

SI EDITION

THE SCIENCE AND ENGINEERING OF
MATERIALS
ENHANCED SEVENTH EDITION



DONALD R. ASKELAND
WENDELIN J. WRIGHT

Chapter 2

Atomic Structure

Chapter Learning Objectives

- Define four quantum numbers for electrons and explain the significance of each.
- Explain arrangement of elements in the periodic table.
- State the electronic structure of elements.
- Explain role of electronegativity in bonding.
- Define four different mechanisms of bonding in materials.
- Describe how interactions between atoms or between ions influence materials properties.
- Explain how allotropes can display different materials properties based on their structure even though they are composed of the same element.

Chapter Outline

Sections

- 2-1 The Structure of Materials: Technological Relevance
- 2-2 The Structure of the Atom
- 2-3 The Electronic Structure of the Atom
- 2-4 The Periodic Table
- 2-5 Atomic Bonding
- 2-6 Binding Energy and Interatomic Spacing
- 2-7 The Many Forms of Carbon: Relationships between Arrangements of Atoms and Materials Properties

2-1 Structure of Materials: Technological Relevance

- Structure on various levels/length scales can profoundly influence a material's properties, behavior, and applications.
- The 5 main levels of structure are:
 - Atomic structure
 - Short- and Long-range atomic arrangements
 - Nanostructure
 - Microstructure
 - Macrostructure

2-2 The Structure of the Atom

- The atomic structure may be familiar from introductory chemistry courses.
- An atom consists of a nucleus (protons & neutrons) orbited by electrons.
- Electrons (-) and protons (+) are held together by electrostatic attraction, since both carry opposite charges.
 - Atomic number = number of protons in nucleus
 - Atomic mass = mass of protons + neutrons in atom

2-3 The Electronic Structure of the Atom

- Electrons occupy discrete energy levels within the atom.
- Only 2 electrons may occupy the same energy level. Each electron's energy level is identified by 4 quantum numbers.
 - Principal quantum number $n = 1, 2, 3, \dots$ for shells
 - Azimuthal quantum number $l = 0, 1, \dots, n-1$ for orbitals
 - Magnetic quantum number $m_l = 2l+1$ for each l
 - Spin quantum number $m_s = 1/2$ or $-1/2$

2-3 The Electronic Structure of the Atom

- Pauli's Exclusion Principle states that no 2 electrons in an atom can have the same 4 quantum numbers.
- The energy levels of quantum shells do not fill in strict numerical order.
- The Aufbau Principle predicts deviations from the expected ordering of energy levels. Not all elements follow the Aufbau Principle (e.g., Cu)

2-3 The Electronic Structure of the Atom

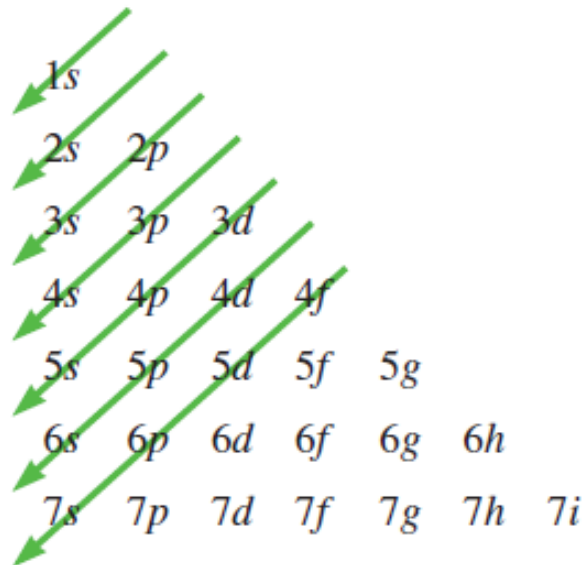
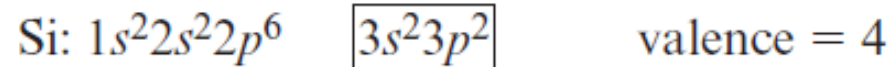
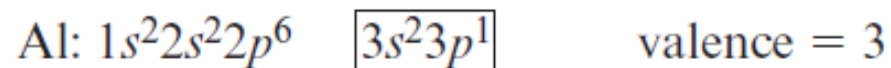
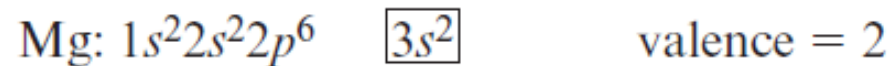


