CHEM110 – Chapter 7
Condensed Phases: Liquids and Solid

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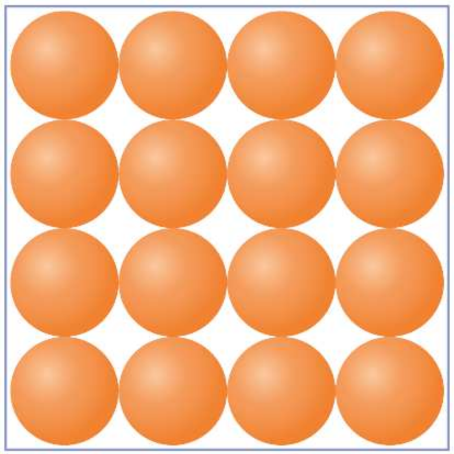
7.4 Order in Solids

- Molecules in gases and liquids can move relatively freely
- The atoms, molecules or ions in a solid are in fixed positions
- Their motions are restricted to vibrations about these fixed positions

7.4 Order in Solids

- Close-packed structures
  - Assume we can approximate a metal atom with a sphere
  - A hexagonal arrangement of identical spheres is the most dense packing that can be achieved in one layer of spheres



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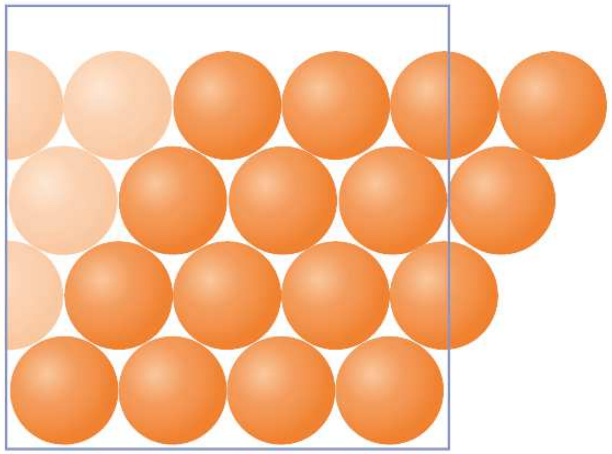
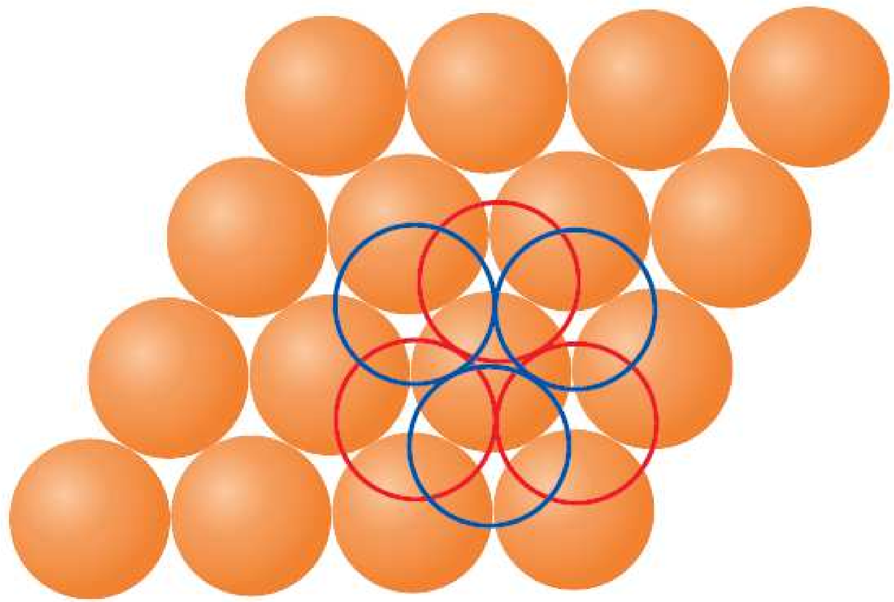


(b)

