

PHY2009 Physics of Crystals

22 lectures by Rob Hicken

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Text Books

Core text book is:

Kittel C., *Introduction to Solid State Physics*, Wiley, ISBN 0-471-11181-3
(12 copies, in library, various editions) Very complete, covers all undergraduate Solid State modules.

Supplementary Reading:

Hook J.R. and Hall H.E. (1991), *Solid State Physics* (2nd edition), Wiley, ISBN 0-471-928054 (UL: 530.41 HOO, 4 copies). Well suited to this module but doesn't go far enough for later modules.

Ashcroft N.W. and Mermin N.D. (1976), *Solid State Physics*, Holt-Saunders, ISBN 0-03-083993-9 (UL: 530.41 ASH, 3 copies). Very thorough, more mathematical and my favorite. Use for reference only.

Rosenberg H.M. (1988), *The Solid State*, (Oxford) ISBN 0198518706 (UL: 530.41 ROS, 3 copies). Easy to read, full of insight, but a bit simple.

Others, not used by myself:

Christman J.R. (1988), *Fundamentals of Solid State Physics*, Wiley, ISBN 0-471-81095-9 (UL: 530.41 CHR, 3 copies)

Burns G. (1985), *Solid State Physics*, Academic Press, ISBN 0121460703 (UL: 530.41 BUR, 4 copies)



Synopsis

(With references to Kittel (K) and Hook & Hall (H))

I. Review of Bonding in Solids (K3, H1.6)

1. Interatomic bonding in solids: ionic, covalent, metallic, van de Waals and Hydrogen bonds; central core repulsion

II. Crystal Lattices (K1, H1.1-1.3)

1. Crystal structure as lattice plus basis. Lattice symmetries. (K1, H1.2)

2. Two-dimensional and three-dimensional lattices: General features, Bravais lattices, crystal systems; Positions, directions and planes in crystals (K1, H1.2)

3. Typical Crystal Structures: Cubic and hexagonal close-packed structures; Body-centred cubic structure; Rock-salt structure; structures of ionic solids; Diamond and zincblende structures (K1, H1.3)

III. Elastic Scattering of Waves (K2, H1.4, H11.1-11.2)

1. General features of scattering of waves in solids

2. Scattered-wave amplitude (H1.4, 11.1)

3. Laue conditions for diffraction (H11.2)

4. Reciprocal lattice and Brillouin zones (H11.2)

5. Structure factor (H11.2)



Synopsis

IV. Atomic Vibrations (K4, H2)

1. Lattice vibrations of the monatomic linear chain
2. Diatomic linear chain
3. Lattice vibrations of three-dimensional crystals; plotting of dispersion relations

V. Electrons in crystals (K6, K7, H3, H4)

1. The free-electron model: Free electron Fermi gas, dispersion relation, group velocity and effective mass (K6)
2. Density of states and Fermi distribution (K6, H3.2)
3. Electrical conductivity (K6, H3.3)
4. The nearly-free-electron model: Qualitative discussion of the dispersion curves: energy gaps, group velocity and effective mass
5. Consequences for electrical conductivity: Band picture classification of metals insulators and semiconductors (K7, H4)



Aim of this lecture

- To review the origin and properties of bonds in solids



Introduction

Overall aim:

to relate the **properties** of solids to their **structure**

i.e. to understand the origin of complexity in nature:

How do ~100 elements lead to enormous variety of different materials?

Answer: its how they fit together – **STRUCTURE**



Introduction

Overall aim:

to relate the **properties** of solids to their **structure**

e.g. change in structure can convert:

Graphite	→	diamond
Insulator	→	superconductor
common-cold virus	→	deadly virus

Mechanical, electrical, optical and thermal properties all affected



I. Review of Bonding in Solids

Definition of a solid:

Atoms vibrate with small amplitudes about fixed equilibrium positions

Sections I, II, IV and V of this module assume atoms fixed

Section III discusses the vibrations (normal modes, Phonons)



1. Inter-atomic bonding in solids

The atom looks like:

- a sphere having a net positive charge consisting of the nucleus plus inner core electrons, and
- a few outer valence electrons orbiting

Only the latter are involved in bonding



Ionic Bonding

Complete transfer of electrons from one atom to another
(compounds only, not elemental solids)

Bond comes from electrostatic attraction between ions

- Bond is strong (→ high melting point, large elastic modulus)
- Not directional (→ high density, high coordination number)
- Compounds only
- Good insulators (except near melting point)
- transparent up to UV (strong bonds → electrons need a lot of energy to become free)



Ionic Bonding

Complete transfer of electrons from one atom to another

Bond comes from electrostatic attraction between ions

Mathematical form: Energy $\sim 1/r$

Example: Sodium Chloride



Covalent Bonding

Equal sharing of electrons between atoms

→ both atoms have full shells

- Bond is strong (→ high melting point, large elastic modulus)
- directional (from orientation of QM orbitals) → low density
- Saturable (limited number of bonds per atom) → low density
- Good insulators



Covalent Bonding

Equal sharing of electrons between atoms

→ both atoms have full shells

Example: Diamond, Silicon

Note continuum of behaviour, ionic → covalent

e.g. III-V compounds GaAs, InSb, are partially covalent and partially ionic.



Metallic Bonding

Positive ions plus gas (sea) of electrons.

Think of this as the limiting case of ionic bonding in which the negative ions are electrons.

BUT: electrons can't be forced to sit at lattice points

(from Uncertainty principle: $\Delta p \Delta x \geq \frac{h}{2}$)

but for electrons m is small so the zero point energy $\Delta E = \frac{\Delta p^2}{2m}$ is very large

- the electrons would shake themselves free and are therefore delocalised)



Metallic Bonding

Positive ions plus gas (sea) of electrons.

- Bonds are non directional (→ high coordination number, high density, malleable and ductile)
- Variable strength
- Free electrons → high electrical conductivity, shiny

(electric field associated with incident light makes free electrons at surface move back and forth, re-radiating the light, as a reflected beam)



Van der Waals Bonding

Even an atom with a full shell, can, at a given instant, have a dipole moment (i.e. one side of the atom more positive than the other).

This instantaneous dipole will induce a dipole in a neighbouring atom, and the resulting dipole-dipole interaction is the origin of the van der Waals bond.

Although the original dipole time-averages to zero, the interaction does not – it is always attractive. $E \sim 1/r^6$



Van der Waals Bonding

- Bond is weak (\rightarrow low melting point, large expansion coefficient)
- non directional so high coordination number BUT
- long bond lengths (\rightarrow low density)

Examples: Solid inert gases (Argon, Neon), molecular solids (solid Oxygen)



Hydrogen Bonding

Hydrogen loses its electron and becomes positively charged particularly easily.

Therefore the region of a molecule around a hydrogen atom is often quite positive, and this allows an electrostatic bond to form between it and negative parts of neighbouring molecules.

Example: ice – the strength of the hydrogen bond explains the anomalously high melting point of ice.



Central Core Repulsion

Overlap of orbitals rapidly increases the energy of the electrons

(Pauli exclusion principle forces energies up as soon as electron wavefunctions start to overlap).

Present in all cases – need a repulsion to give an equilibrium separation.

Characterised mathematically by a high power law, or an exponential – but this is empirical.



Summary of this lecture

- We have reviewed the origin of the following bonds:
 - Ionic
 - Covalent
 - Metallic
 - van der Waals
 - Hydrogen
- and discussed the consequent properties of solids possessing these bonds
- We have discussed the origin of central-core repulsion