Figure 2-7 The Aufbau Principle. By following the arrows, the order in which the energy levels of each quantum level are filled is predicted: $1s$, $2s$, $2p$, $3s$, $3p$, etc. Note that the letter designations for $l = 4, 5, 6$ are g , h , and i .

2-3 The Electronic Structure of the Atom

- Valence is the number of electrons in an atom that participate in bonding/chemical reactions.
- Usually, valence is the number of electrons in outer *s* and *p* orbitals.



- However, valence also depends on the environment surrounding the atom.

2-3 The Electronic Structure of the Atom

- If an atom has a valence of 0, it is chemically unreactive/inert.
- Electronegativity describes the tendency of atom to gain an electron to achieve a valence of zero.
- Atoms such as chlorine are very electronegative because they have 7 electrons in the outer shell and need only one more to achieve 0 valence.
- Atoms with nearly empty outer shells have low electronegativity since they give up their electrons to achieve 0 valence.

2-3 The Electronic Structure of the Atom

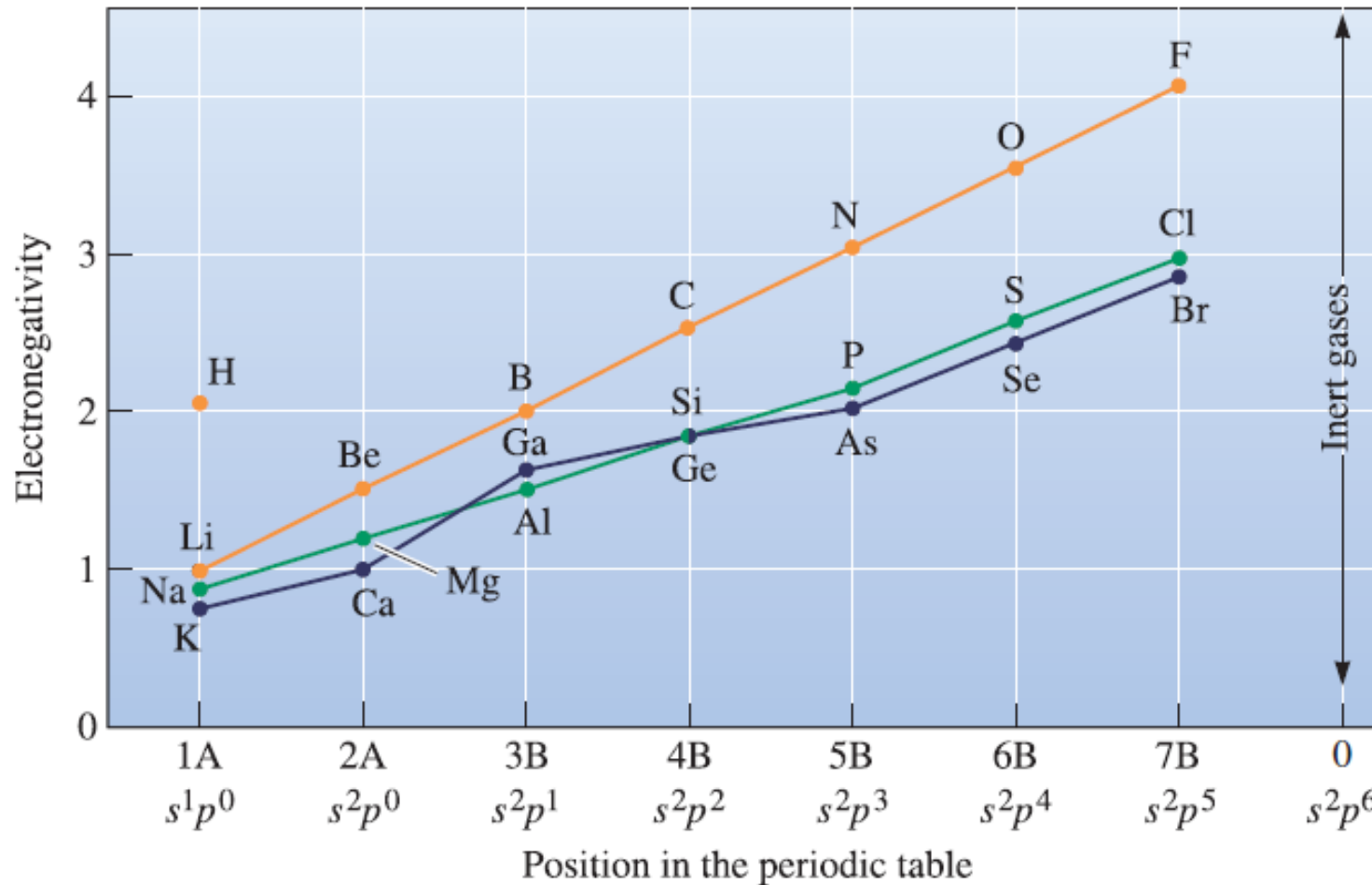


Figure 2-8 The electronegativities of selected elements relative to the position of the elements in the periodic table.

2-4 The Periodic Table

- The periodic table contains information about each element and can identify useful trends in atomic size, reactivity, and melting points.
 - Rows correspond to electron shells
 - Columns refer to the most common valence