7.4 Order in Solids

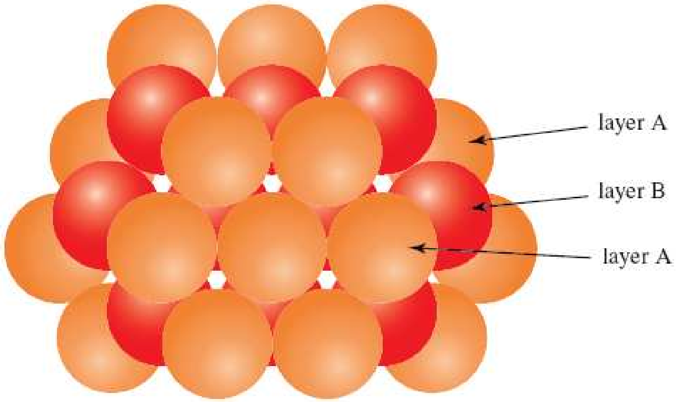
Close-packed structures

- When a second layer is added, to achieve the most compact arrangement, each sphere in layer B sits in one of the 'dimples' between a trio of spheres in layer A
- It is not possible to put a sphere in every 'dimple'



7.4 Order in Solids

- Close-packed structures: maximum space filling
  - When a third layer is added directly above the first, the structure is called hexagonal close-packed (hcp)
  - When the third layer is offset from both of the layers, the structure is called cubic close-packed (ccp)



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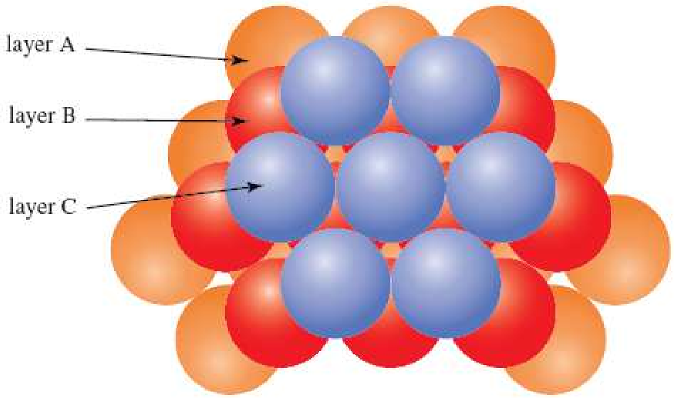

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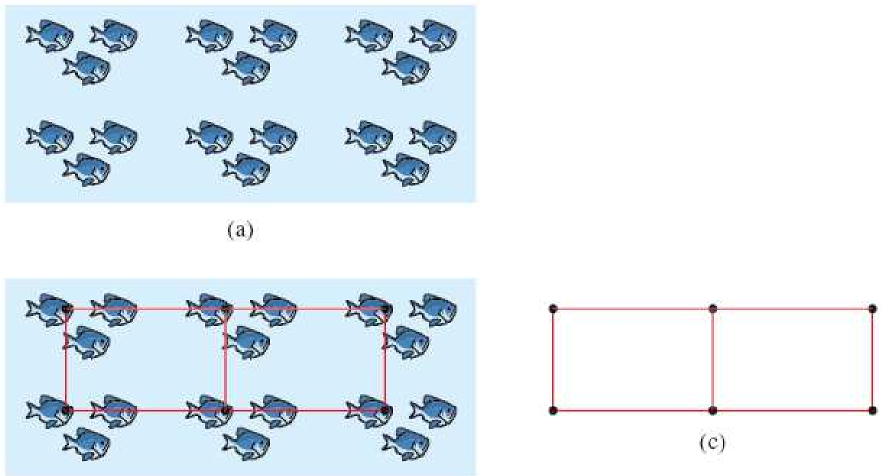
7.4 Order in Solids

- The crystal lattice and the unit cell
  - A lattice is a pattern of points
  - Every individual point is a lattice point

