^{iGx} + e^{-iGx}\right)$$

$$= 2\sum_{G>0} U_G \cos(Gx)$$

G : reciprocal lattice vector

Inverse $\longrightarrow$ $$U_G = \frac{1}{a}\int_0^a dx U(x)\cos(Gx)$$

Using $$E_g = \frac{2}{L}\int_0^L dx U(x) \cos\left(\frac{2\pi x}{a}\right)$$

$$\longrightarrow \boxed{E_g = 2U_{2\pi/a} = 2U_{G1}}$$

Energy gap is equal to the Fourier component of crystal potential.

For instance,

$$U(x) = -U_0 \cos\left(\frac{2\pi x}{a}\right)$$

$$E_g = \left|\frac{2}{L}\int_0^L dx(-u_0)\cos\left(\frac{2\pi x}{2}\right)\cos\left(\frac{2\pi x}{2}\right)\right|$$

$$= \frac{2}{L}\left(U_0 \frac{1}{2} L\right) = U_0$$

The average of total energy

$$E = \int_0^L dx \psi^* H \psi \Longrightarrow \boxed{\begin{array}{l} E_+ = \int_0^L dx \psi_+^* H \psi_+ \\ E_- = \int_0^L dx \psi_-^* H \psi_- \end{array}}$$

Hence

$$E_+ = \int_0^L dx \psi_+^* H \psi_+ = \frac{2}{L}\int_0^L dx \cos\left(\frac{\pi x}{a}\right)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - U_0\cos\left(\frac{2\pi x}{a}\right)\right]\cos\left(\frac{\pi x}{a}\right)$$

$$= \frac{2}{L}\left[\frac{\hbar^2(\pi/a)^2}{2m}\int_0^L dx \cos^2\left(\frac{\pi x}{a}\right) - U_0\int_0^L dx \cos\left(\frac{2\pi x}{a}\right)\cos^2\left(\frac{\pi x}{a}\right)\right]$$

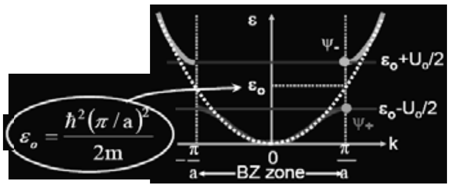
$$= \frac{2}{L}\left[\frac{\hbar^2(\pi/a)^2}{2m}\left(\frac{L}{2}\right) - U_0\left(\frac{L}{4}\right)\right]$$

$$= \frac{\hbar^2(\pi/a)^2}{2m} - \frac{U_0}{2}$$

The first-order energy

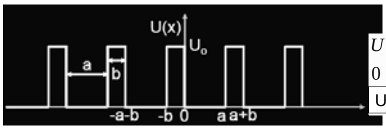
$$E_- = \int_0^L dx\psi_-^* H\psi_- = \frac{2}{L}\int_0^L dx(-i)\sin\left(\frac{\pi x}{a}\right)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - U_0\cos\left(\frac{2\pi x}{a}\right)\right] i\sin\left(\frac{\pi x}{a}\right)$$

$$= \frac{\hbar^2(\pi/a)^2}{2m} + \frac{U_0}{2}$$



Kronig-Penny Model

--Square well periodic potential by Kronigand Penney



$U(x)$:

$0 \quad where \quad 0 < x < a$

$U_0 \quad where \quad -b < x < 0$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = \varepsilon\psi(x)$$

square well U(x) →

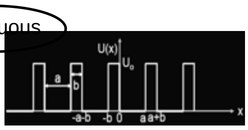
$$0 < x < a, \psi(x) = Ae^{i\mathbf{K}x} + Be^{-i\mathbf{K}x} \quad w/. \quad \varepsilon = \frac{\hbar^2\mathbf{K}^2}{2m}$$

$$-b < x < 0, \psi(x) = Ce^{qx} + De^{-qx} \quad w/. \quad \varepsilon = U_0 - \frac{\hbar^2 q^2}{2m}$$

Boundary conditions : continuous

(1) x=0

A+B = C+D
i**K**(A-B) = q(C-D)



How about other boundaries ?

x = a? What is ψ (a<x<a+b) ?

x = -b? What is ψ (-a-b<x<-b) ?

By Bloch theorem $\Psi_k(\mathbf{r}+\mathbf{R}) = \exp(i\mathbf{k}\bullet\mathbf{R})\Psi(\mathbf{r})$

$$\psi(a < x < a+b) = \psi(-b < x < 0)\,e^{ik(a+b)}$$

$$\psi(-a-b < x < -b) = \psi(-0 < x < a)\,e^{ik(a+b)}$$

(2) x=a

$$Ae^{i\mathbf{k}x} + Be^{-i\mathbf{K}x} = \left(Ce^{-qb} + De^{qb}\right)e^{ik(a+b)}$$

$$i\mathbf{K}\left(Ae^{i\mathbf{K}x} - Be^{-i\mathbf{K}x}\right) = q\left(Ce^{-qb} - De^{qb}\right)e^{ik(a+b)}$$

Solving (1) and (2)

The determinant of the coefficients of A,B, C,D vanishes

$$\left(\frac{q^2-\mathbf{K}^2}{2q\mathbf{K}}\right)\sinh(qb)\sin(\mathbf{K}a) + \cosh(qb)\cos(\mathbf{K}a) = \cos(ka+kb)$$

The result can be simplified by a periodic delta potential

b →0 and U_o→∞

Hence, bU_o is finite and $bU_0 = b\left(\varepsilon + \frac{\hbar^2 q^2}{2m}\right) \to \frac{\hbar^2 bq^2}{2m}$

$$\frac{q^2-\mathbf{K}^2}{2q\mathbf{K}} \to \frac{q^2}{2q\mathbf{K}} = \frac{q}{2\mathbf{K}}$$

remain finite !

Due to sinh(qb) →qb and cosh(qb) →1

$$\left(\frac{q^2ba}{2\mathbf{K}a}\right)\sin(\mathbf{K}a) + \cos(\mathbf{K}a) = \cos(ka)$$

P : a measure of strength of the barrier

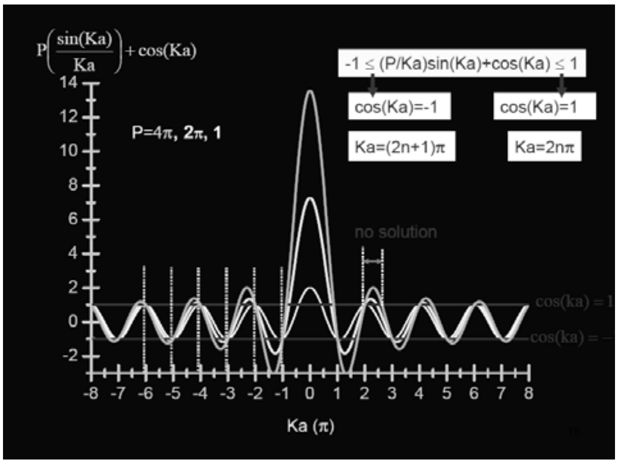
$$P = \frac{q^2ab}{2} = \frac{(U_0-\varepsilon)mab}{\hbar^2} \approx \lim_{\substack{b\to 0\\ U_0\to\infty}}\left(bU_0\frac{ma}{\hbar^2}\right)$$

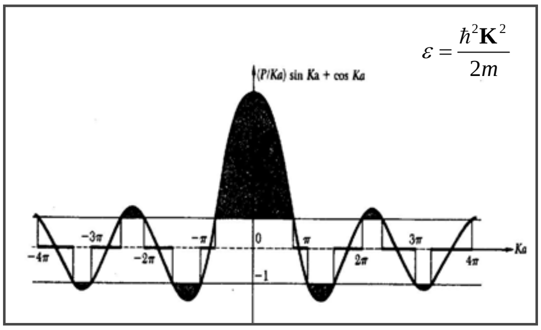
$$P\left(\frac{\sin(\mathbf{K}a)}{\mathbf{K}a}\right) + \cos(\mathbf{K}a) = \cos(ka)$$

(1) P→0 implying that K→k free electron

(2) P→∞ $\Rightarrow \frac{\sin(\mathbf{K}a)}{\mathbf{K}a} \Rightarrow \mathbf{K}a = n\pi$

$$\Rightarrow \boxed{E = \frac{n^2\pi^2\hbar^2}{2ma^2}}$$

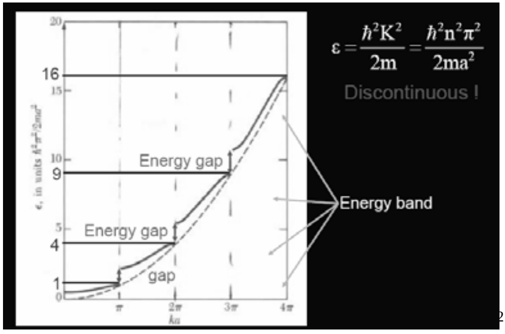




$$\varepsilon = \frac{\hbar^2 \mathbf{K}^2}{2m}$$

$$P\left(\frac{\sin(\mathbf{K}a)}{\mathbf{K}a}\right)+\cos(\mathbf{K}a)=\cos(ka)$$

Discontinuity occurs at Ka=n π (corresponding to ka=nπ) where n$\in$Z



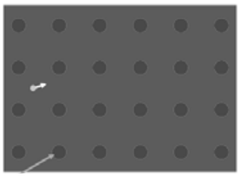
Conclusion

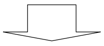
- **This model can be solved in terms of elemental functions.**
- **The results have shown that the energy form the energy band in periodic field.**
- **The model can be develop to discuss the surface state and the multiple layer film.**

Review

1. Nearly free electron model

--add the periodic potential of the ion cores to free electrons





Energy Band Theory

2. Bloch's theorem

$$\boxed{\Psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})\exp(i\mathbf{k}\bullet\mathbf{r})} \quad u_k(\vec{r}) = u_k(\vec{r}+\vec{R})$$

$$\boxed{\Psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = \exp(i\mathbf{k}\bullet\mathbf{R})\Psi(\mathbf{r})}$$

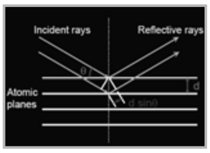
3. Origin of the energy band and gap

energy band: due to the periodicity of lattice

energy gap:due to Bragg reflection of Bloch waves

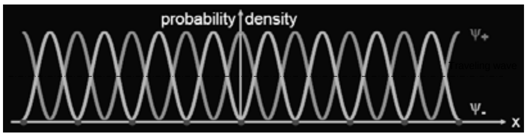
$$2a\sin\theta = n\lambda \quad \Longrightarrow \quad \lambda = \frac{2a}{n} \quad \Longrightarrow \quad k = \frac{n\pi}{a}$$

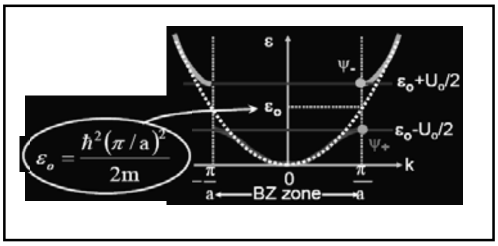
$$\Psi_k \; e^{i\vec{k}\bullet\vec{r}} \pm e^{-i\vec{k}\bullet\vec{r}}$$



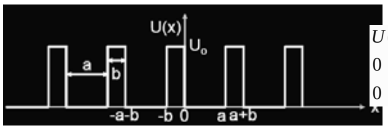
k = ± π /a (BZ)

$$\begin{cases} 2\cos\left(\vec{k}\bullet\vec{r}\right) = 2\cos\left(\dfrac{\pi x}{a}\right) \approx \psi_+ \\ i2\sin\left(\vec{k}\bullet\vec{r}\right) = i2\sin\left(\dfrac{\pi x}{a}\right) \approx \psi_- \end{cases}$$





4. Kronig-Penny Model



$U(x)$:

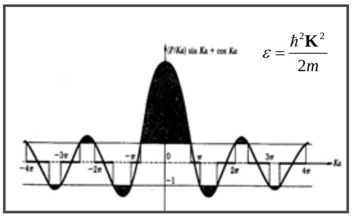
$0 \quad where \quad 0 < x < a$

$0 \quad where \quad -b < x < 0$

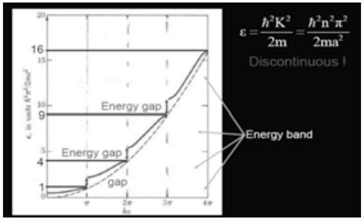
b →0 and U_o→∞

$$\boxed{P\left(\frac{\sin(\mathbf{K}a)}{\mathbf{K}a}\right) + \cos(\mathbf{K}a) = \cos(ka)}$$

$$P\left(\frac{\sin(\mathbf{K}a)}{\mathbf{K}a}\right)+\cos(\mathbf{K}a)=\cos(ka)$$



$$\varepsilon=\frac{\hbar^2\mathbf{K}^2}{2m}$$



$$\varepsilon=\frac{\hbar^2\mathrm{K}^2}{2\mathrm{m}}=\frac{\hbar^2\mathrm{n}^2\pi^2}{2\mathrm{ma}^2}$$

Discontinuous !