- Materials of engineering interest are:
 - Polymers (based on carbon in Group 4B)
 - Ceramics (combinations of elements from Groups 1-5B and oxygen, carbon, or nitrogen)
 - Metallic materials (Groups 1, 2, and transition metal elements)

2-4 The Periodic Table

n	s^1	s^2	Transition Metals ($(n-1)d$)														np															
			d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}		p^1	p^2	p^3	p^4	p^5	p^6													
1	1 H	2 He																														
2	3 Li	4 Be															5 B	6 C	7 N	8 O	9 F	10 Ne										
3	11 Na	12 Mg	Inner Transition Metals ($(n-2)f$)														13 Al	14 Si	15 P	16 S	17 Cl	18 Ar										
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr														
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe														
6	55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr															

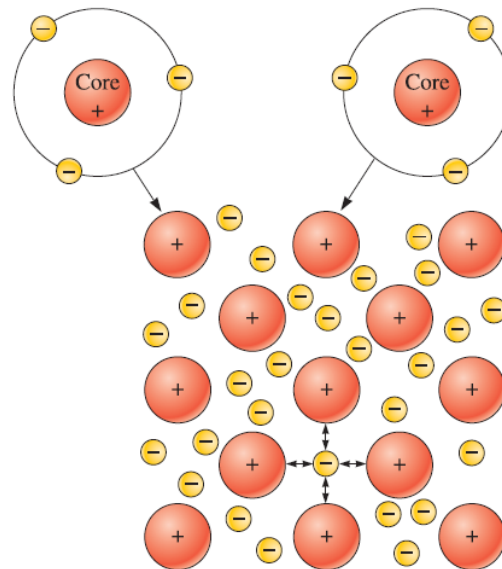
Figure 2-10 The periodic table for which the rows of the Lathanoid and Actinoid series are inserted into their correct positions. The column heading indicates the particular orbital being filled by each additional electron as the atomic number increases.

2-5 Atomic Bonding

- There are 4 important mechanisms by which atoms are bonded in engineering materials:
 - Metallic bonds
 - Covalent bonds
 - Ionic bonds
 - Van der Waals bonds
- The first 3 types are strong and called primary bonds. Van der Waals bonds are secondary bonds and weaker.