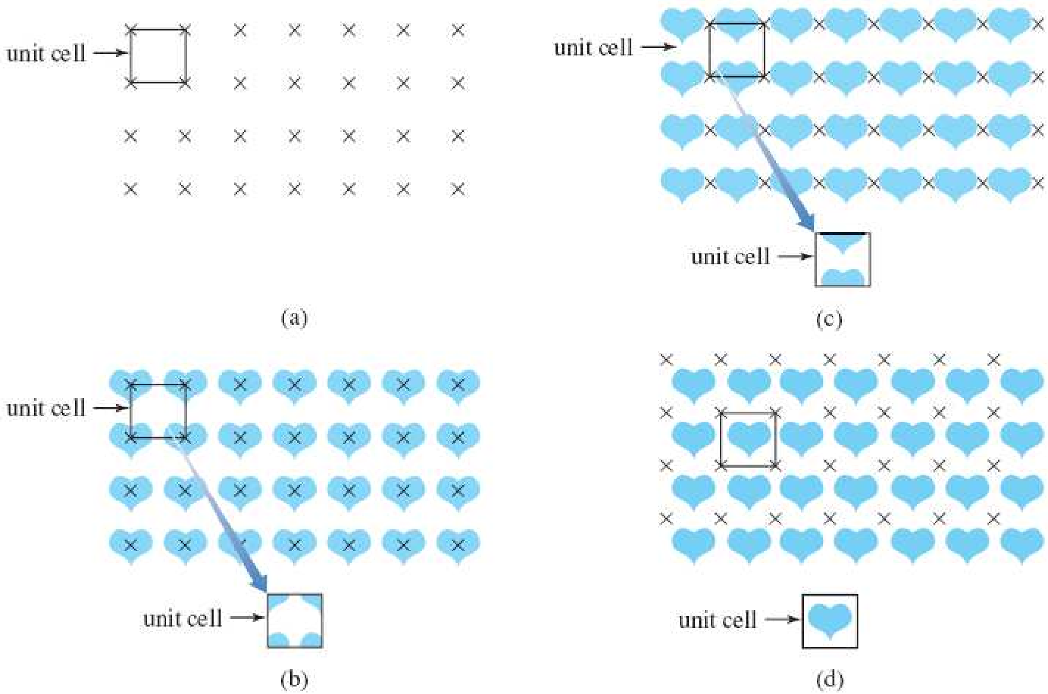


(a) (b) (c)

  - The unit cell is the smallest unique repeating unit of a lattice

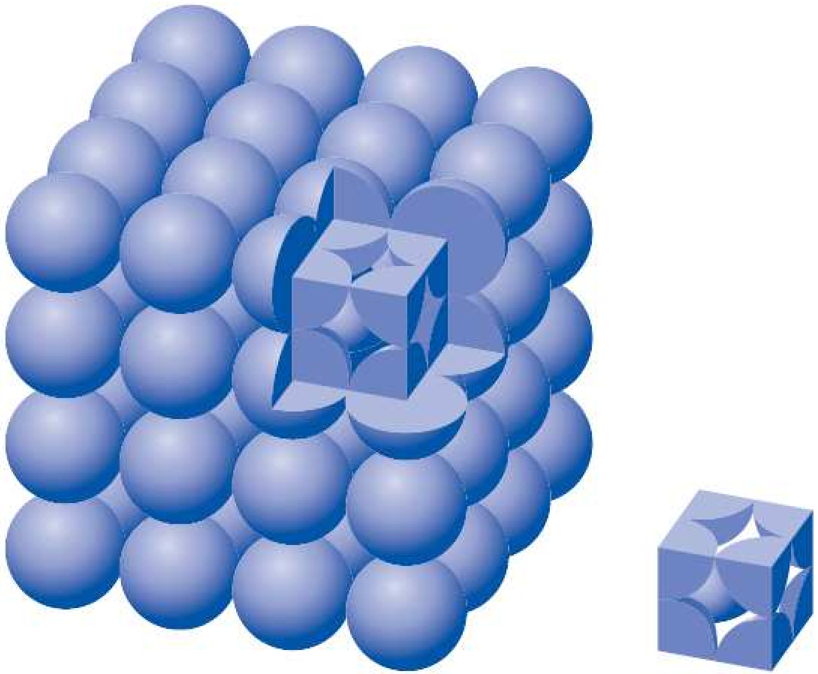
7.4 Order in Solids

- The crystal lattice and the unit cell
  - The same lattice can be used to describe many different designs or structures



