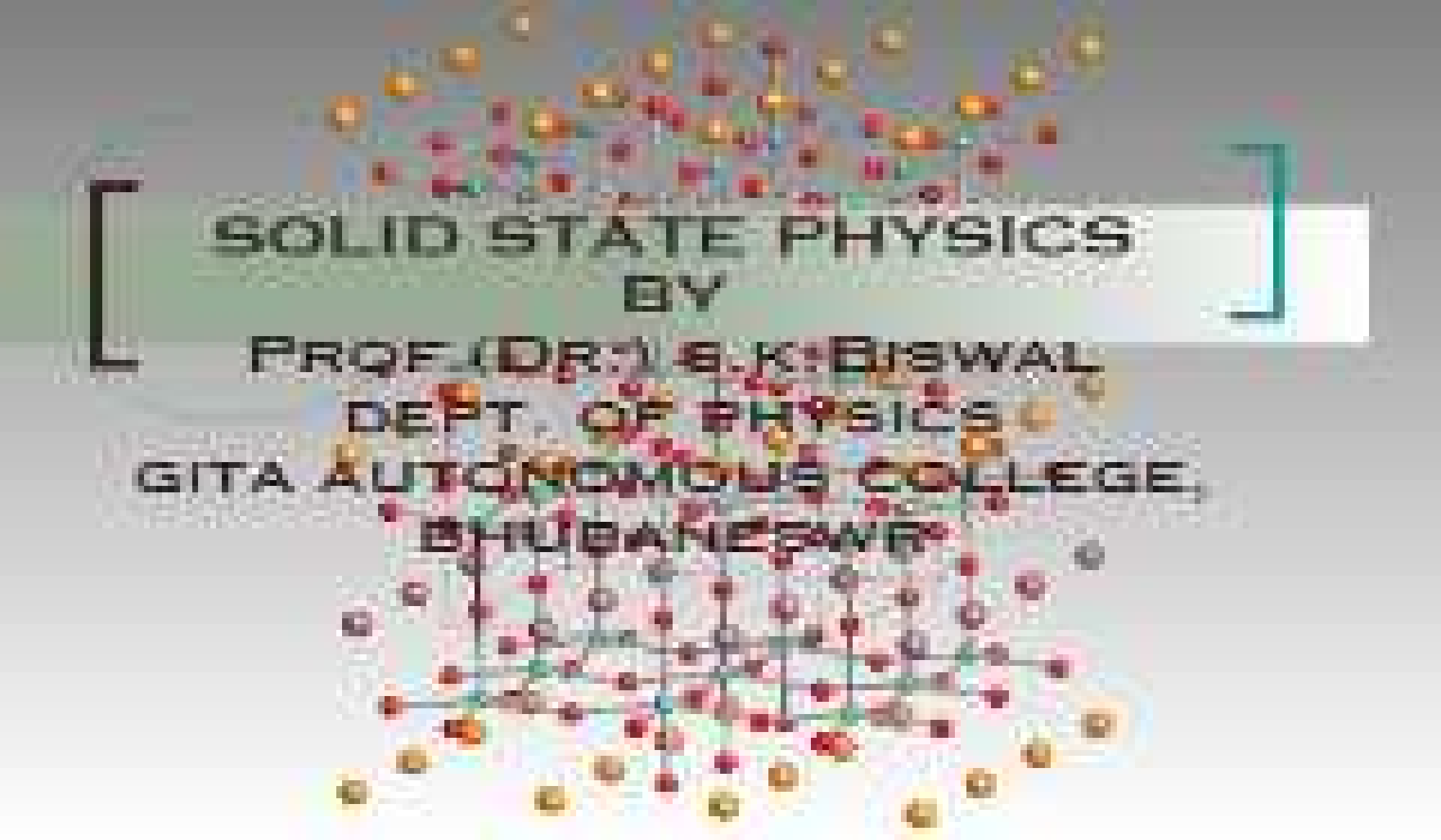

SOLID STATE PHYSICS

BY

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BHUBANESWAR

Matter

- Gases
- Liquids and liquid crystals
- Solids

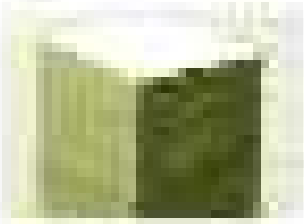
CLASSIFICATION OF SOLIDS

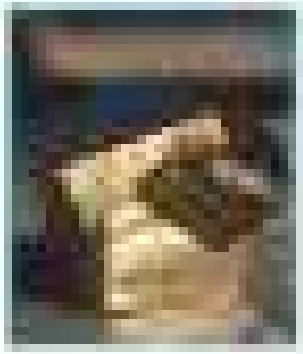
SOLID MATERIALS

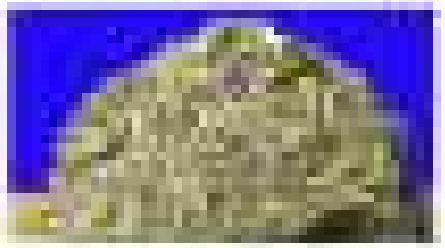
CRYSTALLINE

Single Crystal

POLYCRYSTALLINE







Solids can broadly be classified into two types based on the arrangement of units of matter.
The units of matter may be atoms, molecules or ions.
They are,

- Crystalline solids and
- Non-crystalline (or) Amorphous solids

CRYSTALLINE SOLIDS

A substance is said to be crystalline when the arrangement of units of matter is regular and periodic.

A crystalline material has directional properties and therefore called as anisotropic substance.

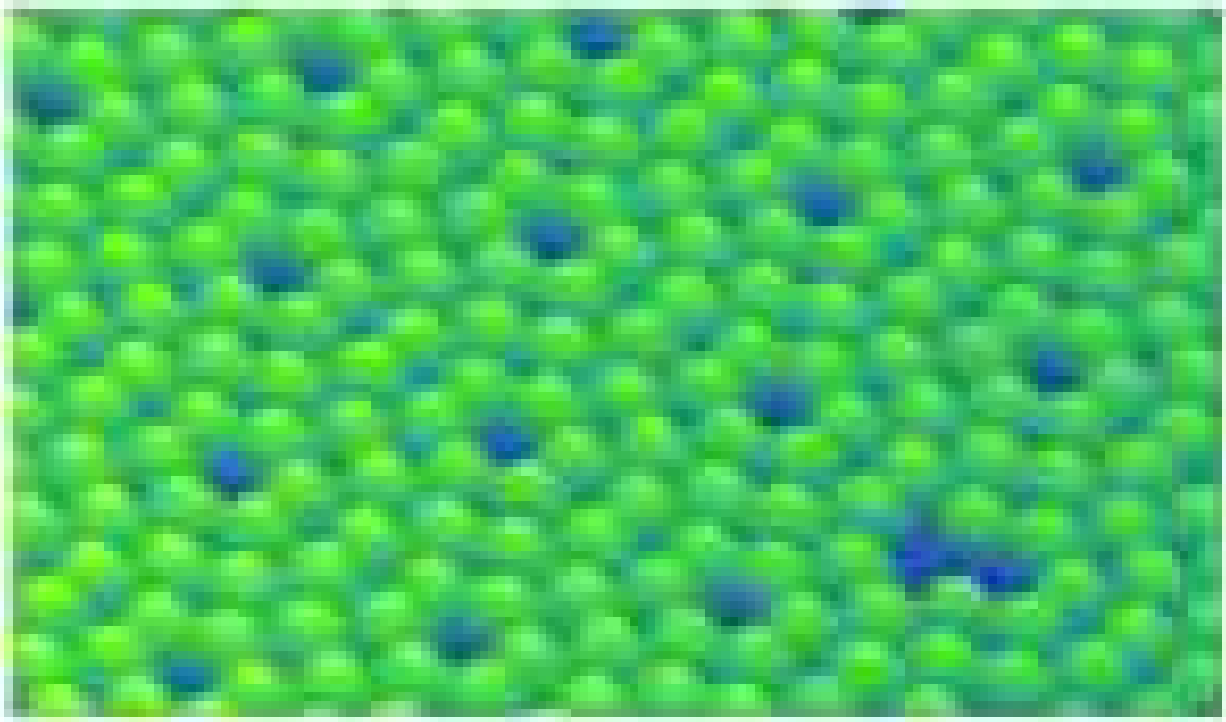
A crystal has a sharp melting point.

It possesses a regular shape and if it is broken, all broken pieces have the same regular shape.