Quiz

1. The wave functions of the electron will satisfy the Bloch theorem. Supposing *a* represent the lattice constant. The wave functions of electron are listed below. Calculate the wave vector in these states.

   (i) $\psi_k(x)=\sin\frac{x}{a}\pi$

   (ii) $\psi_k(x)=i\cos\frac{3x}{a}\pi$

2. Kronig-Penny Model. Considering the limit *b*=∞,U_0= ∞ derive the expression about the energy, then analyses this result.

Review

1. Nearly free electron model

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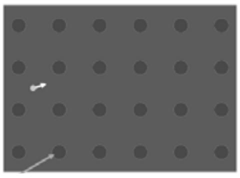

⇩

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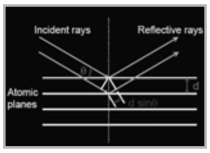

k = ± π /a (BZ)

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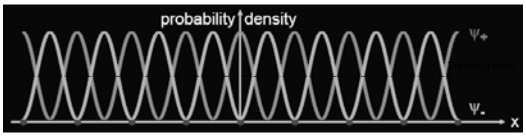
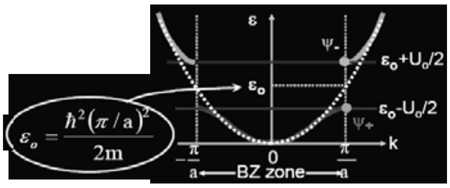
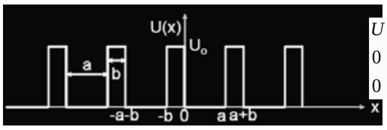




4. Kronig-Penny Model



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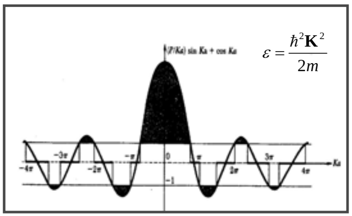
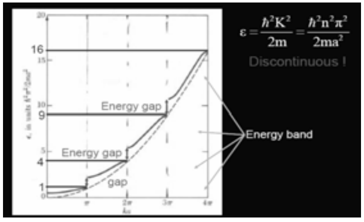


$$\varepsilon=\frac{\hbar^2\mathbf{K}^2}{2m}$$



$$\varepsilon=\frac{\hbar^2\mathrm{K}^2}{2\mathrm{m}}=\frac{\hbar^2\mathrm{n}^2\pi^2}{2\mathrm{ma}^2}$$

Discontinuous !

Electrons in a weak periodic potential

General approach to the Schrodinger equation when the potential is weak.

1. The electron-ion interaction is strongest at small separations, but the conduction electrons are forbidden from entering the immediate neighborhood of the ions because this region is already occupied by the core electrons.

2. In the region in which the conduction electrons are allowed, their mobility further diminishes the net potential any single electron experiences, for they can screen the fields of positively charged, diminishing the total effective potential.

Wave equation of electron in periodic potential

Equation of motion

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+U(x)\psi(x)=\varepsilon\psi(x)$$

$\psi(x)$ ⇨ **The motion of one electron in potential of the ion cores and in the average potential of the other conduction electrons.**

Bloch theorem $\psi(\vec{r})=e^{i\vec{k}\bullet\vec{r}}u(r)$

Born-von Karman boundary condition

$$\psi(\vec{r}+N_i a_i)=\psi(\vec{r})$$

For a general potential, U(r) is periodic in the lattice

$$U(x)=\sum_G U_G e^{iGx}$$

Fourier series

The Fourier coefficients U$_G$

$$U_G=\frac{1}{v}\int_{cell} dre^{-iG\bullet\vec{r}}U(r)$$

U(r) is real ⇨ $\boxed{U_G=U_{-G}=U_G^*}$

Wave function obeying the Born-von Karman boundary condition

$$\psi(\vec{r}+N_i a_i)=\psi(\vec{r})$$

⇩

$$\psi(\vec{r})=\sum_{\vec{k}} C_{\vec{k}}e^{i\vec{k}\bullet\vec{r}} \qquad k=n\left(\frac{2\pi}{L}\right)$$

$$\psi(x)=\sum_k C_k e^{ikx}$$
$$U(x)=\sum_G U_G e^{iGx}$$

⇨ **Wave equation**

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+U(x)\psi(x)=\varepsilon\psi(x)$$

One dimension

The kinetic energy term $-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}=\frac{\hbar^2}{2m}\sum_k k^2C_k e^{ikx}$

The potential energy term $\left(\sum_G U_G e^{iGx}\right)\psi(x)=\sum_G\sum_k U_G e^{iGx}C_k e^{ikx}$

⇓

$$\sum_k \frac{\hbar^2}{2m}k^2C_k e^{ikx}+\sum_G\sum_k U_G e^{iGx}C_k e^{ikx}=\varepsilon\sum_k C_k e^{ikx}$$

$$\sum_k\left(\left(\frac{\hbar^2}{2m}k^2-\varepsilon\right)C_k\right)e^{ikx}=-\sum_k\sum_G U_G C_k e^{i(k+G)x}=-\sum_{k'}\left(\sum_G U_G C_{k'-G}\right)e^{ik'x}$$

⇓

$$=-\sum_k\left(\sum_{G'}U_{G'}C_{k-G'}\right)e^{ikx}$$

⇓

k ⟶ **q**

For convenient to write q in the form **q=k-G**

$$\left(\frac{\hbar^2}{2m}(k-G)^2-\varepsilon\right)C_{k-G}+\sum_{G'}U_{G'-G}C_{k-G'}=0$$

the central eq.

- **G is a reciprocal lattice vector**
- **k lies in the fist Brillouin zone**

The original problem has separated into N independent problem

For fixed k

$\psi(\vec r)=\sum_{\vec k}C_{\vec k}e^{i\vec k\bullet\vec r}$ ⇒ $\psi_k(x)=\sum_G C_{k-G}e^{i(k-G)x}$

⇓

⇓ **Proof of Bloch theorem**

$$u_k(x)=u_k(x+R)$$

$$u_k(x+R)=\sum_G C_{k-G}e^{-iG(x+R)}=\cancelto{0}{e^{-iGR}}u_k(x)=u_k(x)$$

Case 1 **The Kronig-Penney model**

---- A periodic delta-function potential

$U(x)=\sum_G U_G e^{iGx}$ ⟶ $=\sum_{G>0}U_G(e^{iGx}+e^{-iGx})=2\sum_{G>0}U_G\cos Gx$

Real function

$$U(x)=Aa\sum_s\delta(x-sa)$$

$$U_G=\int_0^1 dxU(x)\cos Gx=Aa\sum_s\int_0^1 dx\delta(x-sa)\cos Gx$$

⇒ $=Aa\sum_s\cos Gsa=A$

According to the central eq.

$(\lambda_k-\varepsilon)C_k+\sum_G U_G C_{k-G}=0$ $\lambda_k=\hbar^2k^2/2m$

$$(\lambda_k-\varepsilon)C(k)+A\sum_n C(k-2\pi n/a)=0$$

$$f(k)=\sum_n C(k-2\pi n/a)$$

$$C(k)=-\frac{(2mA/\hbar^2)f(k)}{k^2-(2m\varepsilon/\hbar^2)}$$

$$f(k)=f(k-2\pi n/a)$$

$$\Rightarrow \quad C(k-2\pi n/a) = -\frac{(2mA/\hbar^2)\,f(k)}{(k-2\pi n/a)^2-(2m\varepsilon/\hbar^2)}$$

$$\Downarrow$$

$$\sum_n C(k-2\pi n/a) = \sum_n -\frac{(2mA/\hbar^2)\,f(k)}{(k-2\pi n/a)^2-(2m\varepsilon/\hbar^2)}$$

$$\Downarrow \qquad f(k)=\sum_n C(k-2\pi n/a)$$

$$\boxed{(\hbar^2/2mA) = -\sum_n \frac{1}{(k-2\pi n/a)^2-(2m\varepsilon/\hbar^2)}}$$

$$(\hbar^2/2mA) = -\sum_n \frac{1}{(k-2\pi n/a)^2-(2m\varepsilon/\hbar^2)}$$

$$\mathrm{ctg}(x)=\sum_n \frac{1}{n\pi - x}$$

$$\frac{a^2 \sin Ka}{4Ka(\cos ka-\cos Ka)} \Leftarrow K^2 = 2m\varepsilon/\hbar^2$$

$$\Rightarrow \quad (mAa^2/2\hbar^2)(Ka)^{-1}\sin Ka+\cos Ka=\cos ka$$

Kronig-Pennney model

Case 2

U(*x*) = *2U cos2πx/a = U exp(2πix/a)+U exp(-2πix/a)*

$$= \sum_{G=g,-g} U_G e^{iGx}$$

There are only 2 components $U_g=U_{-g}=U$ ($g=2\pi/a$)

$$\boxed{\left(\frac{\hbar^2}{2m}(k-G)^2-\varepsilon\right)C_{k-G}+\sum_{G'}U_{G'-G}C_{q-G'}=0}$$

Matrix form of the central eq.

$$\begin{pmatrix} \ddots & & & & \\ \lambda_{k-2g}-\varepsilon & U & 0 & 0 & 0 \\ U & \lambda_{k-g}-\varepsilon & U & 0 & 0 \\ 0 & U & \lambda_k-\varepsilon & U & 0 \\ 0 & 0 & U & \lambda_{k+g}-\varepsilon & U \\ 0 & 0 & 0 & U & \lambda_{k+2g}-\varepsilon \\ & & & & \ddots \end{pmatrix}\begin{pmatrix} \vdots \\ C(k-2g) \\ C(k-g) \\ C(k) \\ C(k+g) \\ C(k+2g) \\ \\ \end{pmatrix}=0$$

Approximate solution near a zone boundary

1. Considering a wavevector exactly at zone boundary at first Brillouin zone boundary ½ g

k=0.5 g= π/a

C(½ g) and C(k- ½ g) is important coefficients.

$$\begin{pmatrix} \ddots & & & & \\ \lambda_{k-2g}-\varepsilon & U & 0 & 0 & 0 \\ U & \boxed{\lambda_{k-g}-\varepsilon \quad U} & & 0 & 0 \\ 0 & \boxed{U \quad \lambda_k-\varepsilon} & & U & 0 \\ 0 & 0 & U & \lambda_{k+g}-\varepsilon & U \\ 0 & 0 & 0 & U & \lambda_{k+2g}-\varepsilon \\ & & & & \ddots \end{pmatrix}\begin{pmatrix} \vdots \\ C(k-2g) \\ \boxed{C(k-g)} \\ \boxed{C(k)} \\ C(k+g) \\ C(k+2g) \\ \\ \end{pmatrix}=0$$

k=0.5 g $\Rightarrow$ ħ²(k-g)²/2m= ħ²(g/2)²/2m

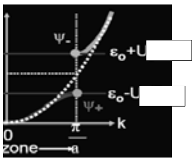
$$\Downarrow$$

$$\lambda_g = \lambda_{k-g}$$

Central equation :

$$\boxed{\begin{aligned}(\lambda-\varepsilon)C_{\frac{G_1}{2}}+UC_{-\frac{G_1}{2}}&=0\\ (\lambda-\varepsilon)C_{-\frac{G_1}{2}}+UC_{\frac{G_1}{2}}&=0\end{aligned}} \Rightarrow \begin{vmatrix}\lambda-\varepsilon & U \\ U & \lambda-\varepsilon\end{vmatrix}=0$$

$$\varepsilon=\lambda\pm U=\frac{\hbar^2}{2m}\left(\frac{g}{2}\right)^2\pm U$$



$$\boxed{\begin{aligned}(\lambda-\varepsilon)C_{\frac{G_1}{2}}+UC_{-\frac{G_1}{2}}&=0\\(\lambda-\varepsilon)C_{-\frac{G_1}{2}}+UC_{\frac{G_1}{2}}&=0\end{aligned}} \Rightarrow \frac{C(-1/2g)}{C(1/2g)}=\frac{\varepsilon-\lambda}{U}=\pm1$$