7.4 Order in Solids

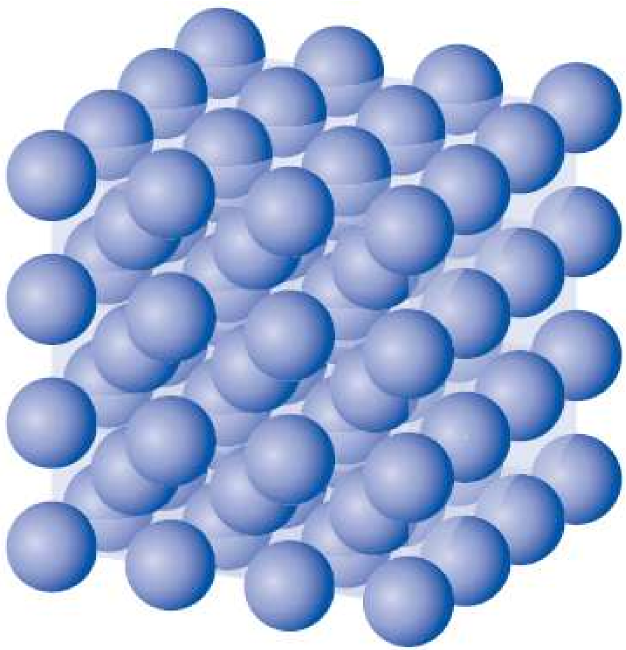
- Cubic structures: primitive cubic structure
  - Layers of atoms stack one directly above another, so that all atoms lie along straight lines at right angles



1 atom per unit cell
(8 × 1/8)

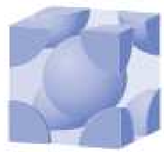
7.4 Order in Solids

- Cubic structures: body-centred cubic lattice (bcc)
  - Simple cube with one entire atom in the center of the cube (in the body; bcc)



(a)

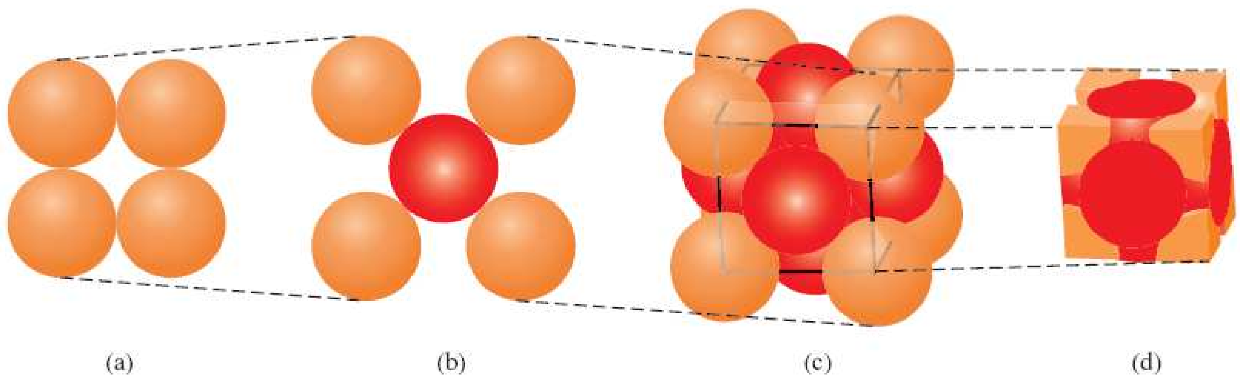
2 atoms per unit cell
(1 + 8 × 1/8)



(b)

7.4 Order in Solids

- Cubic structures: face-centred cubic structure (fcc)
  - simple cube with atoms in the center of each face of the cube