Examples:

Metallic crystals – Cu, Ag, Al, Mg etc,

Non-metallic crystals – Carbon,Silicon,Germanium, NaCl, Diamond

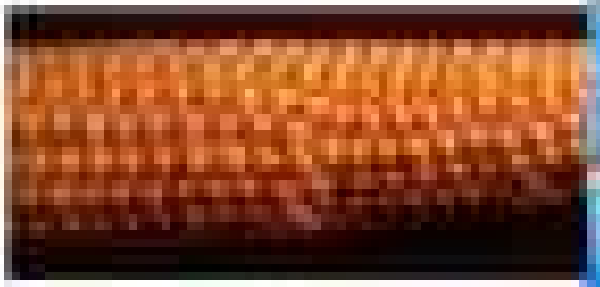


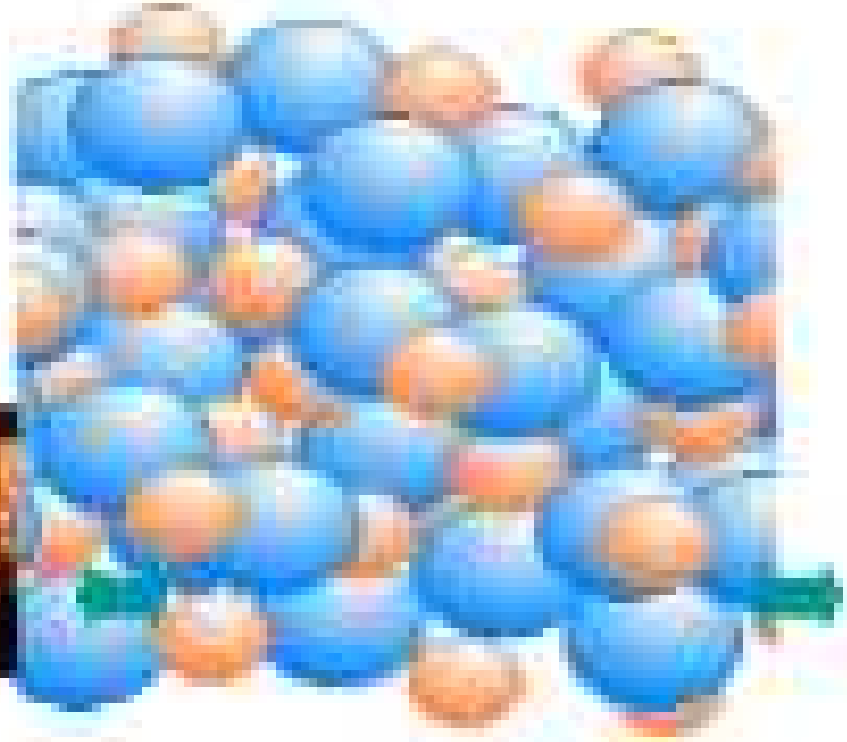
In amorphous solids, the constituent particles are not arranged in an orderly manner. They are randomly distributed.

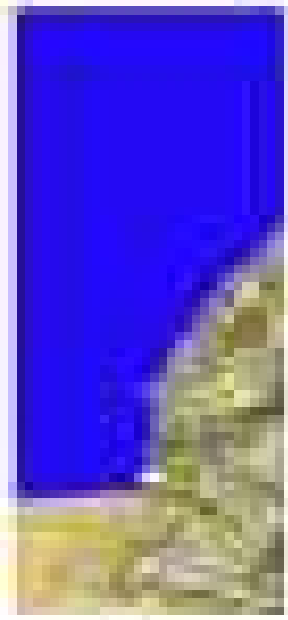
They do not have directional properties and so they are called as "isotropic" substances.

They have wide range of melting point and do not possess a regular shape.

- Examples:
- Glass,
  Plastics,
  Rubber etc.,







SPACE LATTICE

A lattice is a regular and periodic arrangement of points in three dimensions.

Crystal Lattice

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

Crystal Structure

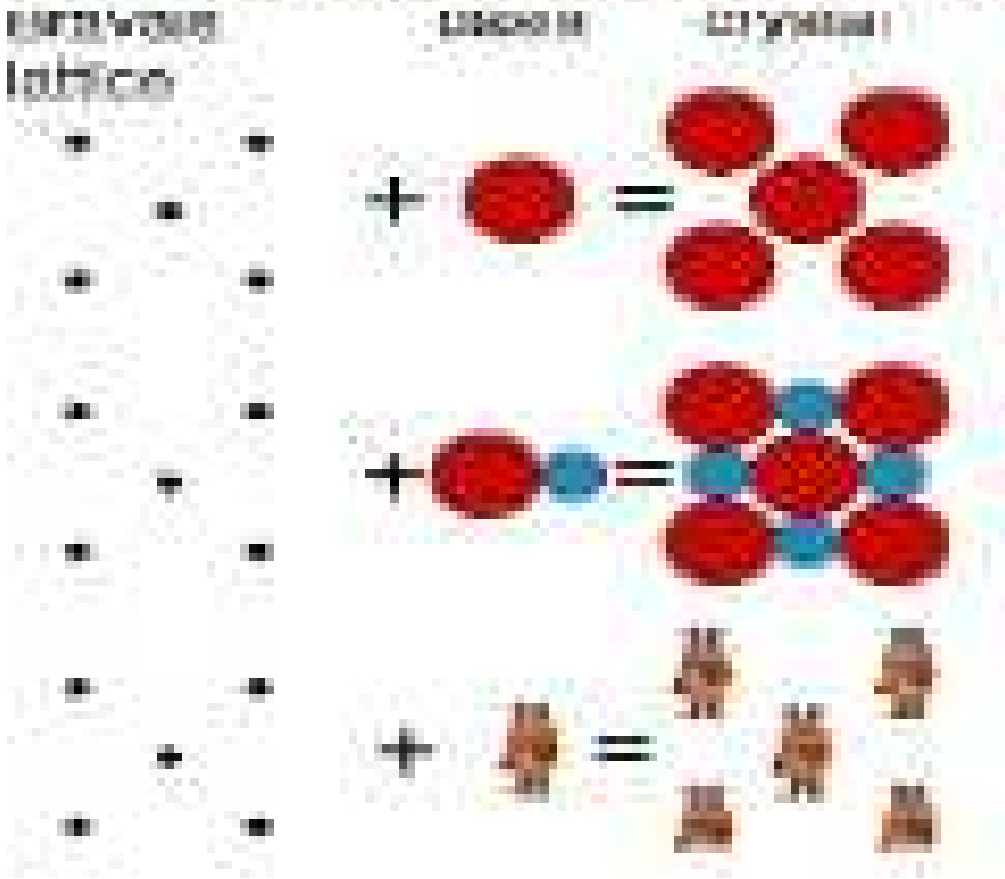
- Crystal structures can be obtained by attaching atoms, groups of atoms or molecules which are called basis (motif) to the lattice sides of the lattice point

Crystal Structure = Crystal Lattice + Basis

UNIT CELL

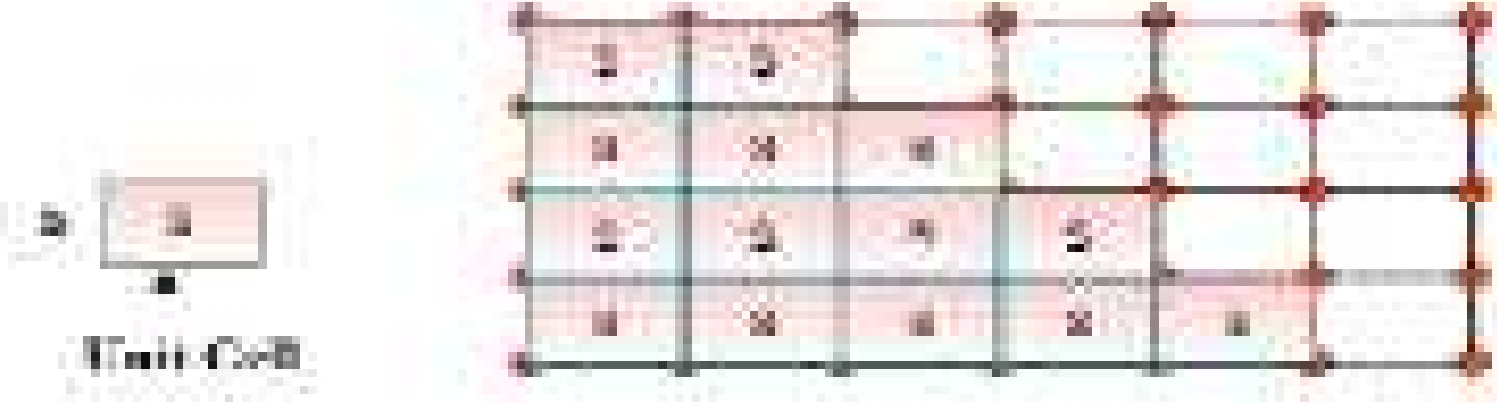
A unit cell is defined as a fundamental building block of a crystal structure, which can generate the complete crystal by repeating its own dimensions in various directions.