Wave function at first Brillouin zone boundary

$$\psi(x)=\exp(igx/2)\pm\exp(-igx/2)$$

Standing waves,

identical to previous discussion

Empty lattice approximation

Empty simple cubic lattice, $\varepsilon(k)$ in the reduced zone

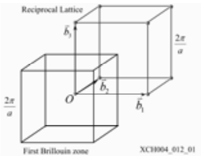
free electron

Look for a *G* $\Rightarrow$ $\vec{k}'+\vec{G}=\vec{k}$

k : unstricted and is true free electron wave vector in empty lattice

free electron energy In the 1st BZ

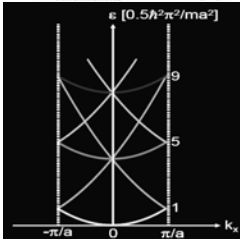
$$\varepsilon(k_x,k_y,k_z)=\frac{\hbar^2}{2m}(k+G)^2=\frac{\hbar^2}{2m}((k_x+G_x)^2+(k_y+G_y)^2+(k_z+G_z)^2)$$

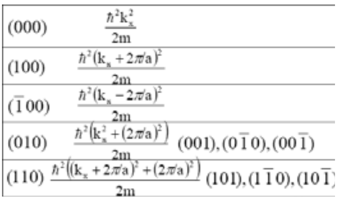


Along [100] direction,

$$\boxed{\varepsilon(k_x,k_y,k_z)=\frac{\hbar^2}{2m}((k_x+G_x)^2+(G_y)^2+(G_z)^2)}$$

$$\text{SC, } \vec{G}(hk\ell)=h\frac{2\pi}{a}\hat{x}+k\frac{2\pi}{a}\hat{y}+\ell\frac{2\pi}{a}\hat{z}$$





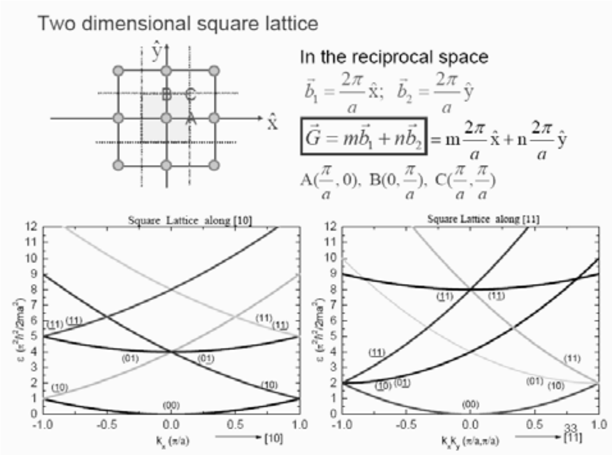
(000)	$\frac{\hbar^2 k_x^2}{2m}$	
(100)	$\frac{\hbar^2(k_x+2\pi/a)^2}{2m}$	
$(\bar{1}00)$	$\frac{\hbar^2(k_x-2\pi/a)^2}{2m}$	
(010)	$\frac{\hbar^2(k_x^2+(2\pi/a)^2)}{2m}$	$(001),(0\bar{1}0),(00\bar{1})$
(110)	$\frac{\hbar^2((k_x+2\pi/a)^2+(2\pi/a)^2)}{2m}$	$(101),(1\bar{1}0),(10\bar{1}$

For other directions, change k_x, k_y, k_z

For other lattices, must use proper Gs

To get band structure of real crystals, turn on weak periodic potential

$\longrightarrow$ Band gap opens up at the BZ boundary



Two dimensional square lattice

In the reciprocal space

$$\vec{b}_1=\frac{2\pi}{a}\hat{x};\quad \vec{b}_2=\frac{2\pi}{a}\hat{y}$$

$$\boxed{\vec{G}=m\vec{b}_1+n\vec{b}_2}=m\frac{2\pi}{a}\hat{x}+n\frac{2\pi}{a}\hat{y}$$

$$A(\frac{\pi}{a},0),\ B(0,\frac{\pi}{a}),\ C(\frac{\pi}{a},\frac{\pi}{a})$$

Square Lattice along [10]

Square Lattice along [11]

Review

Wave equation

$$\psi(x)=\sum_k C_k e^{ikx}$$
$$U(x)=\sum_G U_G e^{iGx}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+U(x)\psi(x)=\varepsilon\psi(x)$$

$$\left(\frac{\hbar^2}{2m}(k-G)^2-\varepsilon\right)C_{k-G}+\sum_{G'}U_{G'-G}C_{k-G'}=0$$

$U(x)$ = $2U$ cos$2\pi x/a$ = U exp($2\pi ix/a$)+U exp($-2\pi ix/a$)

$$=\sum_{G=g,-g}U_G e^{iGx}$$

There are only 2 components $U_g=U_{-g}=U$ ($g=2\pi/a$)

$$\left(\frac{\hbar^2}{2m}(k-G)^2-\varepsilon\right)C_{k-G}+\sum_{G'}U_{G'-G}C_{k-G'}=0$$

Matrix form of the central eq.

$$\begin{pmatrix} \ddots & & & & \\ \lambda_{k-2g}-\varepsilon & U & 0 & 0 & 0 \\ U & \lambda_{k-g}-\varepsilon & U & 0 & 0 \\ 0 & U & \lambda_k-\varepsilon & U & 0 \\ 0 & 0 & U & \lambda_{k+g}-\varepsilon & U \\ 0 & 0 & 0 & U & \lambda_{k+2g}-\varepsilon \\ & & & & \ddots \end{pmatrix}\begin{pmatrix} \vdots \\ C(k-2g) \\ C(k-g) \\ C(k) \\ C(k+g) \\ C(k+2g) \\ \\ \end{pmatrix}=0$$

Approximate solution near a zone boundary

1. Considering a wavevector exactly at zone boundary at first Brillouin zone boundary ½ g

k=0.5 g= π/a

k=0.5 g ⇨ $\hbar^2(k-g)^2/2m=\hbar^2(g/2)^2/2m$

⇩

$$\lambda_g=\lambda_{k-g}$$

C(½ g) and C(- ½ g) is important coefficients.

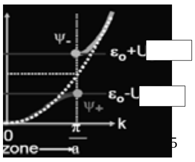
$$\begin{pmatrix} \ddots & & & & \\ \lambda_{k-2g}-\varepsilon & U & 0 & 0 & 0 \\ U & \lambda_{k-g}-\varepsilon & U & 0 & 0 \\ 0 & U & \lambda_k-\varepsilon & U & 0 \\ 0 & 0 & U & \lambda_{k+g}-\varepsilon & U \\ 0 & 0 & 0 & U & \lambda_{k+2g}-\varepsilon \\ & & & & \ddots \end{pmatrix}\begin{pmatrix} \vdots \\ C(k-2g) \\ C(k-g) \\ C(k) \\ C(k+g) \\ C(k+2g) \\ \\ \end{pmatrix}=0$$

Central equation :

$$(\lambda-\varepsilon)C_{\frac{G_1}{2}}+UC_{-\frac{G_1}{2}}=0$$
$$(\lambda-\varepsilon)C_{-\frac{G_1}{2}}+UC_{\frac{G_1}{2}}=0$$

$$\begin{vmatrix} \lambda-\varepsilon & U \\ U & \lambda-\varepsilon \end{vmatrix}=0$$

$$\varepsilon=\lambda\pm U=\frac{\hbar^2}{2m}\left(\frac{g}{2}\right)^2\pm U$$



$$(\lambda-\varepsilon)C_{\frac{G_1}{2}}+UC_{-\frac{G_1}{2}}=0$$
$$(\lambda-\varepsilon)C_{-\frac{G_1}{2}}+UC_{\frac{G_1}{2}}=0$$

$$\frac{C(-1/2g)}{C(1/2g)}=\frac{\varepsilon-\lambda}{U}=\pm1$$

$$\varepsilon=\lambda\pm U=\frac{\hbar^2}{2m}\left(\frac{g}{2}\right)^2\pm U$$

Wave function at first Brillouin zone boundary

$$\psi(x)=\exp(igx/2)\pm\exp(-igx/2)$$

Standing waves,

identical to previous discussion

2. Near the zone boundary

$$(\lambda_k-\varepsilon)C_k+UC_{k-G}=0$$

$$(\lambda_{k-G}-\varepsilon)C_{k-G}+UC_k=0$$

$$\begin{pmatrix} \ddots & & & & \\ \lambda_{k-2g}-\varepsilon & U & 0 & 0 & 0 \\ U & \lambda_{k-g}-\varepsilon & U & 0 & 0 \\ 0 & U & \lambda_k-\varepsilon & U & 0 \\ 0 & 0 & U & \lambda_{k+g}-\varepsilon & U \\ 0 & 0 & 0 & U & \lambda_{k+2g}-\varepsilon \\ & & & & \ddots \end{pmatrix}\begin{pmatrix} \vdots \\ C(k-2g) \\ C(k-g) \\ C(k) \\ C(k+g) \\ C(k+2g) \\ \end{pmatrix}=0$$

where $\lambda_k \equiv \hbar^2k^2/2m$

$$\begin{vmatrix} \lambda_k-\varepsilon & U \\ U & \lambda_{k-G}-\varepsilon \end{vmatrix}=0$$

Two solutions :

$$\boxed{\varepsilon^2=\frac{1}{2}(\lambda_k+\lambda_{k-G})\pm\sqrt{\frac{(\lambda_k-\lambda_{k-G})^2}{4}+U^2}}$$

Introducing a new parameter

$$\tilde{K}\equiv k-\frac{G}{2}$$ difference bet. k and zone boundary

$$\boxed{\varepsilon_k=\frac{1}{2}(\lambda_k+\lambda_{k-G})\pm\sqrt{\frac{(\lambda_k-\lambda_{k-G})^2}{4}+U^2}}$$

$$k\equiv\tilde{K}+\frac{G}{2}$$

$$\varepsilon_{\tilde{K}}=\frac{1}{2}\left(\lambda_{\tilde{K}+\frac{G}{2}}+\lambda_{\tilde{K}-\frac{G}{2}}\right)\pm\sqrt{\frac{\left(\lambda_{\tilde{K}+\frac{G}{2}}-\lambda_{\tilde{K}-\frac{G}{2}}\right)^2}{4}+U^2}$$

First term

$$\frac{1}{2}\left(\lambda_{\tilde{K}+\frac{G}{2}}+\lambda_{\tilde{K}-\frac{G}{2}}\right)=\frac{\hbar^2}{4m}\left(\left(\tilde{K}+\frac{G}{2}\right)^2+\left(\tilde{K}-\frac{G}{2}\right)^2\right)=\frac{\hbar^2}{2m}\left(\tilde{K}^2+\frac{G^2}{4}\right)$$

second term

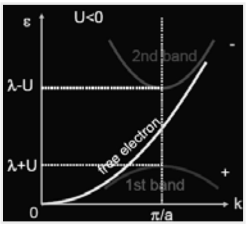
$$\left(\frac{1}{2}\left(\lambda_{\tilde{K}+\frac{G}{2}}+\lambda_{\tilde{K}-\frac{G}{2}}\right)\right)^2=\frac{\hbar^4}{16m^2}\left(\left(\tilde{K}+\frac{G}{2}\right)^2-\left(\tilde{K}-\frac{G}{2}\right)^2\right)^2=\frac{\hbar^4}{4m^2}\left(\tilde{K}^2G^2\right)$$

$$=4\frac{\hbar^2\tilde{K}^2}{2m}\left(\frac{\hbar^2}{2m}\left(\frac{G}{2}\right)^2\right)=4\frac{\hbar^2\tilde{K}^2}{2m}\lambda$$

$$\boxed{\varepsilon_{\tilde{K}}=\frac{\hbar^2}{2m}\left(\tilde{K}^2+\frac{G^2}{4}\right)\pm\sqrt{4\frac{\hbar^2\tilde{K}^2}{2m}\lambda+U^2}}=\left(\frac{\hbar^2\tilde{K}^2}{2m}+\lambda\right)\pm U\sqrt{1+4\frac{\hbar^2\tilde{K}^2}{2m}\frac{\lambda}{U^2}}$$

$$\varepsilon_{\tilde{K}}\approx\left(\frac{\hbar^2\tilde{K}^2}{2m}+\lambda\right)\pm U\left(1+\frac{1}{2}4\frac{\hbar^2\tilde{K}^2}{2m}\frac{\lambda}{U^2}\right)$$

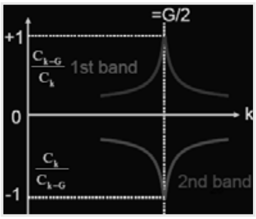
$$\boxed{\varepsilon_{\tilde{K}}=(\lambda\pm U)+\frac{\hbar^2\tilde{K}^2}{2m}\left(1\pm\frac{2\lambda}{U}\right)}$$



$$\psi(x)=C_k\exp(ikx)+C_{k-G}\exp(i(k-G)x)$$

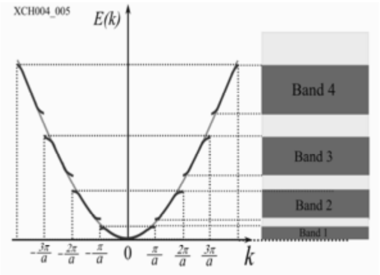
$$(\lambda_k-\varepsilon)C_k+UC_{k-G}=0$$

$$\boxed{\frac{C_{k-G}}{C_k}=-\frac{\lambda_k-\varepsilon}{U}}$$



One component dominates as we move away from the boundary.