4 atoms per unit cell
(6 × 1/2 + 8 × 1/8)

  - cubic closed packed (ccp) structure and fcc have the same arrangement of spheres

7.4 Order in Solids

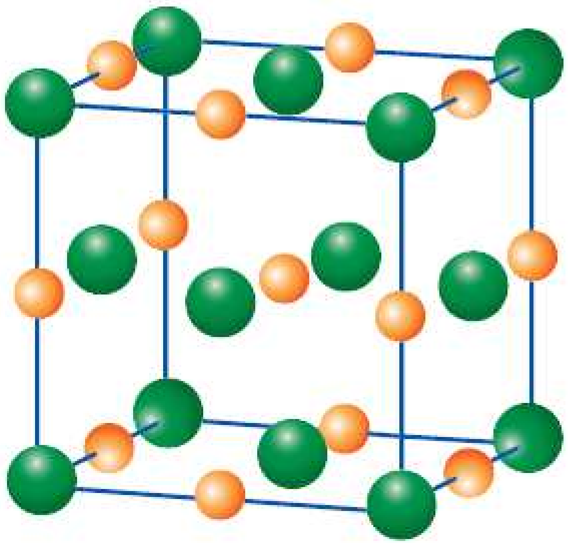
- Ionic solids
  - The packing in ionic crystals requires that ions of opposite charge alternate with one another to maximise attractions and minimise repulsions
  - The cations and anions are usually different sizes
  - Adopt a variety of structures that depend on the stoichiometry and relative sizes of the ions
  - Can understand ionic structures by assuming that the closed-packed structure is formed by larger ions

  - the smaller ions fill the interstitial sites

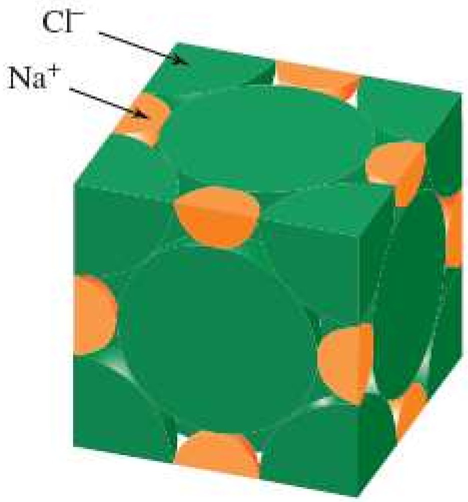
  (spaces between the spheres in the closed-packed structure)

7.4 Order in Solids

- Ionic solids: sodium chloride
  - fcc of large anion (chloride) with small cation (sodium) in octahedral holes



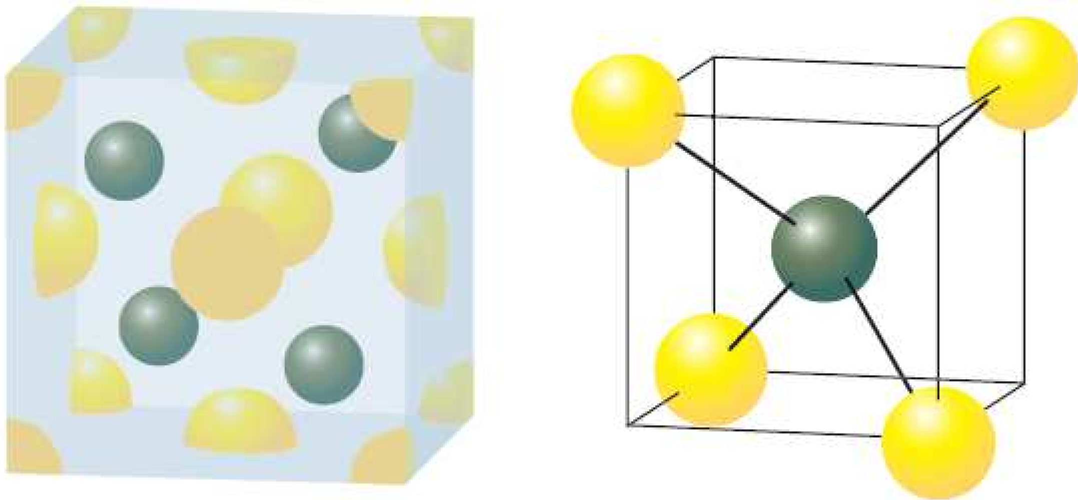
(a)