A two-dimensional Bravais lattice with different choices for the basis

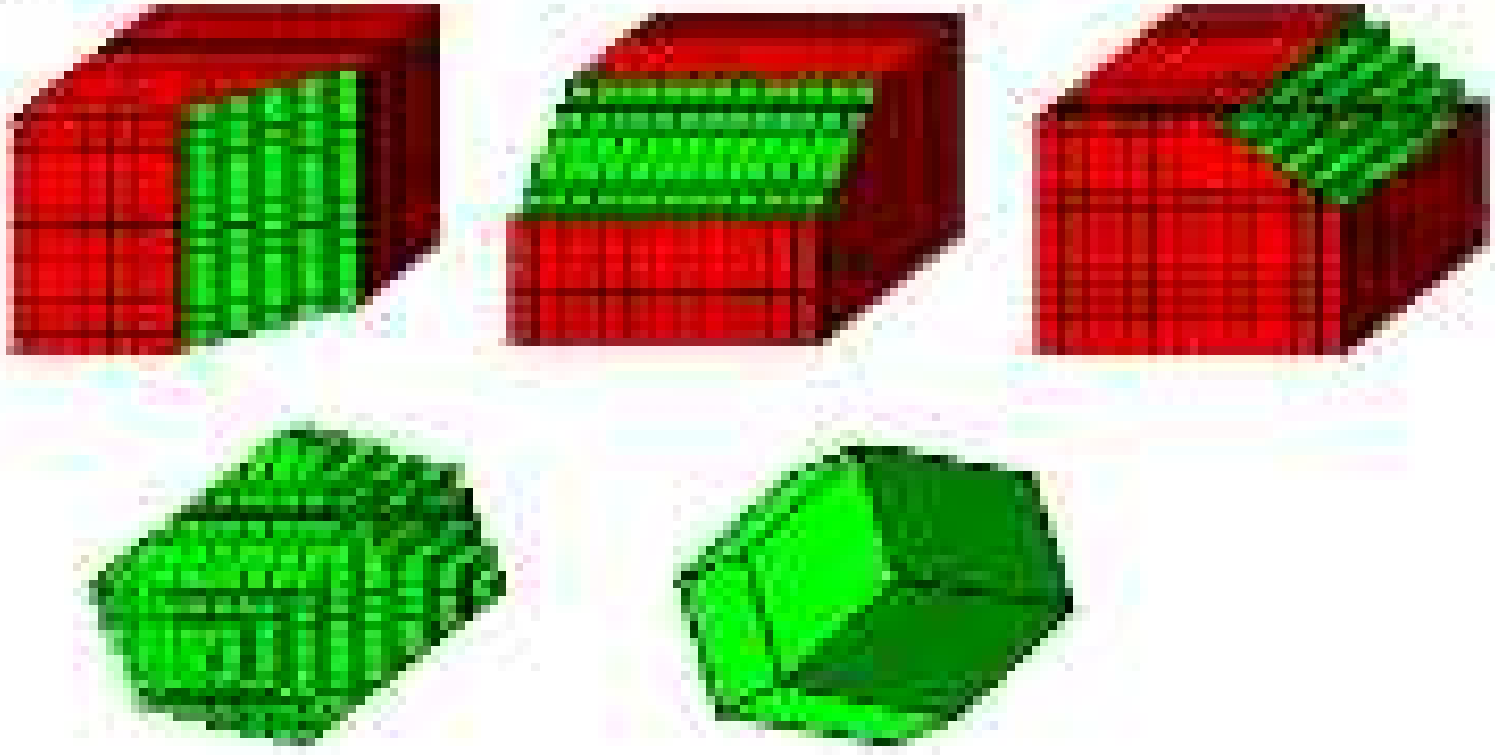


Unit Cell in 2D

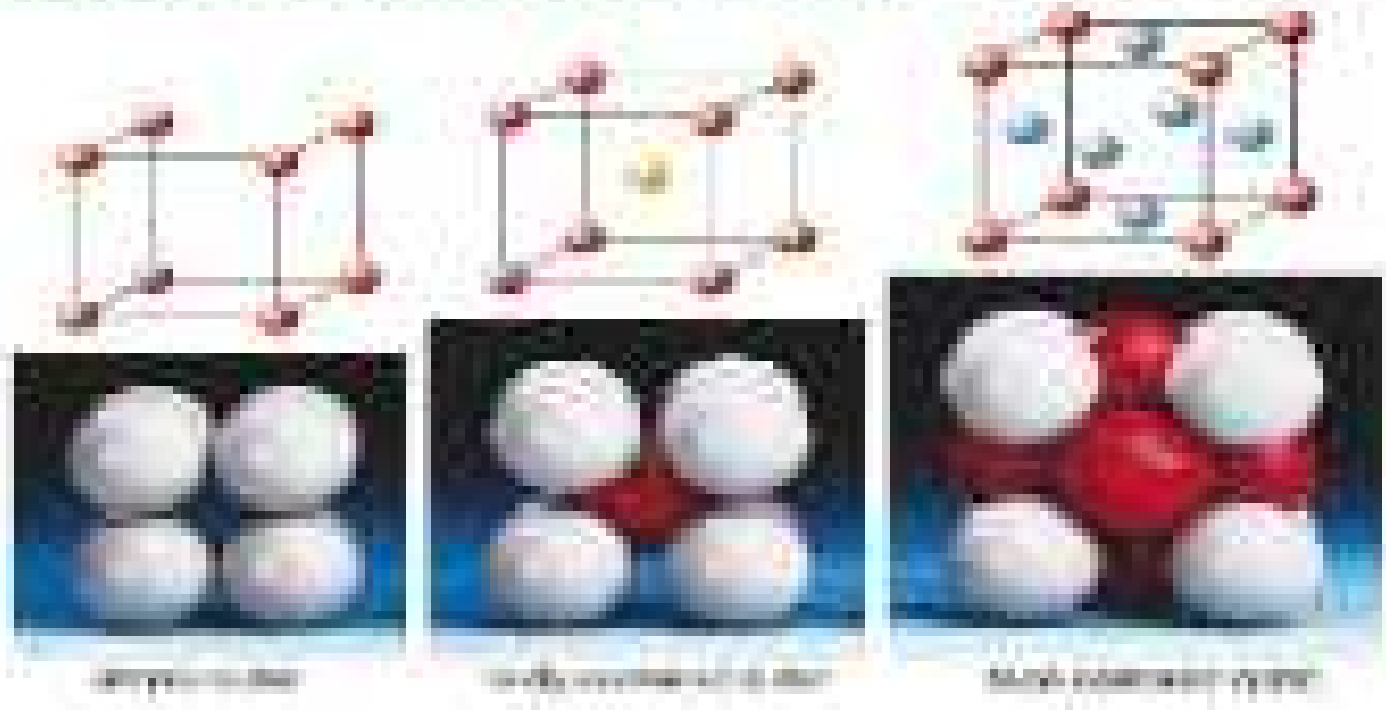
- The smallest component of the crystal (group of atoms, ions or molecules), which when stacked together with pure translational repetition reproduces the whole crystal.



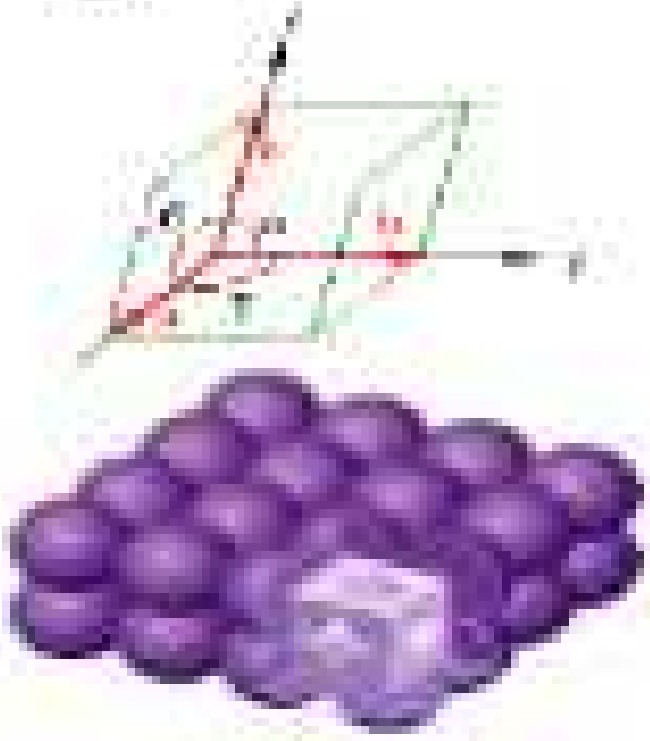
Unit Cell In 3D



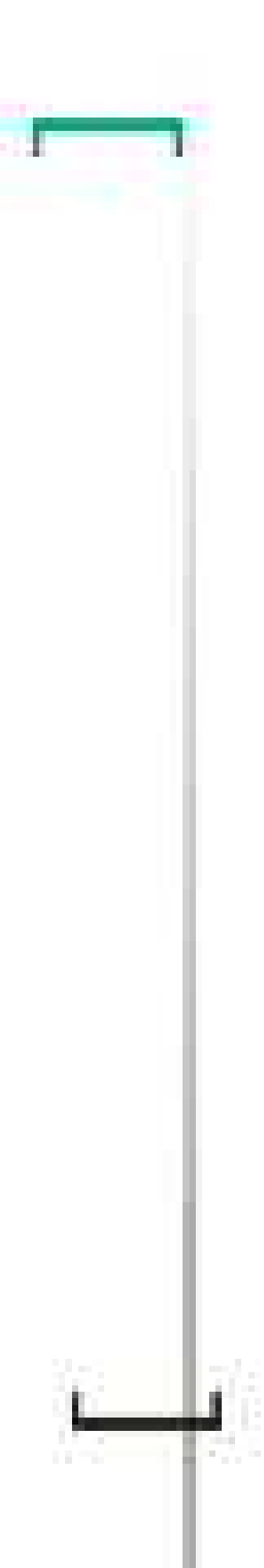
Three common Unit Cells in 3D



Unit Cell



- The unit cell and, consequently, the entire lattice is uniquely determined by the six lattice constants: a, b, c, α, β and γ
- Only 1/8 of each lattice point in a unit cell can actually be assigned to that cell.
- Each unit cell in the figure can be associated with 8 × 1/8 = 1 lattice point.