2-5 Atomic Bonding

- Metallic bonds confer the following properties on metals:
 - Good conductivity: electrons are not fixed in place
 - Good ductility: metallic bonds are non-directional
 - High melting points, electropositive character (prone to corrosion/oxidation), etc.



2-5 Atomic Bonding

- Covalently bonded materials have:
 - Low conductivity: Valence electrons are locked
 - Low ductility: Bonds are directional
 - Very high strengths & melting points

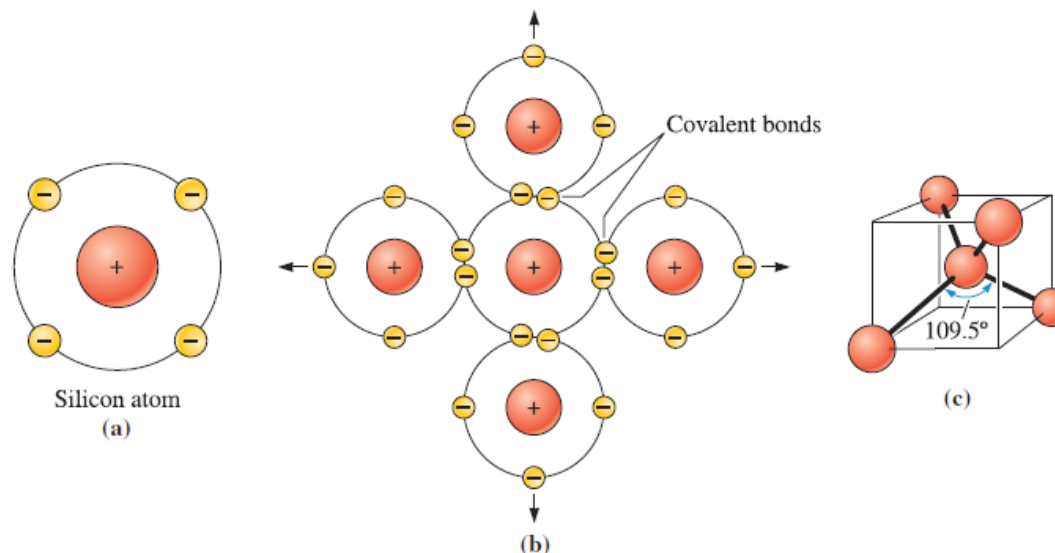


Figure 2-12 (a) Covalent bonding requires that electrons be shared between atoms in such a way that each atom has its outer *sp* orbitals filled. (b) In silicon, with a valence of four, four covalent bonds must be formed. (c) Covalent bonds are directional. In silicon, a tetrahedral structure is formed with angles of 109.5° found between any pair of covalent bonds.

2-5 Atomic Bonding

- Ionic bonds form between materials with different electronegativities.
- An ionic bond consists of cations (+ve) and anions (-ve) which are formed after electron transfer between atoms.