(b)

7.4 Order in Solids

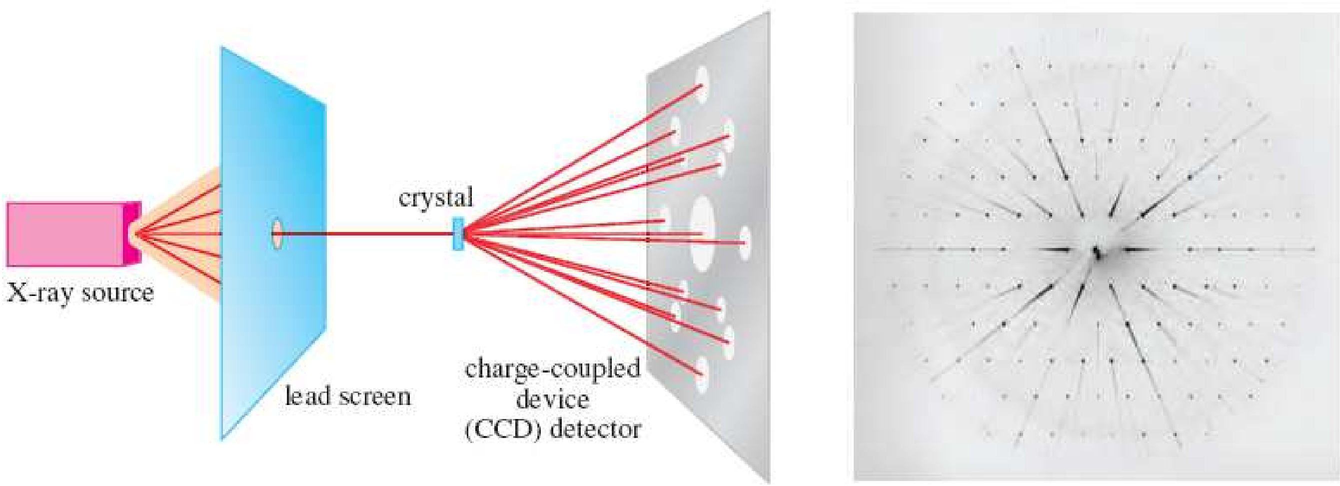
- Ionic solids: zinc sulfide
  - fcc of large anion (sulfide) with small cation (zinc) in half the tetrahedral holes



(a) (b)

7.5 X-ray Diffraction

- When the crystal is exposed to X-rays, diffracted beams due to constructive interference appear only in specific directions leading to a diffraction pattern
- Can be used to determine the arrangement of atoms, ions or molecules in a crystalline structure