Energy bands of nearly free electron calculation



k is unrestricted and is true free electron wavevector.

Bloch Theorem

$$\psi_k(x) = \sum_G C_{k-G} e^{i(k-G)x} \Rightarrow \boxed{\psi_k(x) = u_k(x) e^{ikx}}$$

$$\Downarrow$$

$$\psi_{k+G}(x) = \psi_k(x)$$
$$\varepsilon_{k+G} = \varepsilon_k$$

Check !

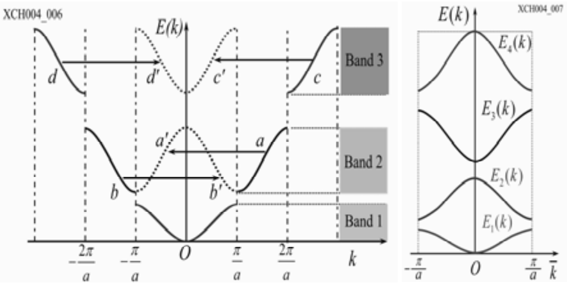
$$\Downarrow$$

The eigenstates and eignvalues are periodic functions of k in the reciprocal lattice.

Look for $k' + G = k$

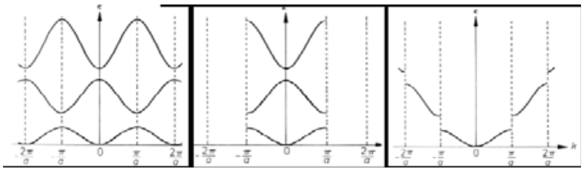
k’ in the first zone

Reduced wavevetor



Reduced zone

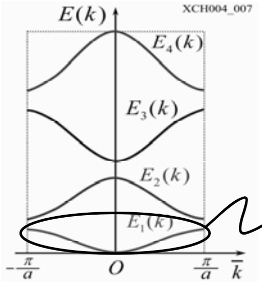
Extended, reduced, and periodic Brillouinzone schemes



Periodic zone Reduced zone Extended zone

All allowed states correspond to k-vectors in the first Brillouin Zone.

Can draw ε (k) in 3 different ways



- Each segment of ε versus k is an *energy band*
- Energy bands are separated by an *energy gaps*: $2U_G$

Separate
Or
Continue

?

Number of orbitals in a band

Linear crystal constructed of an even number *N* of primitive cell of lattice constant *a*.

Na=L

$\psi_k(x) = \psi_k(x + Na)$

$\psi_k(x) = \sum_G C_{k-G} e^{i(k-G)x}$

k = 0, ± 2π/L , ± 4π/L , ± 6π/L…Nπ/L

Number of states per band ?

Density of state (DOS)

D(k)= L/2 π

Δ k(BZ)=2 π **/a**

$N_{band} = D(k)\Delta k(BZ) = \frac{L}{2\pi}\frac{2\pi}{a} = \frac{L}{a} = N_{cell}$

- **Each primitive cell contributes exactly one independent value of k to each energy band.**
- **there are 2N independent orbitals in each energy band with account taken of the two independent orientations of the electron spin.**

Single atom of valence one in each cell

Single atom of valence two in each cell

Two atoms of valence one in each cell

What determines if the crystal will be a metal, or an insulator?

In terms of band theory of solids,

the absence of metallic conductivity implies that no partially filled bands.

In insulator, every band is either completely filled or completely empty.

Why?

Explain:

Case 1: filled band insulator

Energy of electron : $E_n(\vec{k}) = E_n(-\vec{k})$

velocity of wave vector k electron :

velocity of wave vector -k electron :

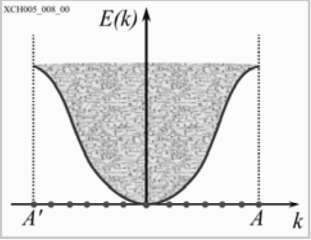
$\vec{v}(\vec{k}) = -\vec{v}(-\vec{k})$

i. no electric field

$\vec{v}(\vec{k}) = -\vec{v}(-\vec{k})$

$I = \sum_N \frac{1}{2} N[q\vec{v}(\vec{k}) + q\vec{v}(-\vec{k}) = 0$

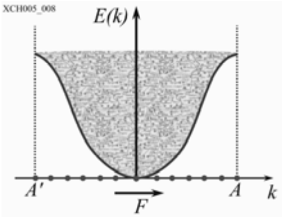
No net current



ii with external electric field

$\frac{d\vec{k}}{dt} = -\frac{1}{\hbar} q\vec{E}$

There is no continuous way to change the total momentum of the electrons if every accessible state is filled.



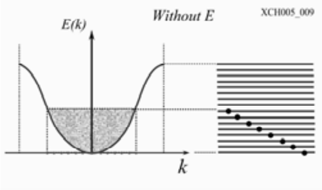
An external electron field will not cause current flow for filled band case.

Case 1: partly filled band

i. no electric field

$$I=\sum_N \frac{1}{2} N[q\vec{v}(\vec{k})+q\vec{v}(-\vec{k})=0$$

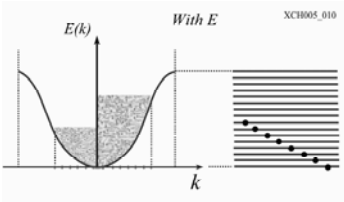
No net current



ii with external electric field

An external electric field will change distribution of electronic state.

net current≠0



Monovalent ***Li*(3)、*Na*(11)、*K*(19)、*Cu*(29)、*Ag*(47)**

⟹ 1/2 band filled

Trivalent ***Al*(13)** ⟹ 3/2 band filled

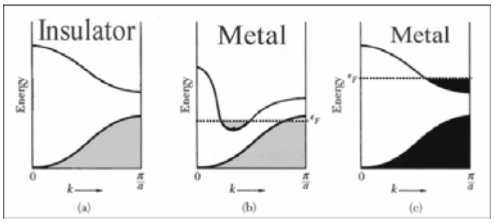
Crystal with an odd number of electrons per cell must be metallic.

Divalent ⟹ 1 band filled (insulator ?)

Crystal with an even number of electrons per cell must be insulator?

Alkaline earth metal ***Be*(4)、*Mg*(12)、*Zn*(30)** Divalent

Bands overlap ⟹ metal



Occupied states and band structures giving (a) an insulator, (b) a metal or a senimetal because of band overlap, and (c)a metal because of electron concentration. If the overlap is small, with relatively few states involved, we speak of a semimetal.

Crystal with an even number of electrons per cell may be either metallic or insulating.

Metals

Overlapping bands

Be,Mg,Ca,Sr,Ba…

Both 3S and 3P bands are partially filled.

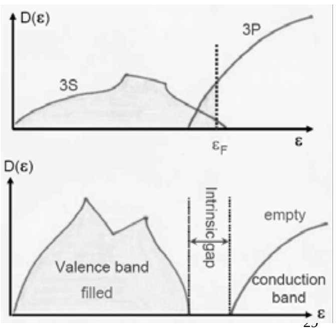
Insulators

No overlap of bands

Si, Ge, …

Valence band filled

Conduction band empty



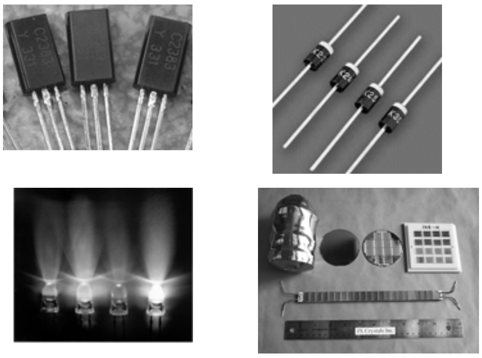
Homework

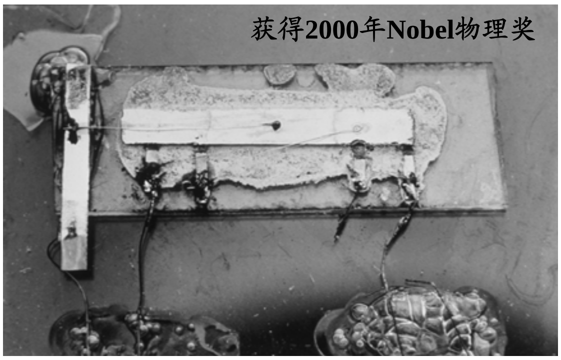
P 195

7.1 7.2 7.3 7.4 7.6

Chapter 8
Semiconductor Crystal

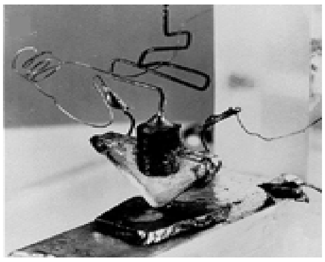
1) **Band gap**
2) **Equations of motion**
3) **Intrinsic carrier concentration**
4) **Impurity conductivity**
5) **Thermoelectric effects**
6) **Semimetals**
7) **Superlattices**





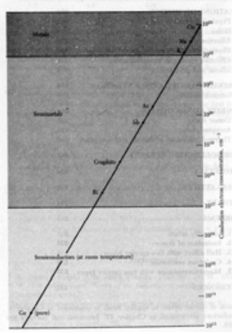
1958年第一块集成电路：TI公司的Kilby，12个器件，Ge晶片

1947年12月23日
第一个晶体管
NPN Ge晶体管
W. Schokley
J. Bardeen
W. Brattain



获得1956年Nobel物理奖

Useful nomenclature



Elements :Group IV

C(graphite) 1S22S22P2

Si 1S22S22P63S23P2

Ge

1S22S22P63S23P63d104S24P2

Compounds :

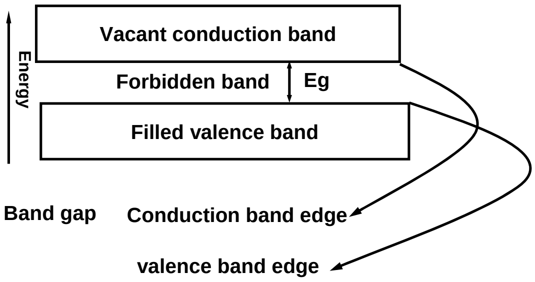
IV-IV: SiC

III-V: GaAs, InSb, GaP, ..