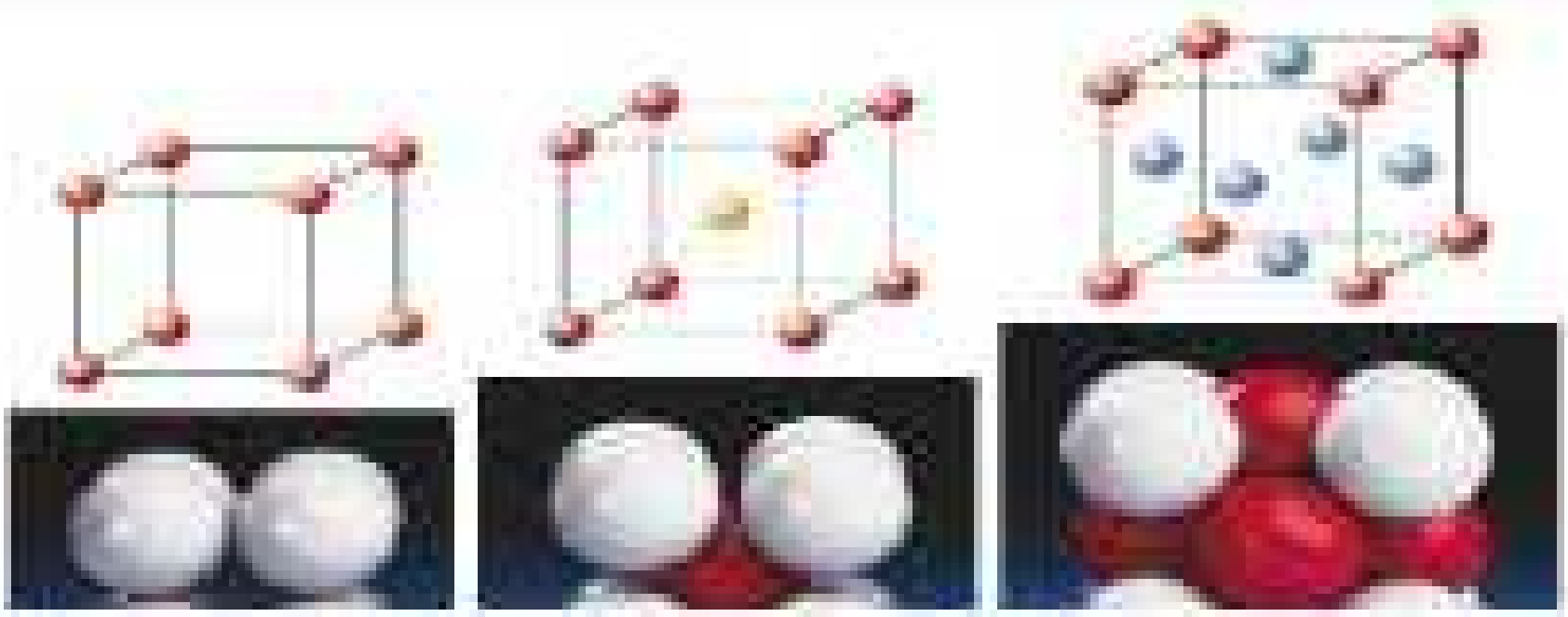


Seven unit cell shapes

Cubic	a=b=c			=	=	=90°	
Tetragonal	a=b	c		=	=	=90°	
Orthorhombic	a	b	c	=	=	=90°	
Monoclinic	a	b	c	=	=90°,		90°
Triclinic	a	b	c			90°	
Hexagonal	a=b	c		=	=90°	=120°	
Rhombohedral	a=b=c			=	=	90°	

Think about the shapes that these define - look at the models provided.

Four common Unit Cells in 3D



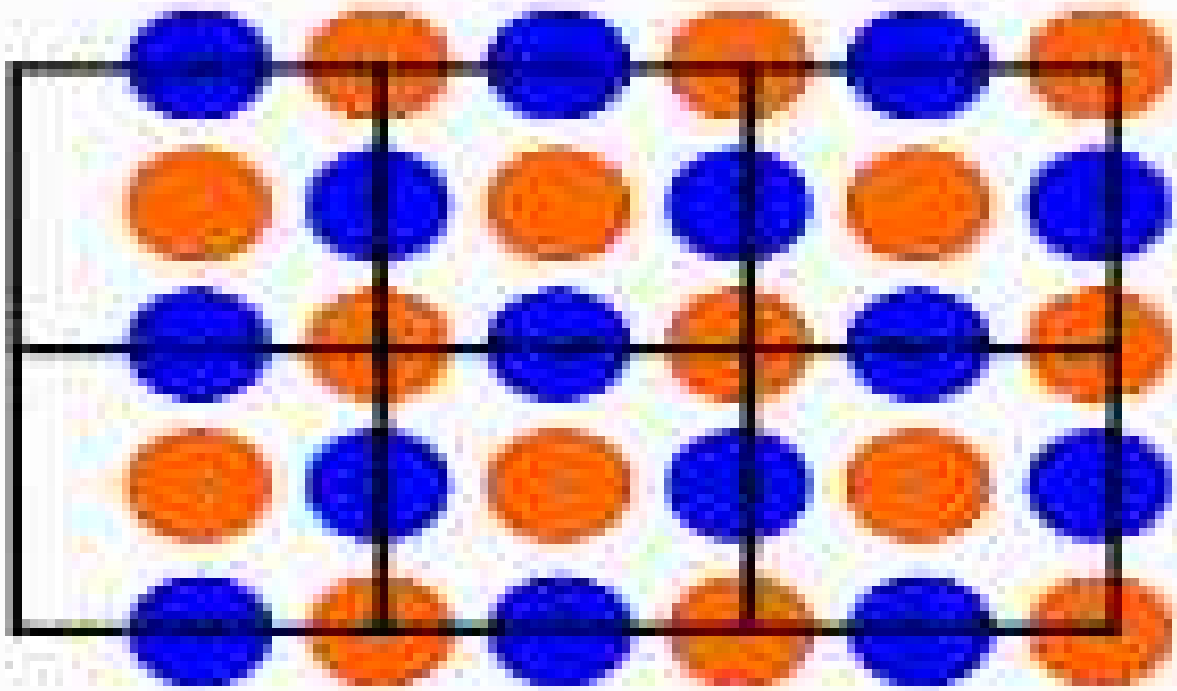
Primitive lattice:P □ having lattice points only at the corners of the unit cell.

Body centred lattice:I □ having lattice points at the corners as well as at the body centre of the unit cell.

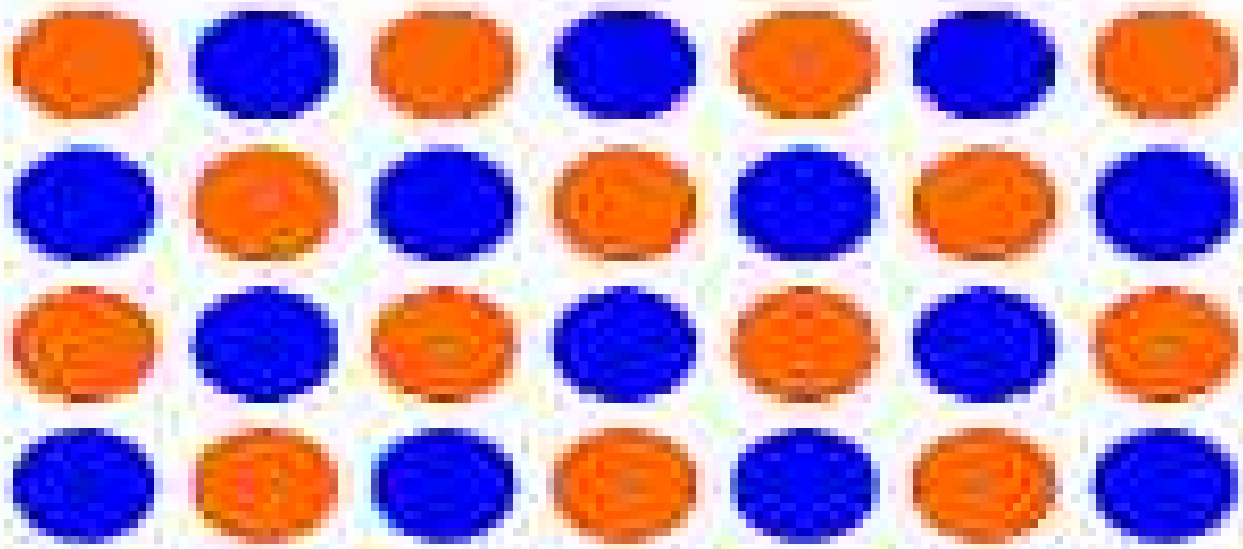
Face centred lattice:F having lattice points at the corners as well as at the face centres of the unit cell.

Base centred lattice:C having lattice points at the corners as well as at the top and bottom base centres of the unit cell.

This is also a unit cell
It doesn't matter if you start from Na or Cl

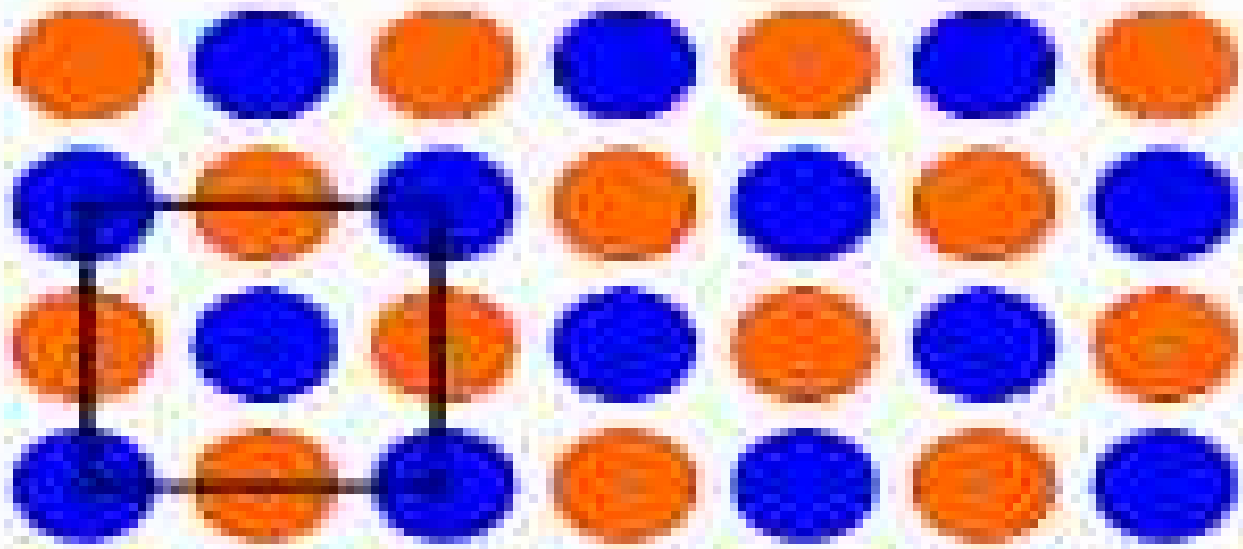


2D example - rocksalt
(sodium chloride, NaCl)