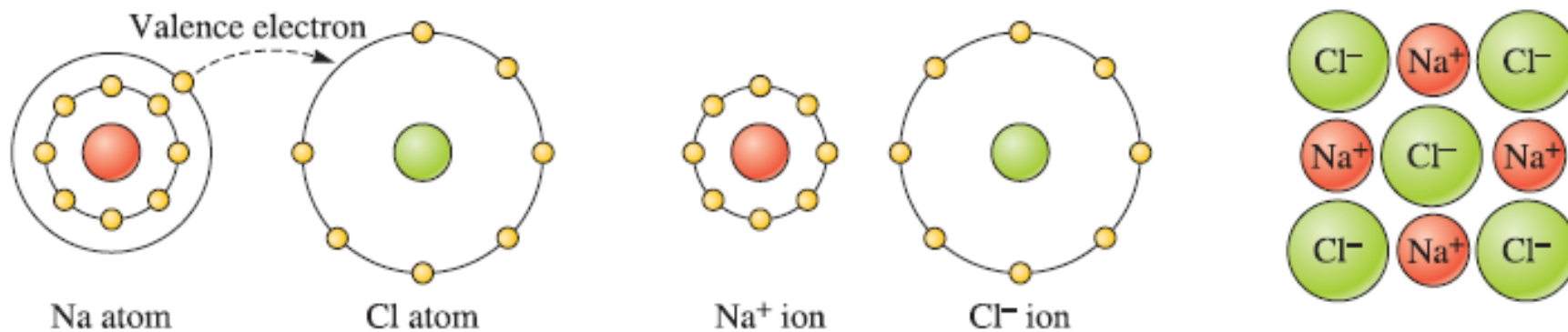


Figure 2-14 An ionic bond is created between two unlike atoms with different electronegativities. When sodium donates its valence electron to chlorine, each becomes an ion, attraction occurs, and the ionic bond is formed.

2-5 Atomic Bonding

- Van der Waals forces exist in all materials and arise due to quantum mechanical effects.
- Van der Waals forces exist because electric dipoles form when an atom interacts with the electric field of a neighboring atom.
- The 3 kinds of van der Waals forces are:
 - London forces (between 2 induced dipoles)
 - Debye interaction (between an induced and a permanent dipole)
 - Keesom interactions/hydrogen bonding (between 2 permanent dipoles)

2-5 Atomic Bonding

- Hydrogen bonding often leads materials (e.g., water) to exhibit higher melting points/surface tension/stronger properties than similar materials.
- Although termed secondary bonding, van der Waals forces play a significant role in influencing materials properties, such as diamond vs. graphite, or the varying strengths of different plastics.

2-5 Atomic Bonding

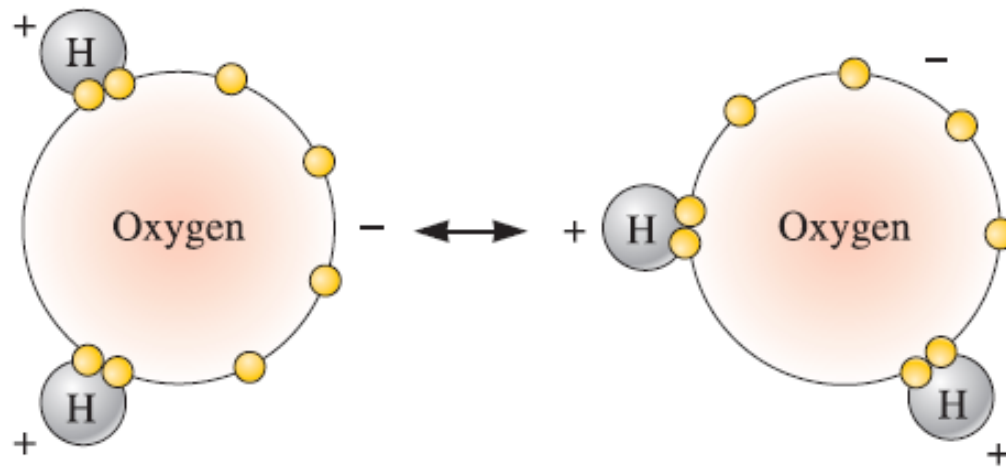


Figure 2-16 The Keesom interactions are formed as a result of polarization of molecules or groups of atoms. In water, electrons in the oxygen tend to concentrate away from the hydrogen. The resulting charge difference permits the molecule to be weakly bonded to other water molecules.

2-5 Atomic Bonding

- Most materials exhibit mixed bonding. Iron is bonded by a combination of metallic and covalent bonding.
- Compounds formed from 2 or more metals may have a combination of metallic & ionic bonds, particularly if electronegativities are different, e.g., AlLi
- Ceramics & semi-conductors have a mixture of ionic & covalent bonding. The fraction of covalent bonds can be found via $\text{Fraction covalent} = \exp(-0.25\Delta E^2)$

2-6 Binding Energy & Interatomic Spacing

- Interatomic spacing is determined by a balance between attractive and repulsive forces.