Ga1S22S22P63S23P63d104S24P1

As 1S22S22P63S23P63d104S24P3

II-VI : ZnS, CdSe, …



Vacant conduction band

Forbidden band **Eg**

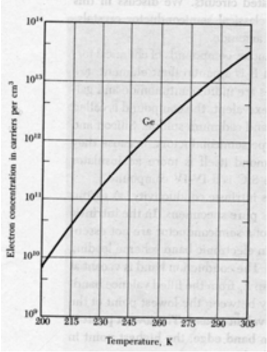
Filled valence band

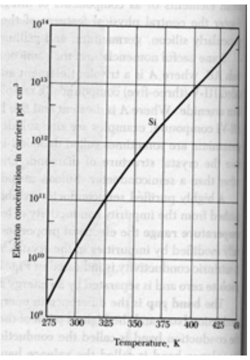
Band gap **Conduction band edge**

valence band edge

zero temperature **zero Conductivity**

finite temperature **finite conductivity**

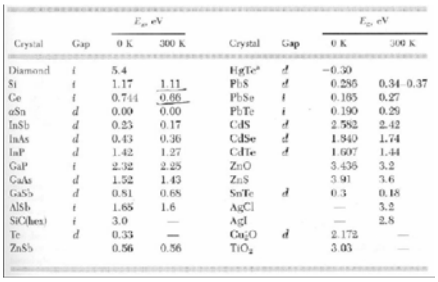




Band gap

determines intrinsic conductivity and intrinsic carrier concentration

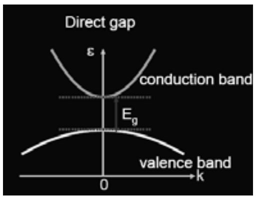
$$\frac{E_g}{k_B T}$$



Crystal	Gap	E_g, eV 0 K	E_g, eV 300 K	Crystal	Gap	E_g, eV 0 K	E_g, eV 300 K
Diamond	i	5.4		HgTe*	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
αSn	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	—

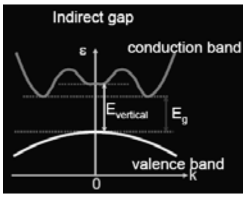
Eg can be obtained by optical absorption

Two types of semiconductors



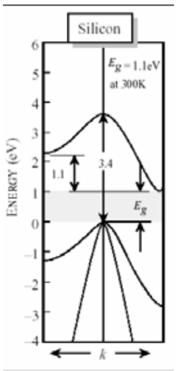
Band edges (extremes) at same k

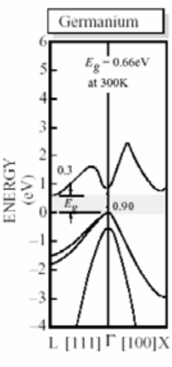
(most compounds)

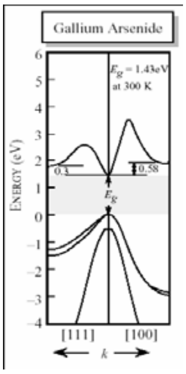


Band edges of valence and conduction bans at different ks

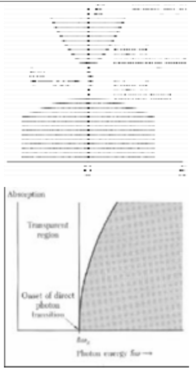
(Ge[111], Si[100], …)





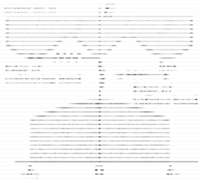


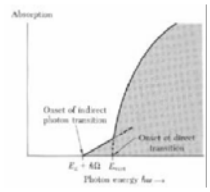
Direct absorption process



$$\hbar\vec{k}' - \hbar\vec{k} = \vec{p}_{photon}$$

Indirect absorption process





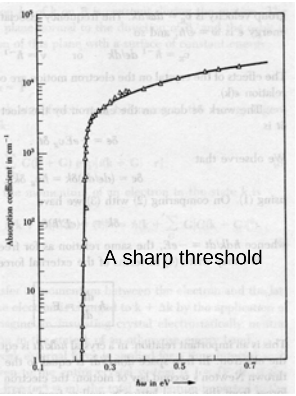
$$\Delta E_k = \hbar\omega \pm \hbar\Omega$$

$$\Delta E_k \approx \hbar\omega$$

$$\hbar\vec{k}' - \hbar\vec{k} = \pm\hbar\vec{q}$$

Optical absorption of InSb

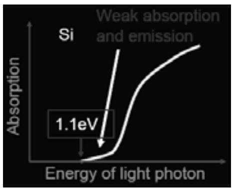
Eg=0.23eV

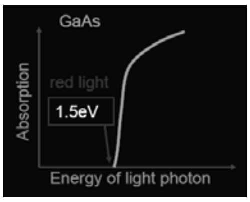


A sharp threshold

Why is your computer chip made of Si, but the laser in your CD player is made of GaAs(GaN in the future)?

Comparison of absorption



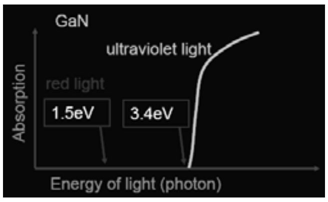


Light emission is related

–very high efficiency in GaAs for excited electron to emit light

–very low efficiency in Si

Why is GaN interesting?



After decades of efforts, finally it is possible to make blue light emitter and laser.

Shorter wavelength light focuses to smaller spot implies higher density of information on a CD.

Equation of motion

In an external electric field E,

The energy gained by the electron in a time interval **Δt**

$$\vec{F} = -e\vec{E} \qquad \Delta\vec{l} = \vec{v}\Delta t$$

$$\Downarrow$$

$$\boxed{\Delta\varepsilon = \vec{F} \bullet \Delta\vec{l} = (-e\vec{E}) \bullet (\vec{v}\Delta t) = (-e\vec{E}) \bullet \frac{1}{\hbar}\cancel{\nabla_{\vec{k}}\varepsilon(\vec{k})}\Delta t}$$

$$= \cancel{\nabla_{\vec{k}}\varepsilon(\vec{k})} \bullet (\Delta\vec{k})$$

$$\Rightarrow \quad \Delta\vec{k} = \frac{-e\vec{E}}{\hbar}\Delta t$$

setting Δ t→0 $d\vec{k} = \frac{-e\vec{E}}{\hbar}dt$

In general, equation of motion for an Bloch electron under Lorentz forces

$$d\vec{k} = \frac{-e\vec{E}}{\hbar}dt \quad \Rightarrow \quad \hbar\frac{d\vec{k}}{dt} = -e\vec{E} = \vec{F}$$

Newton's 2nd law

$$\Downarrow$$

$$\hbar\frac{d\vec{k}}{dt} = \vec{F}_{ext} = q\left(\vec{E} + \left(\frac{1}{\hbar}\nabla_{\vec{k}}\varepsilon(\vec{k})\right)\times\vec{B}\right)$$

Weak external forces such that band structure still holds.

Real momentum

$$P_{el} = \left\langle k\left|\hat{p}\right|k\right\rangle = \left\langle k\left|\frac{\hbar}{i}\nabla\right|k\right\rangle = \frac{\hbar}{i}\sum_G i(k+G)\left|C_{k+G}\right|^2$$

$$\boxed{= \hbar\vec{k} + \sum_G \hbar\vec{G}\left|C_{k+G}\right|^2}$$

where

$$\left|k\right\rangle = \psi_k(r) = \sum_G C_{k+G}e^{i(k+G)\bullet r}$$

$$\left\langle k \mid k\right\rangle = \sum_G \left|C_{k+G}\right|^2 = 1$$

Under a weak external force F,

Impulse = the change of momentum of the crystal

$$\vec{J} = \int \vec{F}dt = \Delta\vec{P}_{total} = \Delta\vec{P}_{eletron} + \Delta P_{lattica}$$

$$= \hbar\vec{k} + \sum_G \hbar\vec{G}\left|C_{k+G}\right|^2$$

$$\Downarrow$$

$$\Delta P_{electron} = (\Delta_{\vec{k}}\vec{P}_{electron})\bullet\Delta\vec{k} = \hbar\Delta\vec{k} + \sum_G \hbar\vec{G}\left(\nabla_{\vec{k}}\left|C_{\vec{k}+\vec{G}}\right|^2\bullet\Delta\vec{k}\right)$$

Momentum of electron

$$\hbar\vec{k} \quad \Rightarrow \quad \hbar(\vec{k}+\vec{G})$$

Momentum of lattice $-\hbar\vec{G}$

$$p_{lat} = < k \,|-\hbar G|\, k >$$

$$\Downarrow$$

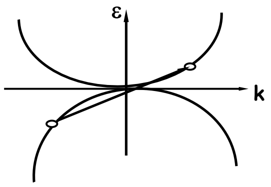
$$\Delta P_{lattice} = -\sum_G \hbar\vec{G}\left(\nabla_{\vec{k}}\left|C_{\vec{k}+\vec{G}}\right|^2\bullet\Delta\vec{k}\right)$$

$$\Rightarrow \quad \vec{J} = \hbar\Delta\vec{k} \quad \Rightarrow \quad \boxed{\hbar\frac{d\vec{k}}{dt} = \vec{F}}$$

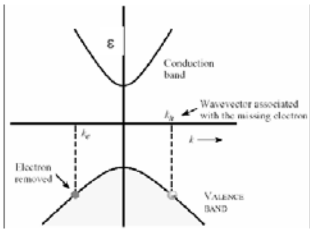
same as for free electrons

Holes in semiconductors

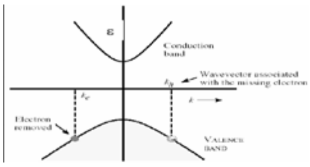
- In a completely filled band (valence band), no current can flow since electrons are Fermions and obey the Pauli exclusion principle.
- The empty states in the valence band are called "*holes*".



- The electrons can "move"if there is an empty state (a hole) available.
- A hole acts under the external forces as if it has a positive charge *+e*.



Missing electron = producing hole

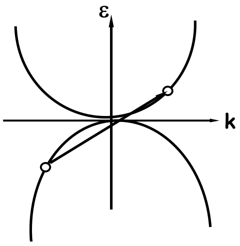


In a full band : all pairs of states $(\vec{k},-\vec{k})$ are filled and $\sum \vec{k}=0$

If an electron of wave vector k_e is missing, $\sum \vec{k}=-\vec{k}_e$

Alternatively speaking,

a hole of wave vector $\vec{k}_h$ is produced and $\vec{k}_h=-\vec{k}_e$



- Setting the energy of the top of valence band is zero,
- the lower in the band the missing electron lies, the higher the energy of the system.

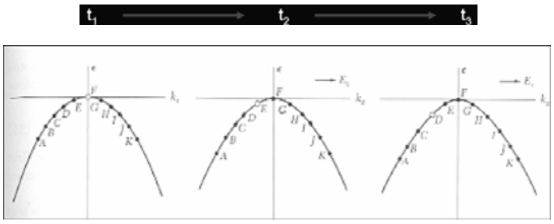
The band is symmetric :

$$\boxed{\varepsilon_e(\vec{k}_e)=\varepsilon_e(-\vec{k}_e)=-\varepsilon_h(\vec{k}_h)}$$

$$v_h=\frac{1}{\hbar}\nabla_{\vec{k}_h}\varepsilon_h=\frac{1}{\hbar}\left(-\nabla_{\vec{k}_e}\right)(-\varepsilon_e)=v_e$$

The group velocity of the hole is the same as that of the electron.

How does a hole move?



$$j=(-e)v(G)=(-e)[-v(E)]=ev(E)$$

the equation of a motion for ***an electron***

$$\hbar\frac{d\vec{k}_e}{dt}=(-e)\left(\vec{E}+\frac{1}{\hbar}\nabla_{\vec{k}_e}\varepsilon_e(\vec{k}_e)\times\vec{B}\right)$$

Applying to a missing electron: creation of a hole

$$\hbar\frac{d(-\vec{k}_h)}{dt}=(-e)\left(\vec{E}+\frac{1}{\hbar}\nabla_{\vec{k}_h}\varepsilon_h(\vec{k}_h)\times\vec{B}\right)$$

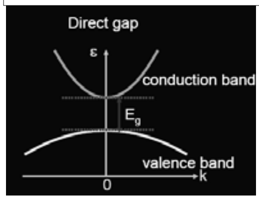
$$\hbar\frac{d\vec{k}_h}{dt}=(+e)\left(\vec{E}+\frac{1}{\hbar}\nabla_{\vec{k}_h}\varepsilon_h(\vec{k}_h)\times\vec{B}\right)$$

exactly the equation of motion for a particle of positive charge

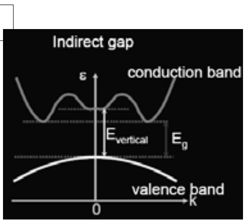
the equation of a motion for ***a hole***

Review

Two types of semiconductors



Band edges (extremes)
at same k
(most compounds)



Band edges of valence
and conduction bans
at different k_s
(Ge[111], Si[100], …)

Holes in semiconductors

- The empty states in the valence band are called “*holes*”.
- The electrons can “move”if there is an empty state (a hole) available.
- A hole acts under the external forces as if it has a positive charge *+e*.