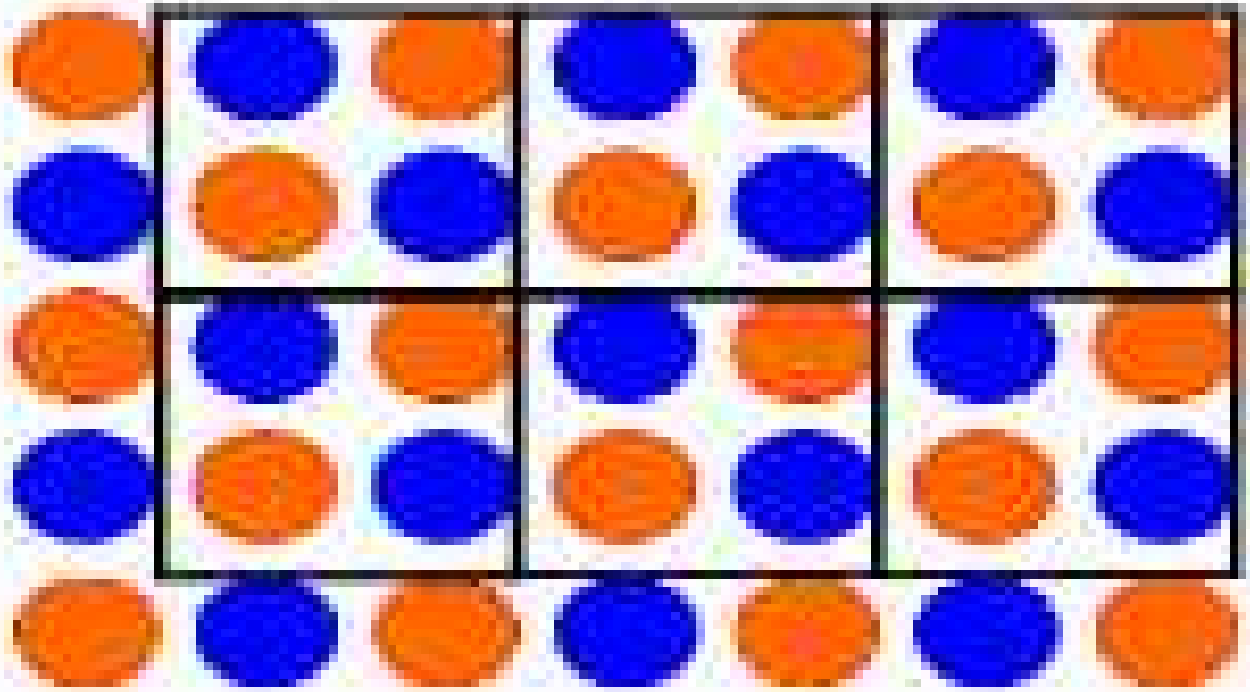


We define **lattice points** ; these are points with *identical environments*

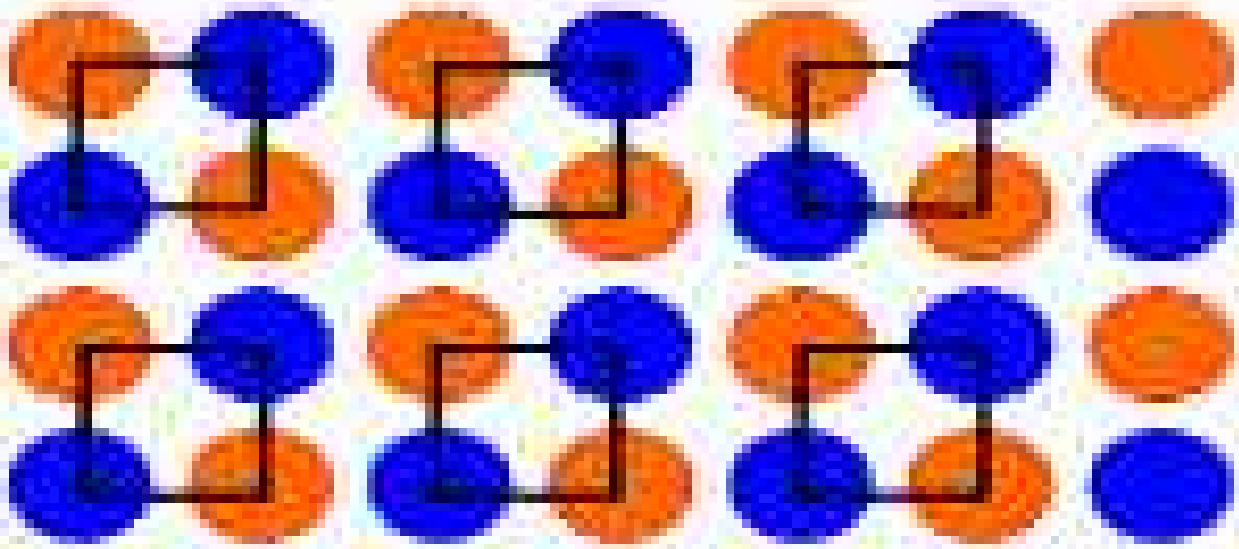
Choice of origin is arbitrary – lattice points need not be atoms – **but** unit cell size should always be the same.



– or if you don't start from an atom

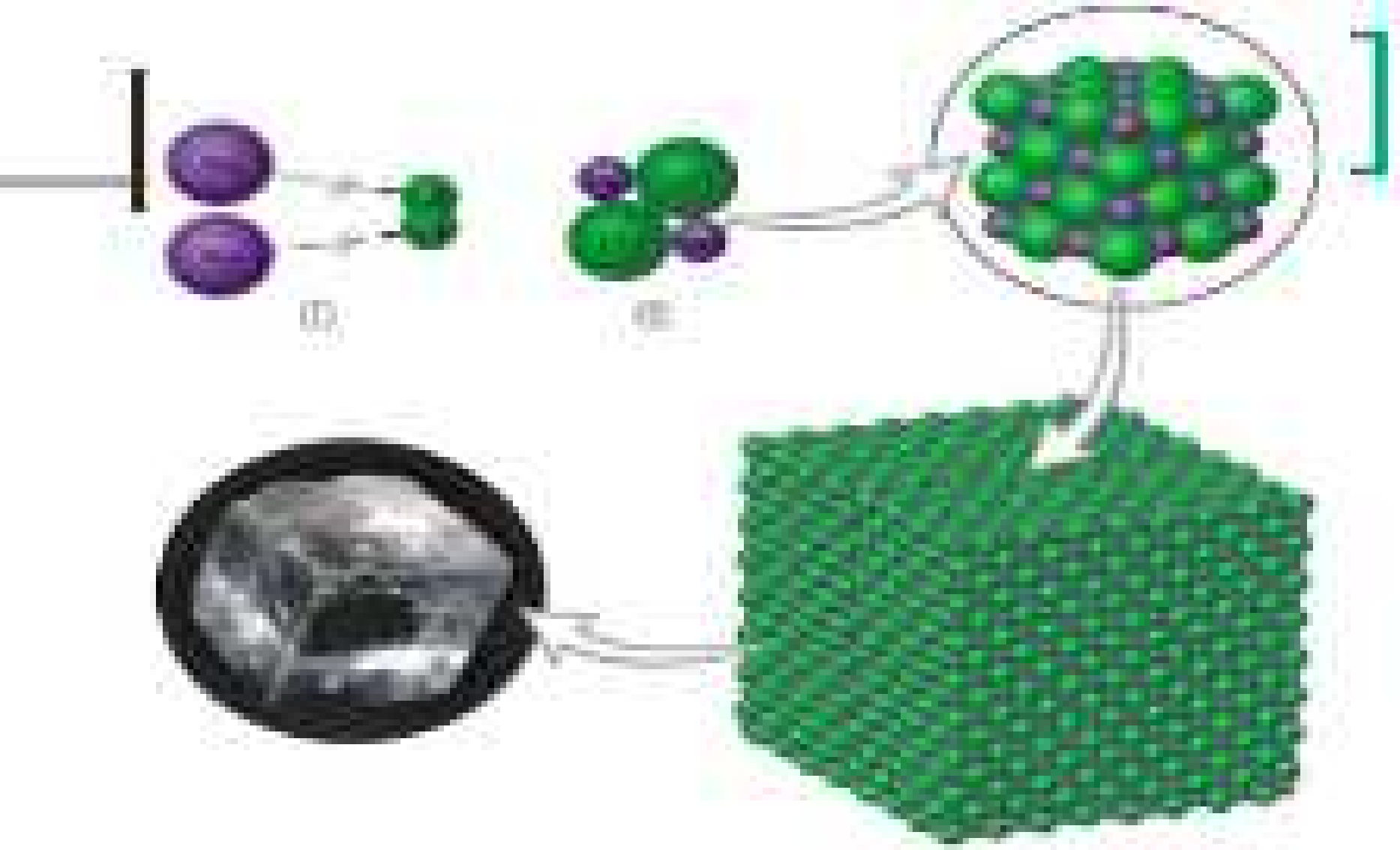


This is NOT a unit cell even though they are all the same – empty space is not allowed!