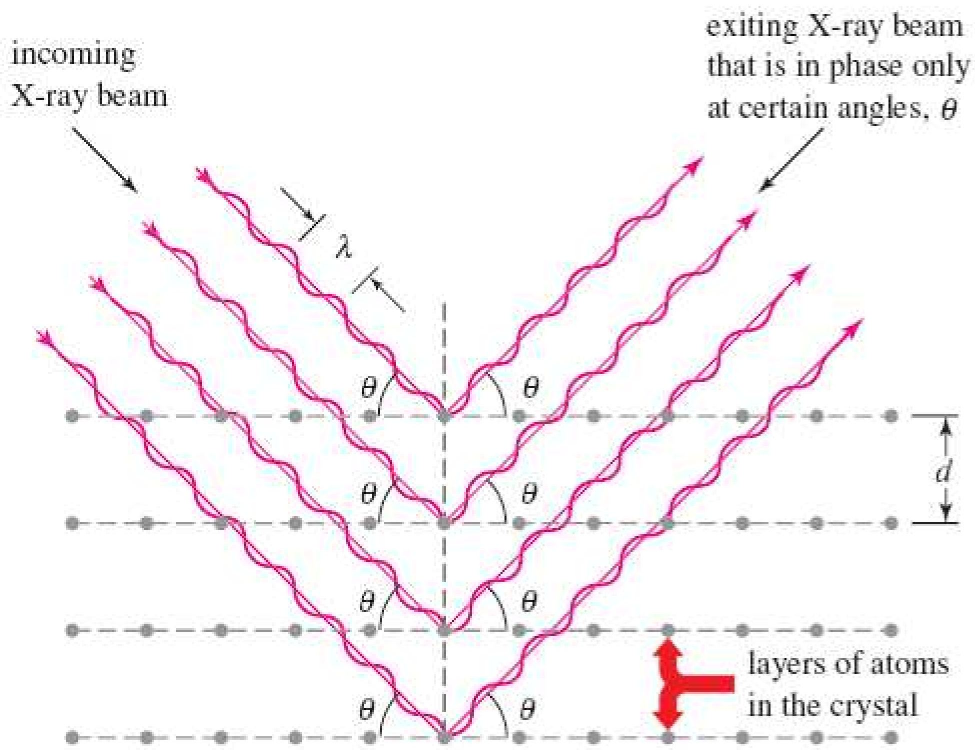


(a) (b)

7.5 X-ray Diffraction

- The Bragg equation relates wavelength (*λ),* angle (θ) and the distance (d) between the planes of atoms:

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



7.5 X-ray Diffraction

- Worked Example 7.4 (Page 279)
- Using X-ray crystal structure data to calculate atomic sizes
- X-ray diffraction measurements reveal that copper crystallises with a face-centred cubic lattice in which the unit cell length is 3.62×10^{-10} m. What is the radius of a copper atom? What is the copper-copper bond length?

7.6 Amorphous Solids

- When a pure liquid or a melt is cooled slowly, it often solidifies as a crystalline solid
- When solids form rapidly, their atoms, ions or molecules may become locked into positions other than those of a regular crystal
- These materials are said to be amorphous, meaning 'without form'
- They do not diffract X-rays
- Glass is an entire family of amorphous solids based on silica, SiO_2

7.7 Crystal Imperfections

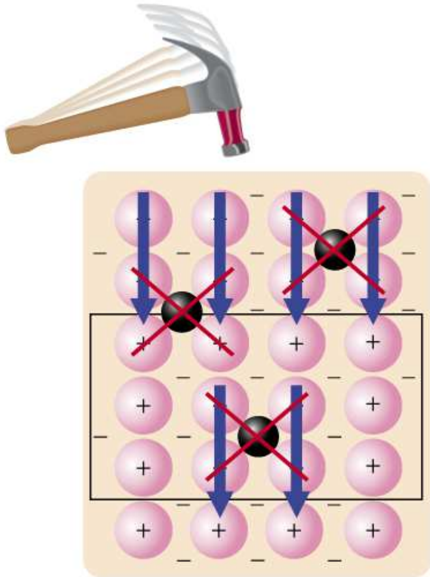
- Many solid materials are crystalline but contain defects which can profoundly alter the properties of a solid material
  - Doped semiconductors are solids into which impurity ‘defects’ are introduced

7.7 Crystal Imperfections

– Some gemstones are crystals containing impurities giving them colour

Colourless Al_2O_3 with Ti^{3+}/Fe^{3+} or Cr^{3+} defects

– The presence of carbon in iron harden the iron into steel



7.8 Modern Ceramics

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- Ceramics are materials composed of inorganic components that have been heat-treated

- Many manufactured ceramics are made from inorganic minerals such as clay, silica (sand) and other silicates