Effective mass (band mass)

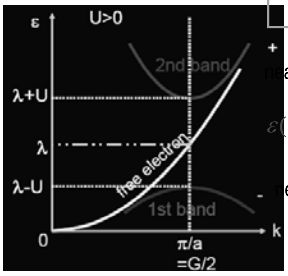
$$\frac{1}{m^*}=\frac{1}{\hbar^2}\frac{d^2\varepsilon(k)}{dk^2}$$

- For a free electron ε(k) = $\hbar^2k^2/2m$ ⇒ m*=m
- For electrons in a band, their masses depend on band curvature.

$$\boxed{\varepsilon_{\tilde K}\approx(\lambda\pm U)+\frac{\hbar^2\tilde K^2}{2m}\left(1\pm\frac{2\lambda}{U}\right)}$$

distance to the zone boundary

$$\boxed{\varepsilon_{\tilde K}\approx(\lambda\pm U)+\frac{\hbar^2\tilde K^2}{2m}\left(1\pm\frac{2\lambda}{U}\right)}$$



near the lower edge of the 2nd band

$$\varepsilon(\tilde K)=\varepsilon_c+\frac{\hbar^2}{2m_e}\tilde K^2$$ where $\varepsilon_c=\lambda+U$

near the top edge of the 1st band

$$\varepsilon(\tilde K)=\varepsilon_v-\frac{\hbar^2}{2m_h}\tilde K^2$$

where $\varepsilon_c=\lambda-U$

$$\boxed{\frac{\hbar^2}{2m_e}\tilde K^2=\frac{\hbar^2}{2m}\tilde K^2\left(1+\frac{2\lambda}{U}\right)}\Rightarrow\boxed{\frac{m_e}{m}=\frac{1}{2\lambda/U+1}}$$

$$\boxed{\frac{\hbar^2}{2m_h}\tilde K^2=\frac{\hbar^2}{2m}\tilde K^2\left(\frac{2\lambda}{U}-1\right)}\Rightarrow\boxed{\frac{m_h}{m}=\frac{1}{2\lambda/U-1}}$$

…………………………………………………………………………………

$$\vec v(\vec k)=\frac{1}{\hbar}\nabla_{\vec k}\varepsilon(\vec k)$$

$$\frac{d\vec v(k)}{dt}=\frac{1}{\hbar}\frac{d\nabla_k\varepsilon(\vec k)}{dt}=\frac{1}{\hbar}\frac{d^2\varepsilon(k)}{dk^2}\frac{d\vec k}{dt}=\frac{1}{\hbar^2}\frac{d^2\varepsilon(k)}{dk^2}\overset{F}{\boxed{\left(\hbar\frac{dk}{dt}\right)}}$$

From Newton’s 2nd law ⇒ $$\frac{1}{m^*}=\frac{1}{\hbar^2}\frac{d^2\varepsilon(k)}{dk^2}$$

Definition of the effective mass

Considering an anisotropic energy surface

$$\left(\frac{1}{m^*}\right)_{\mu\nu}=\frac{1}{\hbar^2}\frac{d^2\varepsilon(k)}{dk_\mu dk_\nu}$$

where μ and ν are Cartesian coordinates.

reciprocal effective mass tensor (3x3)

In three (two) dimensions, constant energy surfaces (lines) are not necessarily spherical (circular), and the effective mass is a tensor:

$$\left(\frac{1}{m^*}\right)_{\mu\nu}=\frac{1}{\hbar^2}\frac{d^2\varepsilon(k)}{dk_\mu dk_\nu}$$

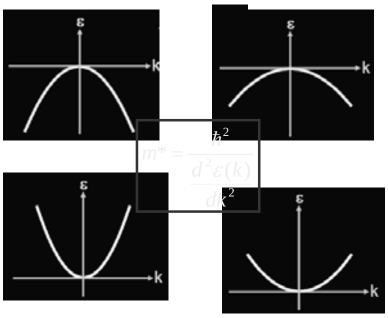
In two dimensions, **free electron**

$$\varepsilon(k_x,k_y)=\frac{\hbar^2}{2m_e}(k_x^2+k_y^2)$$

$$\left(\frac{1}{m^*}\right)_{\mu\nu}=\frac{1}{\hbar^2}\frac{d^2\varepsilon(k)}{dk_\mu dk_\nu}=\frac{1}{m_e}\delta_{\mu\nu} \Rightarrow m^*=\begin{pmatrix} m_e & 0 \\ 0 & m_e \end{pmatrix}$$

m* <0

m* >0



$$m^*=\frac{\hbar^2}{\frac{d^2\varepsilon(k)}{dk^2}}$$

m* can be determined by cyclotron resonance measurements.

The effective mass depends on the *curvature* of the bands

- The flat bands have large effective masses
  The curved bands have small effective masses

- Near the bottom of a band, m* is *positive*
  Near the top of a band, m* is *negative*

Effective mass in semiconductors

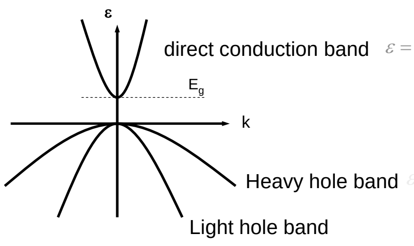
Cyclotron resonance

energy surfaces of the conduction and valence bands near the band edge

$\omega_c=\frac{eB}{m^*}$ where m*is the cyclotron effective mass

Crystal	***Electron (m_e/m)***	***Heavy hole (m_{hh}/m)***	***Light hole (m_{lh}/m)***
GaAs	0.066	0.5	0.082
InAs	0.026	0.39	0.025
Cu_2O	0.99	--	0.58

$$m^*=\hbar^2\Big/\frac{d^2\varepsilon(k)}{dk^2}$$



$$\varepsilon=E_g+\frac{\hbar^2k^2}{2m_e}$$

$$\varepsilon=\frac{\hbar^2k^2}{2m_h}$$

Intrinsic carrier concentration

metallic conductivity **temperature** **dR/dT>0**

conductivity of semiconductor ⟺ **dependent** **temperature**

dR/dT<0

“free”charges must be thermally excited and overcome E_g

Intrinsic ?

charge carrier concentrations n & p have a strong dependence on T.

when "free"electrons and holes can be created only by electronic excitations from the valence band to the conduction band.

Semiconductor are called "intrinsic"

Electron concentration in the conduction band

$$n = \int_{E_c}^{\infty} D_c(\varepsilon) f_e(\varepsilon, T)\, d\varepsilon$$

Hole concentration in the valence band

$$p = \int_{-\infty}^{E_v} D_v(\varepsilon) f_h(\varepsilon, T)\, d\varepsilon$$

Fermi-Dirac distribution

suppose $\boxed{\varepsilon - \mu >> k_B T}$

Electrons

$$\boxed{f_e(\varepsilon) = \frac{1}{\exp\left[(\varepsilon - \mu)/k_B T\right] + 1} \approx \exp\left(-\frac{\varepsilon - \mu}{k_B T}\right)}$$

suppose $\boxed{\mu - \varepsilon >> k_B T}$

Holes

$$\boxed{f_h(\varepsilon) = 1 - f_e(\varepsilon) = \frac{1}{1 + \exp\left[-(\varepsilon - \mu)/k_B T\right]} \approx \exp\left(\frac{\varepsilon - \mu}{k_B T}\right)}$$

Bolzmann

In the parabolic approximation (for simplicity),

The energy of an electron in the conduction band,

$$\varepsilon_k = E_c + \frac{\hbar^2 k^2}{2m_e}$$

Density of states, $D(\varepsilon) = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} \sqrt{\varepsilon - E_c}$

$D_c(\varepsilon)$

$f_e(\varepsilon, T)$

$$\Rightarrow \quad n = \int_{E_c}^{\infty} D_c(\varepsilon) f_e(\varepsilon, T)\, d\varepsilon$$

$$n = \int_{E_c}^{\infty} D_c(\varepsilon) f_e(\varepsilon, T)\, d\varepsilon$$

$$= \int_{E_c}^{\infty} \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)\sqrt{\varepsilon - E_c}\, \exp\left(\frac{\mu - \varepsilon}{k_B T}\right) d\varepsilon$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} \exp\left(\frac{\mu}{k_B T}\right) \boxed{\int_{E_c}^{\infty} \sqrt{\varepsilon - E_c}\, \exp\left(\frac{-\varepsilon}{k_B T}\right) d\varepsilon}$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} \exp\left(\frac{\mu}{k_B T}\right) \int_{E_c}^{\infty} \sqrt{\varepsilon - E_c}\, \exp\left(\frac{-\varepsilon}{k_B T}\right) d\varepsilon$$

$$\int_0^{\infty} \sqrt{\varepsilon}\, \exp\left(\frac{-\varepsilon}{k_B T}\right) d\varepsilon \times \exp\left(\frac{-E_c}{k_B T}\right)$$

$$\Downarrow$$

$$n = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2} \exp\left(\frac{\mu - E_c}{k_B T}\right)$$

$$p = \int_{-\infty}^{E_v} D_v(\varepsilon)\, f_h(\varepsilon, T)\, d\varepsilon$$

$$D(\varepsilon) = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\sqrt{E_v - \varepsilon}$$

$$= \int_{-\infty}^{E_v} \frac{1}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2}\sqrt{E_v - \varepsilon}\,\exp\left(\frac{\varepsilon - \mu}{k_B T}\right) d\varepsilon$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2}\exp\left(\frac{-\mu}{k_B T}\right)\boxed{\int_{-\infty}^{E_v}\sqrt{E_v - \varepsilon}\,\exp\left(\frac{\varepsilon}{k_B T}\right) d\varepsilon}$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2}\exp\left(\frac{-\mu}{k_B T}\right)\int_{-\infty}^{E_v}\sqrt{E_v - \varepsilon}\,\exp\left(\frac{\varepsilon}{k_B T}\right) d\varepsilon$$

$$\int_0^{\infty}\sqrt{\varepsilon}\,\exp\left(\frac{-\varepsilon}{k_B T}\right) d\varepsilon^{*}\exp\left(\frac{E_v}{k_B T}\right)$$

$$\boxed{p = 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2}\exp\left(\frac{E_v - \mu}{k_B T}\right)}$$

$$np = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2}\exp\left(\frac{\mu - E_c}{k_B T}\right) 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2}\exp\left(\frac{E_v - \mu}{k_B T}\right)$$

$$\boxed{= 4\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3}(m_e m_h)^{3/2}\exp\left(\frac{-E_g}{k_B T}\right)}$$

=constant depends on material and temperature

Eg=Ec-Ev

Independent of E_F, (μ)

For an intrinsic semiconductor **n=p,**

$$\boxed{n_i = p_i = 2\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2}(m_e m_h)^{3/4}\exp\left(\frac{-E_g}{2k_B T}\right)}$$

$$\boxed{n = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2}\exp\left(\frac{\mu - E_c}{k_B T}\right)} \qquad \boxed{p = 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2}\exp\left(\frac{E_v - \mu}{k_B T}\right)}$$

Fermi level $\boxed{\mu = \frac{1}{2}E_g + \frac{3}{4}k_B T \ln\left(\frac{m_h}{m_e}\right)}$

$$\boxed{\mu = \frac{1}{2}E_g + \frac{3}{4}k_B T \ln\left(\frac{m_h}{m_e}\right)}$$

At T=0, μ lies half-way between the conduction and valence bands.

As T increases, μ moves toward the band with smaller effective mass

μ does not go far from mid-gap when $m_h \approx m_e$

Intrinsic mobility

Electrical conductivity $\boxed{\sigma = ne\mu}$

$\boxed{\sigma = ne\mu_e + pe\mu_h}$ **∝ n & p**

∝ μ

μ: ⇨ **mobility** ⇨ $\mu = \frac{|v_d|}{E}$

The magnitude of the velocity per unit electron field

SI units m^2/Vs

Drift velocity of a charge q

$$v = q\tau E / m$$

$$\Downarrow$$

$$\mu = \frac{|v_d|}{E} \Rightarrow \boxed{\sigma = ne\mu_e + pe\mu_h}$$

$$\Downarrow$$

$$\boxed{\sigma = \frac{ne^2\tau_e}{m_e} + \frac{pe^2\tau_h}{m_h}}$$

T=300 k

crystal	***μ_e(cm^2/Vs)***	***μ_h(cm^2/Vs)***
GaAs	**8000**	**300**
InAs	**30000**	**450**
Diamond	**1800**	**1200**
Si	**1350**	**480**
Ge	**3600**	**1800**
PbS	**550**	**600**

The hole mobilities are typically smaller than the electron mobilities

because of the occurrence of band degeneracy at the valence band edge at the zone center, thereby making possible interband scattering processes that reduce the mobility.