Summary

- Unit cells must link up - cannot have gaps between adjacent cells
- All unit cells must be identical
- Unit cells must show the full **symmetry** of the structure next section



PART 2
INTERATOMIC FORCES

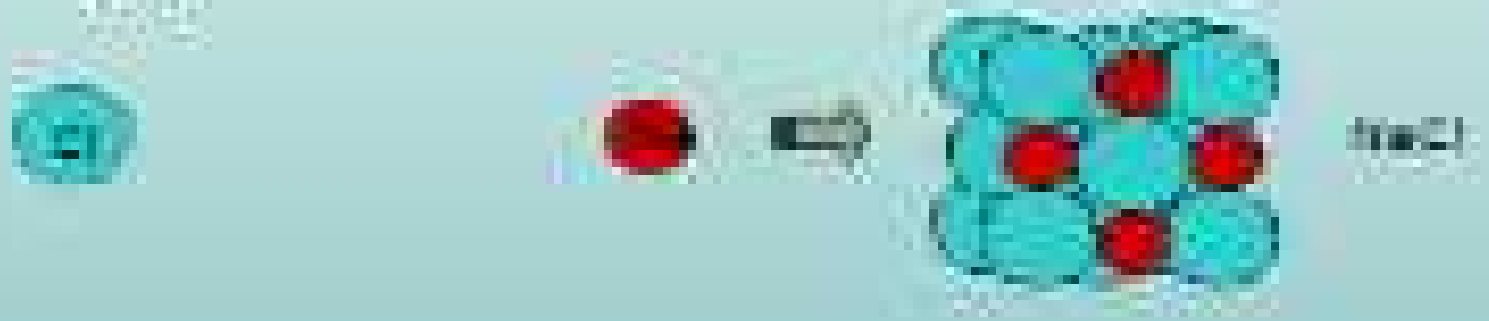
What kind of forces hold the atoms together in a solid?

- Energies of interactions between atoms
- Ionic bonding
  - NaCl
- Covalent bonding
  - Comparison of ionic and covalent bonding
- Metallic bonding
- Van der waals bonding
- Hydrogen bonding

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. This is called the binding (cohesive) energy of the crystal.

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



Types of Bonding Mechanisms

It is conventional to classify the bonds between atoms into different types as

- Ionic
- Covalent
- metallic
- Van der Waals
- Hydrogen

All bonding is a consequence of the electrostatic interaction between the nuclei and electrons.

IONIC BONDING

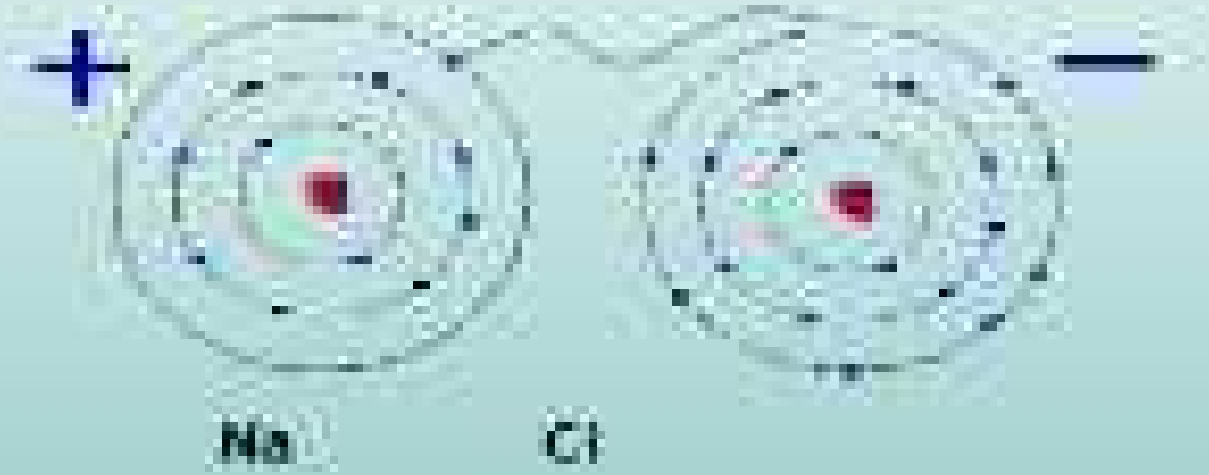
- Ionic bonding is the electrostatic force of attraction between positively and negatively charged ions (between non-metals and metals).

- All ionic compounds are crystalline solids at room temperature.
- NaCl is a typical example of ionic bonding.

Metallic elements have only up to the valence electrons in their outer shell.

When losing their electrons they become positive ions.

Electronegative elements tend to acquire additional electrons to become negative ions or anions.



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

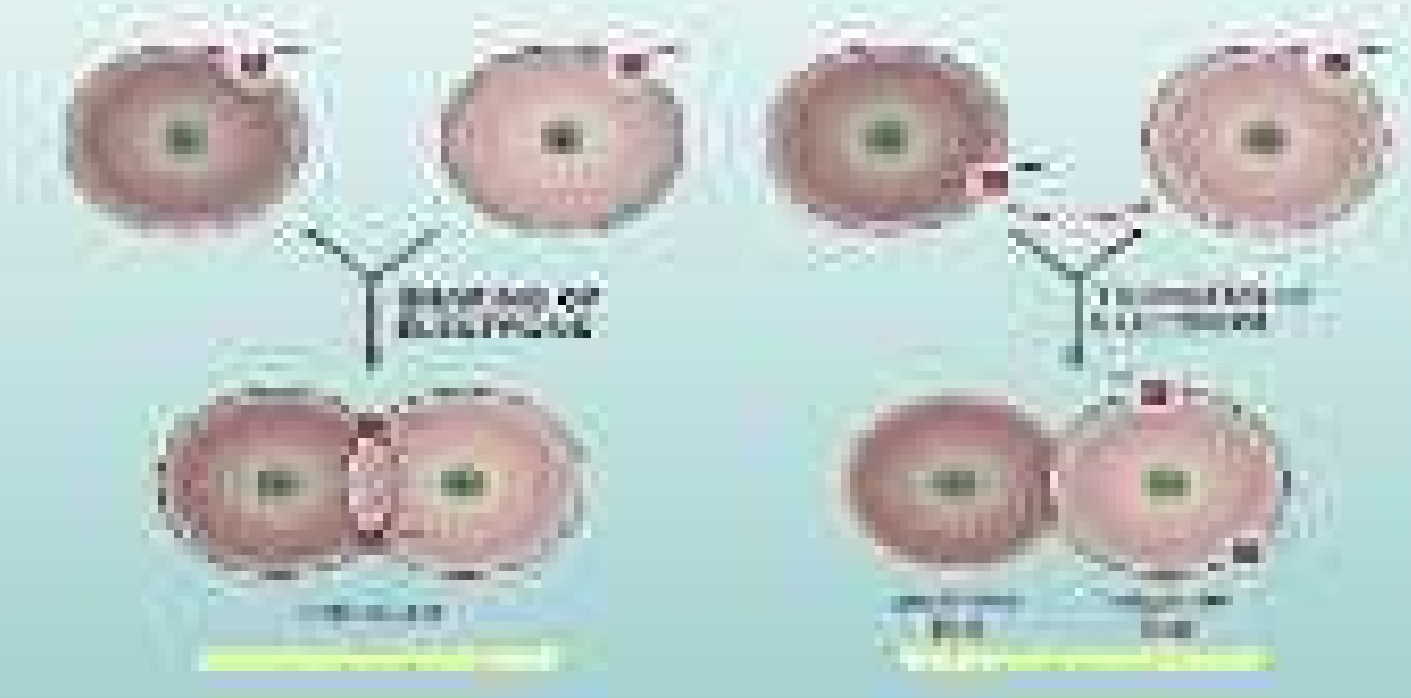
- Pauli exclusion principle has an important role in repulsive force. To prevent a violation of the exclusion principle, the potential energy of the system increases very rapidly.

COVALENT BONDING

- Covalent bonding takes place between atoms with small differences in electronegativity which are close to each other in the periodic table (between non-metals and non-metals).
- The covalent bonding is formed when the atoms share the outer shell electrons (i.e., s and p electrons) rather than by electron transfer.
- Noble gas electron configuration can be attained.

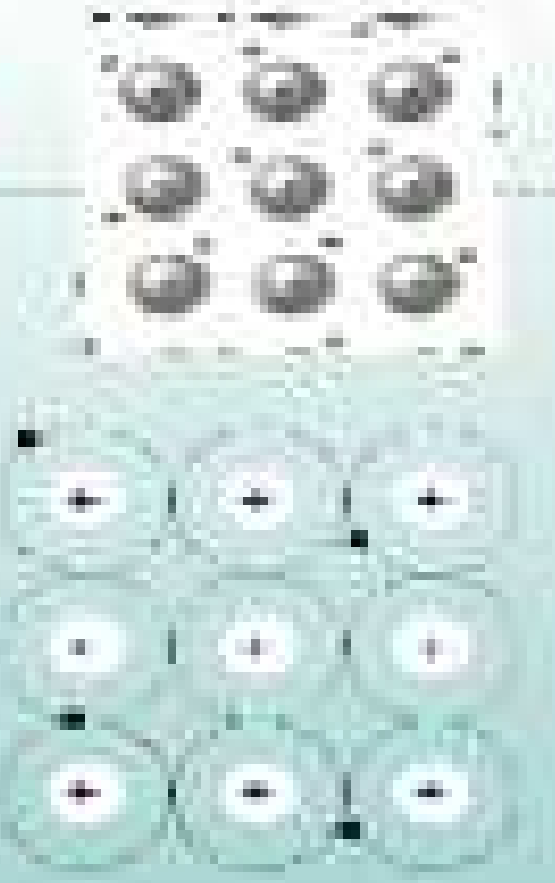
- each electron in a shared pair is attracted to both nuclei involved in the bond. The approach, electron overlap, and attraction can be visualized as shown in the following figure representing the nuclei and electrons in a hydrogen molecule:

Comparison of Ionic and Covalent Bonding



METALLIC BONDING

- Metallic bonding is found in metal elements. This is the electrostatic force of attraction between positively charged ions and delocalised outer electrons.
- The metallic bond is weaker than the ionic and the covalent bonds.
- A metal may be described as a high-density cloud of free electrons.
- Therefore, metals have high electrical and thermal conductivity.