7.8 Modern Ceramics

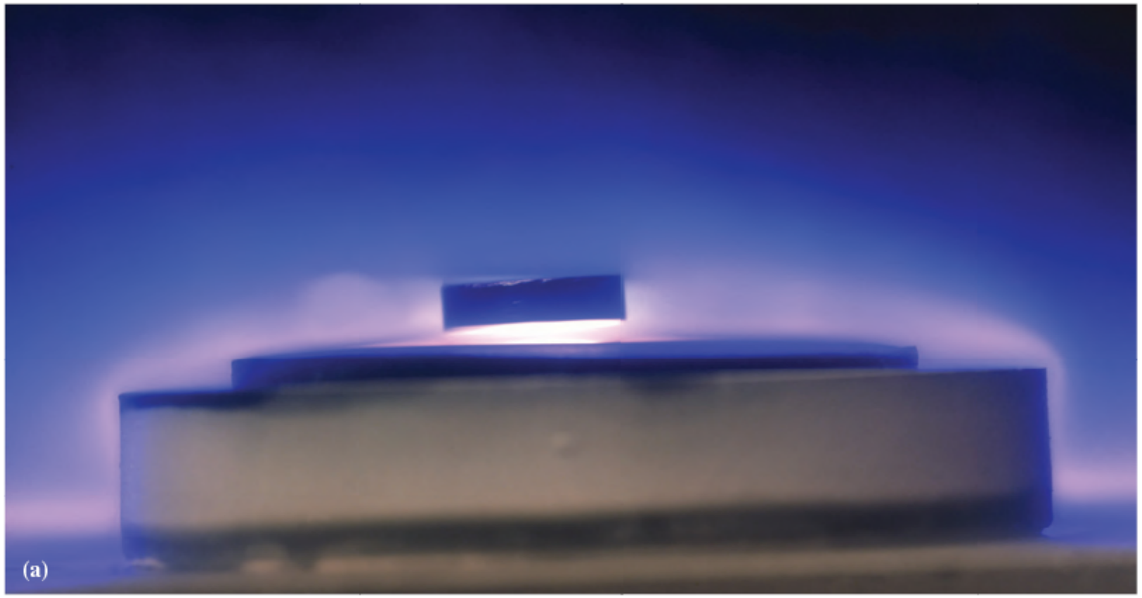
- Properties of ceramics
  - Many ceramic materials are very hard and have very high melting points
  - Most ceramics do not conduct electricity, so they are used as insulators
  - Ceramics generally contain metals in relatively high positive oxidation state and non-metals (e.g. O, N, C) with high negative oxidation states
  - Most ceramics possess substantial covalent bonding between atoms
  - The mixture of ionic and covalent bonding causes both strength and high melting points of ceramics

7.8 Modern Ceramics

- Application of advanced ceramics
  - Thin ceramic films are used as antireflective coatings on optical surfaces
  - Partially stabilised zirconia is used to make portions of hip-joint replacements
  - Boron nitride powder is used in cosmetics
  - Silicon nitride is used to make engine components for diesel engines

7.8 Modern Ceramics

- High-temperature superconductors
  - A superconductor is a material which offers no resistance to the flow of electricity
  - They can be levitated by a magnetic field



Chapter Summary

- Liquids are fluids, but cannot expand or contract significantly
- Viscosity, surface tension and capillary action depend mostly on the strengths of intermolecular attractions within the liquid
- Vapour pressure is the pressure at which the number of molecules escaping into the vapour phase matches the number re-entering
- Solids are rigid
- Solids may be classified as molecular, metallic, network or ionic solids

Chapter Summary

- A phase change occurs when a substance undergoes a transition from one phase to another and required energy to be either supplied or removed
- Temperatures and pressures at which equilibria can exist between phases are shown in a phase diagram
- Supercritical fluids contain properties of both liquids and solids
- Approximating atoms as spheres allows us to visualise their possible close-packed arrangements
- The overall structure of any crystalline solid can be described in terms of a repeating three-dimensional array of lattice points, which is called a lattice

Chapter Summary

- X-ray diffraction can be used to determine the structure of crystalline solids
- Amorphous solids do not have a regular arrangement of atoms, ions or molecules
- The most important example is glass
- Crystalline defects can significantly alter the properties of a solid
- Ceramics are composed of inorganic components that have been heat-treated