Review

Intrinsic carrier concentration

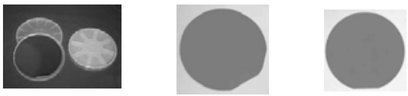
“free”charges must be thermally excited and overcome E_g

$$n = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2} \exp\left(\frac{\mu - E_c}{k_B T}\right)$$

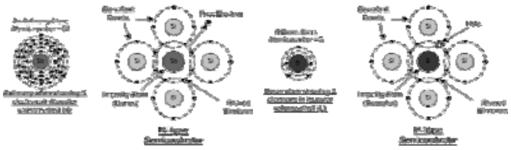
$$p = 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2} \exp\left(\frac{E_v - \mu}{k_B T}\right)$$

$$np = 4\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3} (m_e m_h)^{3/2} \exp\left(\frac{-E_g}{k_B T}\right) \Rightarrow n_i = p_i = 2\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2} (m_e m_h)^{3/4} \exp\left(\frac{-E_g}{2k_B T}\right)$$

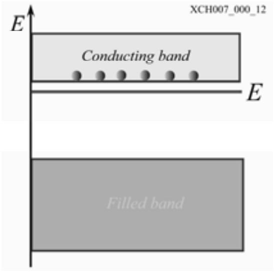
Impurity conductivity



Doping : addition of impurities to the crystal



Increases the conductivity of pure silicon



(1) Donors – Group of V such as N, P, As, Sb

N-type

Substitutional impurity for semiconductor

each dopant atom contribute an electron

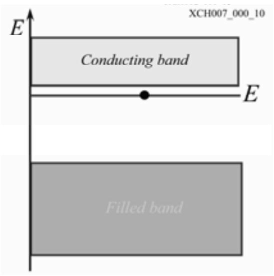
P-type

(2) Acceptors – Group of III such as B, Al, Ga, In

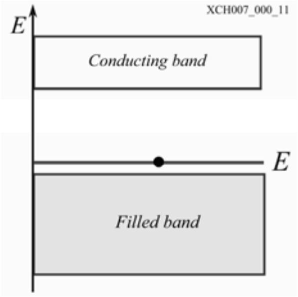
attract electrons from valence band of semiconductor

create a hole per atom

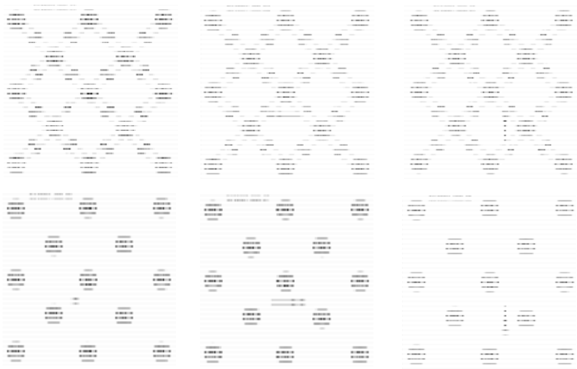
Donors

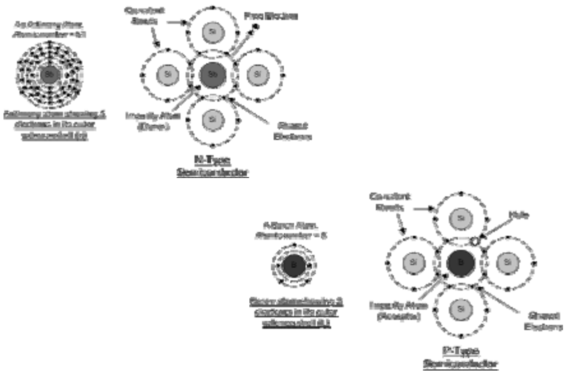


Acceptors



Boron atom ⟹ Silicon atom

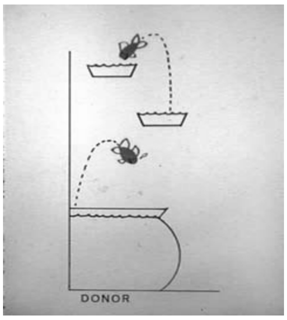




Where do electrons / holes of the dopants go?

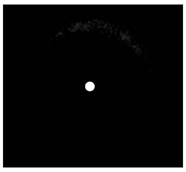
Low T : bound

High T : free



Activated energy –From Bohr model

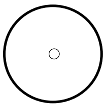
Hydrogen atom



$$F = \frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{mv^2}{r}$$

and $L = mvr = n\hbar$

$$r_n = \frac{4\pi\varepsilon_0\hbar^2}{me^2} n^2 = a_0 n^2$$

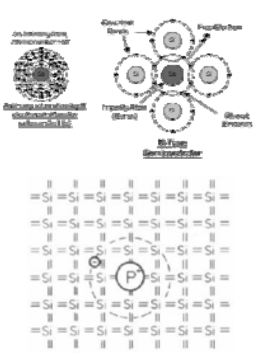


$$E_n = -\frac{e^4 m}{32\pi^2\varepsilon_0^2\hbar^2}\frac{1}{n^2} = -\frac{13.6eV}{n^2}$$

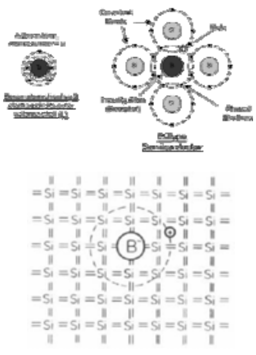
Ionization energy

13.6 eV

N-doped Silicon



P-doped Silicon



The fifth valence electron of P atom is not required for bounding and is thus, only weakly bound. The binding energy can be estimated by treating the system as a hydrogen atom embedded in a dielectric.

Donor

$\varepsilon = \kappa\varepsilon_0$

Dielectric constant

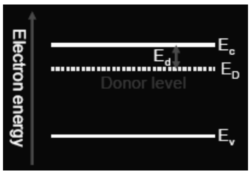
and $2\pi r = n\lambda$

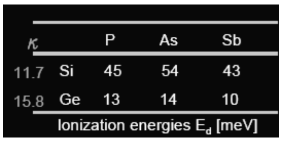
$$a_d = \frac{4\pi\kappa\varepsilon_0\hbar^2}{m_e e^2} = a_0\left(\kappa\frac{m}{m_e}\right)$$

$a_o(10)(10)$

$$E_d = \frac{e^4 m_e}{32\pi^2\kappa^2\varepsilon_0^2\hbar^2} = \frac{13.6eV}{\kappa^2}\left(\frac{m_e}{m}\right)$$

13.6eV$(10^{-2})(10^{-1})$



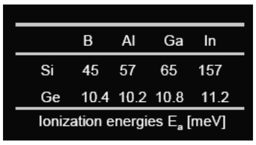


κ		P	As	Sb
11.7	Si	45	54	43
15.8	Ge	13	14	10

Ionization energies E_d [meV]

The valence –three Boron (B) accepts an electron from the Si lattice. The hole that is thereby created in the valence band orbits around the negatively charged impurity.

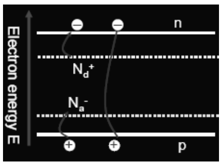
The Bohr model applies qualitatively for holes just as for electrons, but the degeneracy at the top of the valence band complicates the effective mass problem.



	B	Al	Ga	In
Si	45	57	65	157
Ge	10.4	10.2	10.8	11.2

Ionization energies E_a [meV]

In a doped semiconductor,



Density of doped donor

$N_d = N_d^o + N_d^+$

Density of doped acceptor

$N_a = N_a^o + N_a^-$

- an electron in the conduction band can originate either from the valence band or from the ionization of a donor;
- a hoe in a valence band may correspond either to the electron in the conduction band or to the negatively charged acceptor.

Neutrality condition $n + N_a^- = p + N_d^+$

$$N_d^0 = N_d \frac{1}{\exp[(E_D - E_F)/k_BT]+1}$$

$$N_a^0 = N_a \frac{1}{\exp[(E_F - E_A)/k_BT]+1}$$

For pure N-type semiconductor : only donors are available

$n = n_0 \exp\left(\frac{E_F - E_c}{k_BT}\right)$ where and

$N_d = N_d^0 + N_d^+$ And $n = N_d^+ + p$

For the simple case $N_d^+ >> n_i$ $k_BT << E_g$ therefore, $n \sim N_d^+ = N_d - N_d^o$

$$n \approx N_d - N_d^0 = N_d\left(1 - \frac{1}{\exp[(E_D - E_F)/k_BT]+1}\right) = N_d\left(\frac{1}{1+\exp[-(E_D - E_F)/k_BT]}\right)$$

$$\boxed{\frac{n}{n_0}\exp\left(\frac{E_c}{k_BT}\right) = \exp\left(\frac{E_F}{k_BT}\right)}$$

$$n \approx N_d\left(\frac{1}{1+\frac{n}{n_0}\exp[E_c/k_BT]\exp[-E_D/k_BT]}\right)$$

$$n\left(1+\frac{n}{n_0}\exp\left[\frac{E_d}{k_BT}\right]\right) \approx N_d$$

$$\frac{1}{n_0}\exp\left[\frac{E_d}{k_BT}\right]n^2 + n - N_d = 0$$

solution $n = \frac{n_0}{2}\exp\left(-\frac{E_d}{k_BT}\right)\left[-1+\sqrt{1+4\frac{N_d}{n_0}\exp\left(\frac{E_d}{k_BT}\right)}\right]$

At low temperatures, such that $4\frac{N_d}{n_0}\exp\left(\frac{E_d}{k_BT}\right) >> 1$

$$n \approx \sqrt{n_0 N_d}\,\exp\left[-\frac{E_d}{2k_BT}\right]$$

A sufficiently large number of donors still retain their valence electrons,

i.e. are not ionized.

At the intermediate temperatures,such that $4\frac{N_d}{n_0}\exp\left(\frac{E_d}{k_BT}\right) << 1$

The concentration of donor electrons in the conduction band has reached the maximum possible value, equal to the concentration of donor.

All donors are ionized.

At high temperatures,such that $k_BT \approx E_g$

$$n \approx N_d + n_i \approx N_d + n_0 \exp\left(-\frac{E_g}{2k_BT}\right)$$

A semiconductor doped with N_d donor electrons

$k_BT < E_d$

Dopant carriers are thermally excited to conduction band

$n \sim \sqrt{n_0 N_d}\,\exp\left(-\frac{E_d}{2k_BT}\right)$

where $n_0 = 2\left(\frac{m_e k_BT}{2\pi\hbar^2}\right)^{3/2}$

$E_g >> k_BT > E_d$

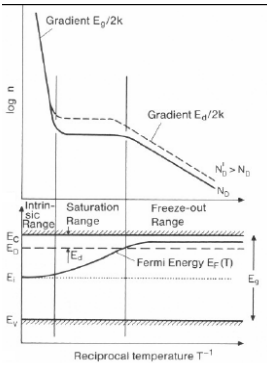
All carriers are excited (Saturation)

$n \sim N_d$

$E_g \sim k_BT$

Intrinsic carriers are excited from valence band

$n \approx N_d + n_i \approx N_d + n_0 \exp\left(-\frac{E_g}{2k_BT}\right)$



A semiconductor doped with N_a acceptor holes

Same results

Low Temperatures, $k_BT<E_a$

$p \sim \sqrt{p_0 N_a}\,\exp\left(-\frac{E_a}{2k_BT}\right)$

where $p_0 = 2\left(\frac{m_h k_BT}{2\pi\hbar^2}\right)^{3/2}$

Intermediate temperatures, $E_g>>k_BT>E_a$

$p=N_a$

High Temperatures, $Eg \sim k_BT$

$p \approx N_a + p_i \approx N_a + p_0 \exp\left(-\frac{E_g}{2k_BT}\right)$

Saturation range(E_d, $E_a< k_BT< E_g$)

N-type : $n \approx N_d >> p$ dominated by electrons

electrical conductivity $\sigma \approx N_d|e|\mu_e + p|e|\mu_h$

Hall coefficient $R_H \approx -\frac{1}{n|e|} \approx -\frac{1}{N_d|e|}$

P-type : $p \approx N_a >> n$ dominated by holes

electrical conductivity $\sigma \approx N_a|e|\mu_h + n|e|\mu_e$

Hall coefficient $R_H \approx \frac{1}{p|e|} \approx \frac{1}{N_a|e|}$

Summary

7/01/2009

Chapter One   Crystal structure

1. Periodic arrays of atom

$$\boxed{\text{Lattice +basis=crystal structure}}$$

Translation operator

$\vec{T} = u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$ Translation vectors $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$

Every lattice point

$\vec{r}' = \vec{r} + u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$ $\vec{a}_1, \vec{a}_2, \vec{a}_3 = \text{lattice vector}$

---

2. Primitive cell -A minimum volume cell

$\vec{a}_1, \vec{a}_2, \vec{a}_3 = \text{lattice vector}$ Primitive translation vectors

Wigner-Seitz Primitive cell

3. Bravais lattices Basis ⟶ One atom

A Bravais lattice is a lattice in which every lattice point has exactly the same environment.