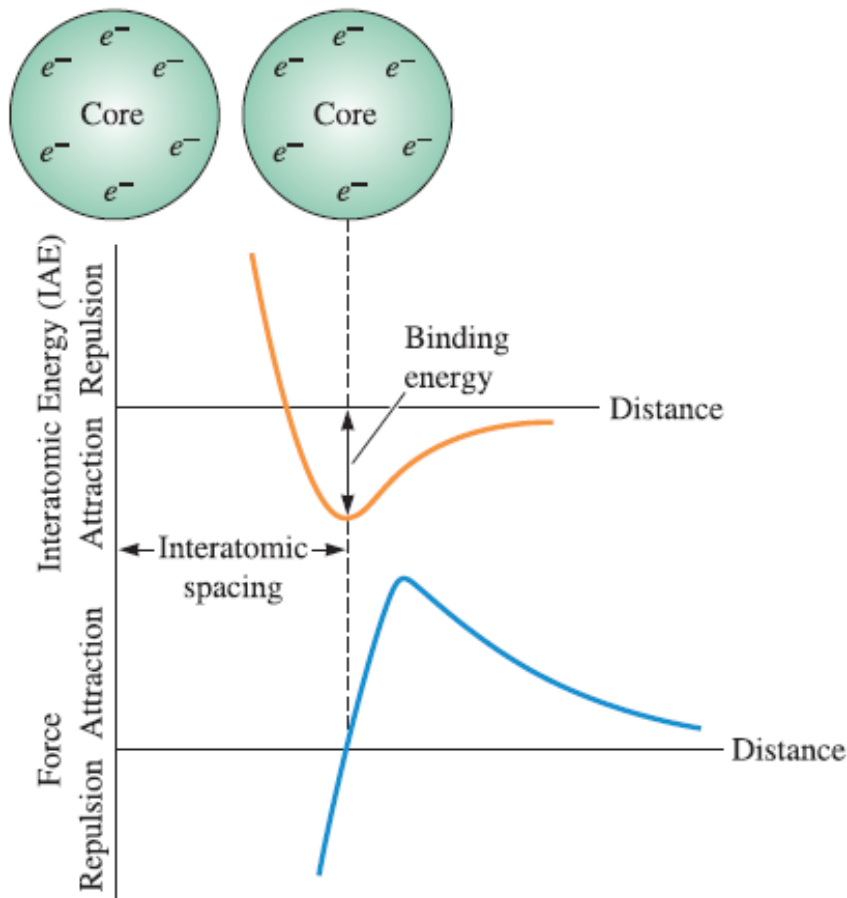


Figure 2-18 Atoms or ions are separated by an equilibrium spacing that corresponds to the minimum interatomic energy for a pair of atoms or ions (or when zero force is acting to repel or attract the atoms or ions).

2-6 Binding Energy & Interatomic Spacing

- Binding energy is the energy required to create/destroy bonds.
 - Materials with high binding energy have high strengths & melting points

Table 2-2 Binding energies for the four bonding mechanisms

Bond	Binding Energy (kcal/mol)
Ionic	150–370
Covalent	125–300
Metallic	25–200
Van der Waals	<10

- Other properties, such as modulus of elasticity and coefficient of thermal expansion (CTE) can also be related to nature of bonding in the material.