VAN DER WAALS BONDING

- These are weak bonds with a typical strength of 0.2 eV/atom.
- Van Der Waals bonds occur between neutral atoms and molecules.
- Weak forces of attraction result from the natural fluctuations in the electron density of all molecules that cause small temporary dipoles to appear within the molecules.
- It is these temporary dipoles that attract one molecule to another. They are called van der Waals forces.

- The **shape** of a molecule influences its ability to form temporary dipoles. Long thin molecules can pack closer to each other than molecules that are more spherical. The bigger the 'surface area' of a molecule, the greater the van der Waal's forces will be and the higher the melting and boiling points of the compound will be.
- Van der Waal's forces are of the order of 1% of the strength of a covalent bond.

Homonuclear molecules, such as iodine, develop temporary dipoles due to natural fluctuations in electron density within the molecule

Heteronuclear molecules, such as HCl have permanent dipoles that also exist in equilibrium with London forces

- These forces are due to the electrostatic attraction between the nucleus of one atom and the electrons of the other.

- Van der waals interaction occurs generally between atoms which have noble gas configuration

HYDROGEN BONDING

- A hydrogen atom, having one electron, can be covalently bonded to only one atom. However, the hydrogen atom can involve itself in an additional electrostatic bond with a second atom of highly electronegative character such as fluorine or oxygen. This second bond permits a ***hydrogen bond*** between two atoms or structures.
- The strength of hydrogen bonding varies from 0.1 to 0.5 ev/atom.

- Hydrogen bonds connect water molecules in ordinary ice. Hydrogen bonding is also very important in proteins and nucleic acids and therefore in life processes.


Types of Bonding
Ionic Bonding
Van Der Waals Bonding
Metallic Bonding
Covalent Bonding
Hydrogen Bonding

PART 3
CRYSTAL DYNAMICS

- [illegible] WAVE A
- LATTICE VIBRATIONS OF 1D CRYSTALS
  - [illegible]
  - [illegible]
- LATTICE VIBRATIONS OF 3D CRYSTALS
- PHONONS
- [illegible] LATTICE VIBRATIONS
- [illegible]
- [illegible]

Crystal Dynamics

- Atomic motions are governed by the forces exerted on atoms when they are displaced from their equilibrium positions.
- To calculate the forces it is necessary to determine the wavefunctions and energies of the electrons within the crystal. Fortunately many important properties of the atomic motions can be deduced without doing these calculations.

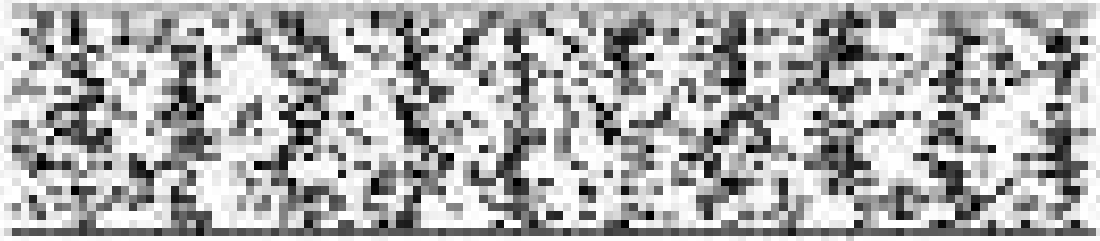
Hooke's Law

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

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.

Longitudinal Waves



Transverse Waves

SOUND WAVES

- Sound waves propagate through solids. They tells us that wavelike lattice vibrations of wavelength long compared to the interatomic spacing are possible. The detailed atomic structure is unimportant for these waves and their propagation is governed by the macroscopic elastic properties of the crystal.
- We discuss sound waves since they must correspond to the low frequency, long wavelength limit of the more general lattice vibrations considered later in this chapter.
- At a given frequency and in a given direction in a crystal it is possible to transmit three sound waves, differing in their direction of polarization and in general also in their velocity.

Speed of Sound Wave

- The speed with which a longitudinal wave moves through a liquid of density ρ is

$$v = \sqrt{\frac{C}{\rho}}$$

C = Elastic bulk modulus
ρ = Mass density

- The velocity of sound is in general a function of the direction of propagation in crystalline materials.
- Solids will sustain the propagation of transverse waves, which travel more slowly than longitudinal waves.
- The larger the elastic modulus and smaller the density, the more rapidly can sound waves travel.

Speed of sound for some typical solids

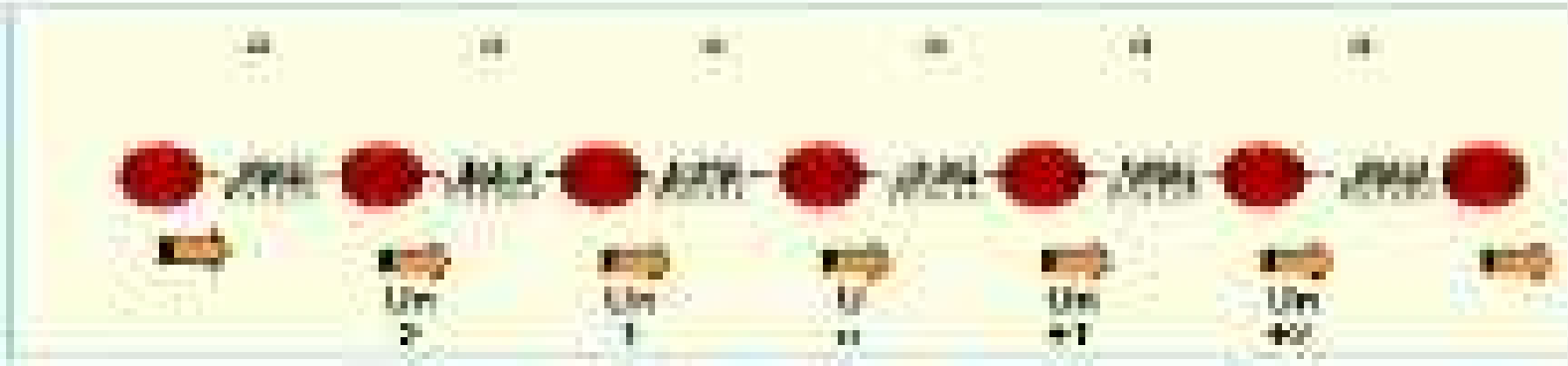
Solid	Structure type	Nearest neighbour distance (Å)	Density of solid ($kg\ m^{-3}$)	Bulk modulus of solid ($10^{11}\ N\ m^{-2}$)	Calculated velocity of sound ($m\ s^{-1}$)	Observed velocity of sound ($m\ s^{-1}$)
Sodium	B.C.C	3.71	970	0.52	2330	2250
Copper	F.C.C	2.55	8960	13.4	3850	3810
Aluminium	F.C.C	2.86	2700	7.38	5230	5110
Lead	F.C.C	3.50	11340	4.34	1960	1320
Silicon	Diamond	2.35	2330	10.1	6600	8450
Germanium	Diamond	2.44	5360	7.9	3830	5400
NaCl	Rock salt	2.82	2170	2.5	3400	4730

- VL values are comparable with direct observations of speed of sound.
- Sound speeds are of the order of 5000 m/s in typical metallic, covalent and ionic solids.

- A lattice vibrational wave in a crystal is a repetitive and systematic sequence of atomic displacements of
  - longitudinal,
  - transverse, or
  - some combination of the two
- An equation of motion for any displacement can be [illegible] considering the restoring forces on [illegible]
- As a result, we can derive the equation relationship between frequency and wavelength or between angular frequency and wavevector

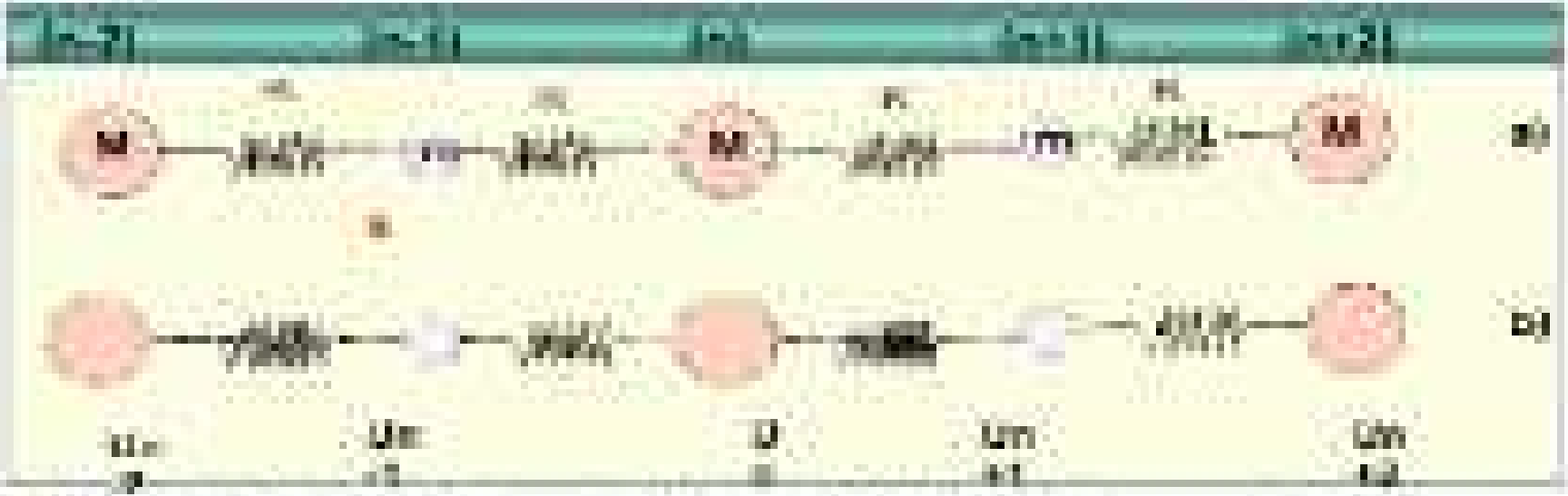
Monoatomic Chain

- 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).