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4. Primitive cell: A minimum volume cell.

conventional cell: more obvious relation with the point symmetry operation

5. Directions and planes in crystals

6. Most common crystal structures :

1. Simple Cubic lattice
2. Body Centered Cubic lattice
3.Face Centered Cubic lattice :

Chapter Two Reciprocal Lattice

1. Various statements of the Bragg condition

$2d\sin\theta = n\lambda$ $\Delta k = G$ $2k \bullet G = G^2$

2. Reciprocal lattices Vectors

$$\vec{b}_1 = 2\pi\frac{\vec{a}_2\times\vec{a}_3}{|\vec{a}_1\bullet\vec{a}_2\times\vec{a}_3|};\ \vec{b}_2 = 2\pi\frac{\vec{a}_3\times\vec{a}_1}{|\vec{a}_1\bullet\vec{a}_2\times\vec{a}_3|};\ \vec{b}_3 = 2\pi\frac{\vec{a}_1\times\vec{a}_2}{|\vec{a}_1\bullet\vec{a}_2\times\vec{a}_3|}$$

Reciprocal lattice vector $\vec{G} = v_1\vec{b}_1 + v_2\vec{b}_2 + v_3\vec{b}_3$

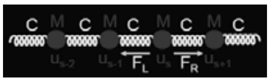
Chapter Three Crystal Binding

Types of bonds

(a) Van der Waals (Molecular)	
	Electrons localized among atoms
(b) Covalent	**Electrons shared by the neighboring atoms**
(c) Metallic	**Electrons free to move through sample**
(d) Ionic	**Electrons transferred to adjacent atoms**

Chapter Four Phonons I Crystal vibrations.

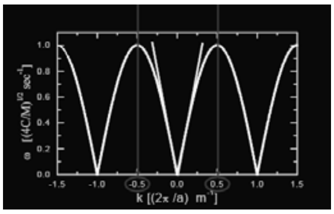
1. Vibrations of crystal with monatomic basis



$$F_s = F_R + F_L = C(u_{s+1} - u_s) + C(u_{s-1} - u_s)$$

$$M\frac{d^2u_s}{dt^2} = C(u_{s+1} + u_{s-1} - 2u_s)$$

Dispersion relation



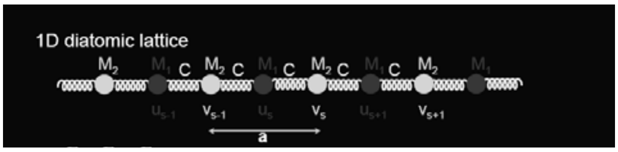
2. Brillouin zone

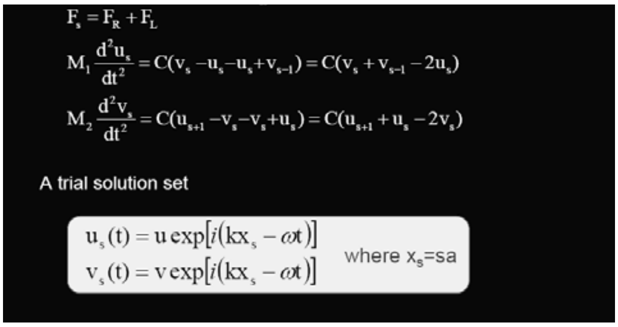
Start at reciprocal lattice

Bisect all G vectors with planes

Enclosed volume is Brillouin zone

3. Two atoms per primitive basis





$$F_s = F_R + F_L$$

$$M_1\frac{d^2u_s}{dt^2} = C(v_s - u_s - u_s + v_{s-1}) = C(v_s + v_{s-1} - 2u_s)$$

$$M_2\frac{d^2v_s}{dt^2} = C(u_{s+1} - v_s - v_s + u_s) = C(u_{s+1} + u_s - 2v_s)$$

A trial solution set

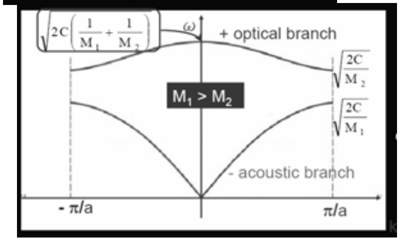
$$u_s(t) = u\exp[i(kx_s - \omega t)]$$
$$v_s(t) = v\exp[i(kx_s - \omega t)]$$

where x_s=sa

Dispersion relation

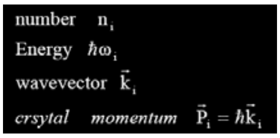
$$\omega^2 = C\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \pm C\sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^2 - \frac{4}{M_1M_2}\sin^2(\frac{ka}{2})}$$

$$\omega^2 = C\left(\frac{1}{M_1} + \frac{1}{M_2}\right)\left(1 \pm \sqrt{1 - \frac{4M_1M_2}{(M_1+M_2)^2}\sin^2(\frac{ka}{2})}\right)$$



4. Periodic boundary conditions (**Born-Karman)**

Phonon: particle-like properties



number n_i

Energy $\hbar\omega_i$

wavevector $\vec{k}_i$

crsytal momentum $\vec{P}_i = \hbar\vec{k}_i$

Chapter Five Phonons II. Thermal Properties

- Phonon heat capacity
- Anharmonic crystal interactions
- Thermal conductivity

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1. Phonon heat capacity

Einstein model(1907)

Einstein model

$$U = 3N\langle n\rangle\hbar\omega = \frac{3N\hbar\omega}{\exp(\hbar\omega/k_BT)-1}$$

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = 3Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2\frac{\exp(\hbar\omega/k_BT)}{(\exp(\hbar\omega/k_BT)-1)^2}$$

Debye model

$$U = \frac{3V\hbar}{2\pi^2 v_g^3}\left(\frac{k_BT}{\hbar}\right)^4\int_0^{x_D} dx\left(\frac{x^3}{e^x-1}\right)$$

$$C_V = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3\int_0^{x_D} dx\,\frac{x^4e^x}{(e^x-1)^2}$$

---

2. Phonon thermal conductivity

The flux of the thermal energy $\vec{j}_U = -\kappa\frac{dT}{dx}$

3. Thermal expansion

$$\langle x\rangle = \frac{3g}{4C^2}k_BT$$

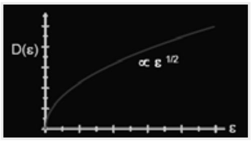
4. Phonon-phonon scattering

Chapter Six Free Electron Fermi Gas

1. Free electron mode
   treat conduction electrons as free particles
2. DOS

In one dimensions $D(\varepsilon) = \frac{\sqrt{mL}}{\sqrt{2}\pi\hbar}\frac{1}{\sqrt{\varepsilon}}$

In three dimensions $D(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}$



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3. Effect of temperature on the Fermi-Dirac distribution

T=0 $f(\varepsilon) = \begin{cases} 1, & \varepsilon \le \varepsilon_F \\ 0, & \varepsilon > \varepsilon \end{cases}$

Finite temperatures

$$f(\varepsilon) = \frac{1}{\exp[(\varepsilon-\mu)/k_BT]+1}$$

---

3. Free electrons contribution to heat capacity

$$C_e = D(\varepsilon_F)k_B^2T\frac{\pi^2}{3} = \frac{\pi^2}{3}\frac{3N}{2k_BT_F}k_B^2T$$
$$= \frac{1}{2}\pi^2Nk_B\frac{T}{T_F}$$

4. Electron conductivity and Ohm's law

$$\vec{J} = -n\frac{e\hbar}{m}\left(\frac{-e\vec{E}}{\hbar}\right)\tau = \frac{ne^2\tau}{m}\vec{E}$$

$$\vec{J} \equiv \sigma\vec{E}$$

5. Motion in magnetic field

$$\vec{F} = q\vec{E} = \hbar \frac{d\vec{k}}{dt}$$

$$\vec{F}_B = q\vec{v} \times \vec{B} = \frac{q\hbar}{m}\vec{k} \times \vec{B} = \hbar \frac{d\vec{k}}{dt}$$

Hall coefficient $R_H \equiv \frac{E_y}{j_x B} = -\frac{1}{ne}$

Hall resistivity $\rho_H = \frac{E_y}{j_x} = BR_H$

6. Thermal conductivity of metal

$$\kappa_e = \frac{1}{3}\pi^2 \frac{nk_B^2}{m} T\tau$$

Chapter Seven Energy Bands

1. Nearly free electron model

add the periodic potential of the ion cores to free electrons

Energy Band Theory

2. Bloch's theorem

$$\boxed{\Psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) \exp(i\mathbf{k} \bullet \mathbf{r})}$$

The alternative form of Bloch theorem

$$\boxed{\Psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \exp(i\mathbf{k} \bullet \mathbf{R})\Psi(\mathbf{r})}$$

The strict proof of Bloch theorem

3. Origin of the energy band and gap

energy band: due to the periodicity of lattice

energy gap:due to Bragg reflection of Bloch waves

4. Kronig-Penny Model

$$\boxed{P\left(\frac{\sin(\mathbf{K}a)}{\mathbf{K}a}\right) + \cos(\mathbf{K}a) = \cos(ka)}$$

5. Wave equation of electron in periodic potential

$$\boxed{\left(\frac{\hbar^2}{2m}(k-G)^2 - \varepsilon\right)C_{k-G} + \sum_{G'} U_{G'-G} C_{k-G'} = 0}$$

6. Empty lattice approximation

7. Brillouin zone of several kinds of lattice

8. Approximate solution near a zone boundary

1. Considering a wavevector exactly at zone boundary at first Brillouin zone boundary ½ g

C(½ g) and C(- ½ g) is important coefficients.

$$\varepsilon = \lambda \pm U = \frac{\hbar^2}{2m}\left(\frac{g}{2}\right)^2 \pm U$$

$$\psi(x) = \exp(igx/2) \pm \exp(-igx/2)$$

2. Near the zone boundary

$$\begin{pmatrix} \ddots & & & & \\ \lambda_{k-2g} - \varepsilon & U & 0 & 0 & 0 \\ U & \lambda_{k-g} - \varepsilon & U & 0 & 0 \\ 0 & U & \lambda_k - \varepsilon & U & 0 \\ 0 & 0 & U & \lambda_{k+g} - \varepsilon & U \\ 0 & 0 & 0 & U & \lambda_{k+2g} - \varepsilon \\ & & & & \ddots \end{pmatrix} \begin{pmatrix} \vdots \\ C(k-2g) \\ C(k-g) \\ C(k) \\ C(k+g) \\ C(k+2g) \\ \\ \end{pmatrix} = 0$$

$$\boxed{\varepsilon_{\tilde{K}} = (\lambda \pm U) + \frac{\hbar^2 \tilde{K}^2}{2m}\left(1 \pm \frac{2\lambda}{U}\right)}$$

3. Number of orbitals in a band

- **Each primitive cell contributes exactly one independent value of k to each energy band.**
- **there are 2N independent orbitals in each energy band with account taken of the two independent orientations of the electron spin.**

Explain: crystal will be a metal, or an insulator?

Chapter 8 Semiconductor Crystal

1.Band gap

Two types of semiconductors

2. Equation of motion

$$\hbar\frac{d\vec{k}}{dt}=\vec{F}_{ext}=q\left(\vec{E}+\left(\frac{1}{\hbar}\nabla_{\vec{k}}\varepsilon(\vec{k})\right)\times\vec{B}\right)$$

3.Holes in semiconductors

A hole acts under the external forces as a positive charge *+e*.

Effective mass (band mass)

$$\frac{1}{m^*}=\frac{1}{\hbar^2}\frac{d^2\varepsilon(k)}{dk^2}$$

4. Intrinsic carrier concentration

$$n=2\left(\frac{m_ek_BT}{2\pi\hbar^2}\right)^{3/2}\exp\left(\frac{\mu-E_c}{k_BT}\right)$$

$$p=2\left(\frac{m_hk_BT}{2\pi\hbar^2}\right)^{3/2}\exp\left(\frac{E_v-\mu}{k_BT}\right)$$

$$np=4\left(\frac{k_BT}{2\pi\hbar^2}\right)^3\left(m_em_h\right)^{3/2}\exp\left(\frac{-E_g}{k_BT}\right)$$

Fermi level $\mu=\frac{1}{2}E_g+\frac{3}{4}k_BT\ln\left(\frac{m_h}{m_e}\right)$

5. Intrinsic mobility

Electrical conductivity $\sigma=ne\mu$

μ: ⇨ **mobility** ⇨ $\mu=\frac{|v_d|}{E}$

6. Impurity conductivity

Donors Acceptors