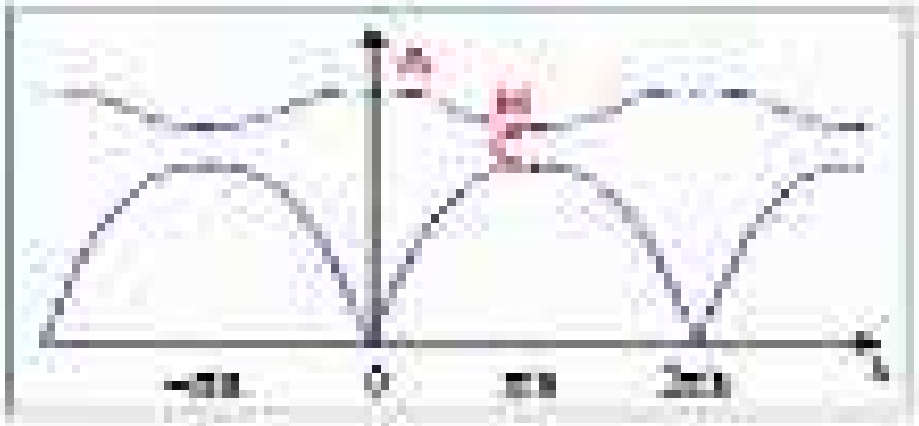


Chain of two types of atom

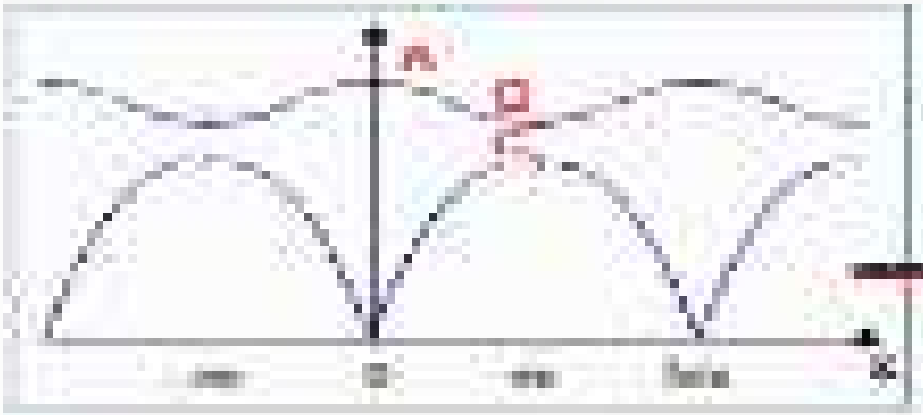
- Two different types of atoms of masses M and m are connected by identical springs of spring constant K.



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


A
B
C
−2π
0
π
2π
x

- As there are two values of ω for each value of k, the dispersion relation is said to have two branches.



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.

- 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 containing an arbitrary number of atoms per unit cell.

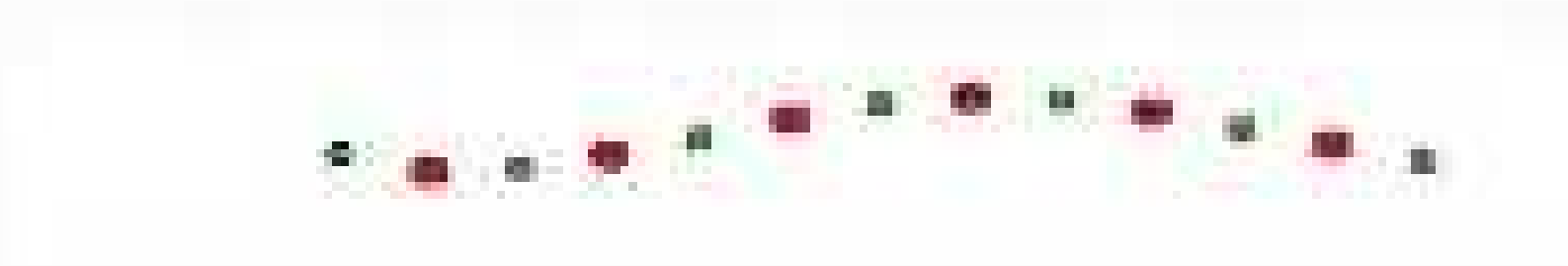
Acoustic/Optical Branches

- The acoustic branch has this name because it gives rise to long wavelength vibrations - speed of sound.
- The optical branch is a higher energy vibration (the frequency is higher, and you need a certain amount of energy to excite this mode). The term "optical" comes from how these were discovered - notice that if atom 1 is +ve and atom 2 is -ve, that the charges are moving in opposite directions. You can excite these modes with electromagnetic radiation (ie. the oscillating electric fields generated by EM radiation)

Transverse optical mode for diatomic chain

Amplitude of vibration is strongly exaggerated!

Transverse acoustical mode for diatomic chain



Phonons

- Consider the regular lattice of atoms in a uniform solid material.
- There should be energy associated with the vibrations of these atoms.
- But they are tied together with bonds, so they can't vibrate independently.
- The vibrations take the form of collective modes which propagate through the material.
- Such propagating lattice vibrations can be considered to be sound waves.
- And their propagation speed is the speed of sound in the material.

- The vibrational energies of molecules are quantized and treated as quantum harmonic oscillators.
- Quantum harmonic oscillators have equally spaced energy levels with separation $\Delta E = h\nu$.
- So the oscillators can accept or lose energy only in discrete units of energy $h\nu$.
- The evidence on the behaviour of vibrational energy in periodic solids is that the collective vibrational modes can accept energy only in discrete amounts, and these quanta of energy have been labelled "phonons".

PHONONS

- Quanta of lattice vibrations
- Energies of phonons are quantized

PHOTONS

- Quanta of electromagnetic radiation
- Energies of photons are quantized as well

Thermal energy and lattice vibrations

- Atoms vibrate about their equilibrium position.
- They produce vibrational waves
- **This motion increases as the temperature is raised.**

In solids, the energy associated with this vibration and perhaps also with the rotation of atoms and molecules is called **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 the 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
- Recall that the specific heat or heat capacity is the thermal energy which is required to raise the temperature of unit mass or 1g mole by one Kelvin

Heat capacity from Lattice vibrations

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
- In magnetic materials: from magnetic ordering.

Atomic vibrations lead to bands of normal mode frequencies from zero up to some maximum value. Calculation of the lattice energy and heat capacity of a solid therefore falls into two parts:

i) the evaluation of the contribution of a single mode, and

ii) the summation over the frequency distribution of the modes.

Plot of as a function of T

Specific heat at constant volume depends on temperature as shown in figure below. At high temperatures the value of Cv is close to 3R, where R is the universal gas constant. Since R is approximately 2 cal/K-mole, at high temperatures Cv is app. 6 cal/K-mole.

This range usually includes RT. From the figure it is seen that Cv is equal to 3R at high temperatures **regardless of the substance**. This fact is known as **Dulong Petit law**. This law states that specific heat of a given number of Atoms of any metal is **independent of temperature** and is the same for **all materials**

Additional Reading

Density of States

According to Quantum Mechanics if a particle is constrained,

- the energy of particle can only have special discrete energy values.
- it cannot increase infinitely from one value to another
- it has to go up in steps.

- These steps can be so small depending on the system that the energy can be considered as continuous.
- This is the case of classical mechanics.
- But on atomic scale the energy can only jump by a discrete amount from one value to another

Distinct energy levels

Steps get small

Energy is continuous

- In some cases each particular energy level can be associated with more than one different state (or wavefunction).
- This energy level is said to be degenerate.

- The density of states is the number of electron states per unit energy interval, and so that the number of states between and will be

Anharmonic Effects

- Any real crystal resists compression to a smaller volume than its equilibrium value more strongly than expansion due to a larger volume.
- This is due to the shape of the interatomic potential curve.
- This is a departure from Hooke's law, since harmonic application does not produce this property.
- This is an anharmonic effect due to the higher order terms in potential which are ignored in harmonic approximations.
- **Thermal expansion is an example to the anharmonic effect.**
- **In harmonic approximations 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.**
- In anharmonic effect phonons collide with each other and these collisions limit thermal conductivity which is due to the flow of phonons.

Phonon-phonon collisions

The coupling of normal modes by the anharmonic terms in the interatomic forces can be pictured as collisions between the phonons associated with the modes. A typical collision process of

Thermal conduction by phonons

- A flow of heat takes place from a hotter region to a cooler region when there is a temperature gradient in a solid.
- The most important contribution to thermal conduction comes from the flow of phonons in an electrically insulating solid.
- Transport property is an example of thermal conductivity.
- Transport property is the process in which the flow of some quantity occurs.
- Thermal conductivity is a transport coefficient and it describes the flow.
- The thermal conductivity of a phonon gas or a solid will be calculated by means of the elementary kinetic theory of the transport coefficients of gases.