2-6 Binding Energy & Interatomic Spacing

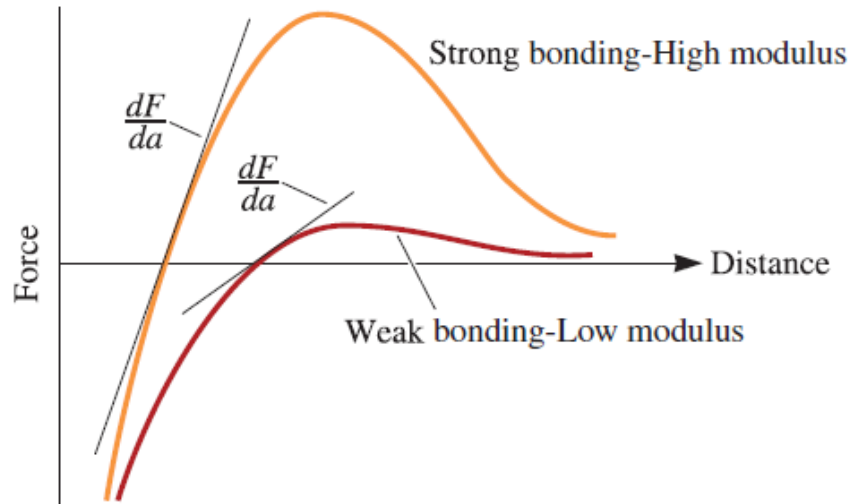


Figure 2-19 The force-distance (F - a) curve for two materials, showing the relationship between atomic bonding and the modulus of elasticity. A steep dF/da slope gives a high modulus.

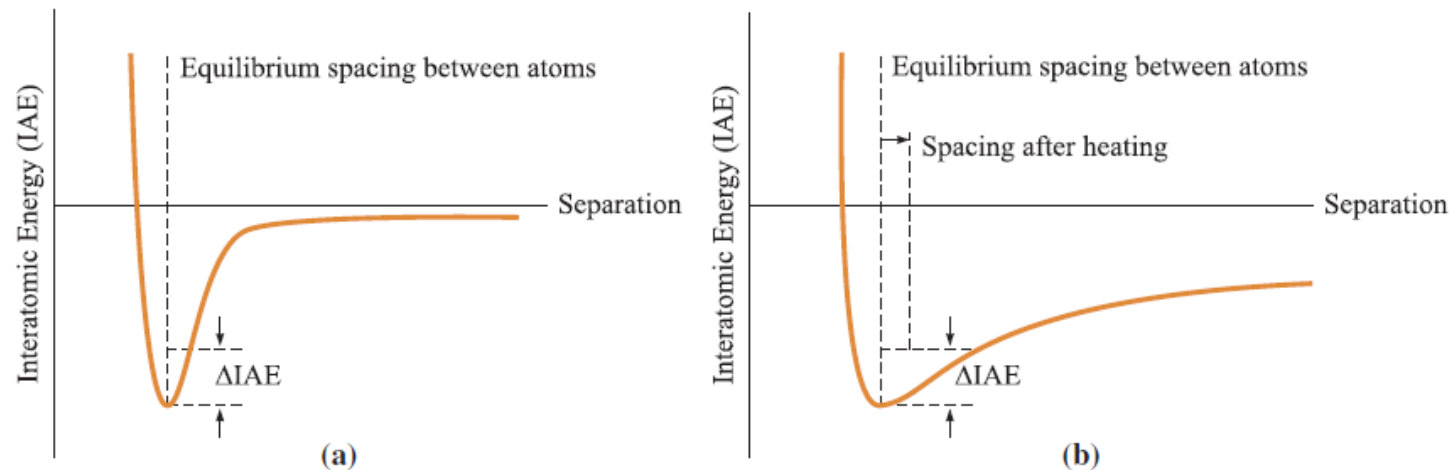


Figure 2-20 The thermal expansion coefficient is related to the shape of the interatomic energy (IAE)—separation curve for two atoms. (a) A symmetric curve has a low (as shown, essentially zero) thermal expansion coefficient. (b) An asymmetric curve has a relatively higher thermal expansion coefficient.

2-7 The Many Forms of Carbon

- Carbon is an abundant element on Earth and is crucial for life and many technological applications.
- Pure carbon exists as several allotropes (same composition, different bonding).
- Carbon has 4 valence electrons. The different bonding structures possible result in distinct allotropes having very different properties.

2-7 The Many Forms of Carbon

- Diamond has 4 covalent bonds. Its properties are:
 - Good thermal conductivity/bad electrical conductivity
 - Very high strength, hardness, stiffness, and melting point

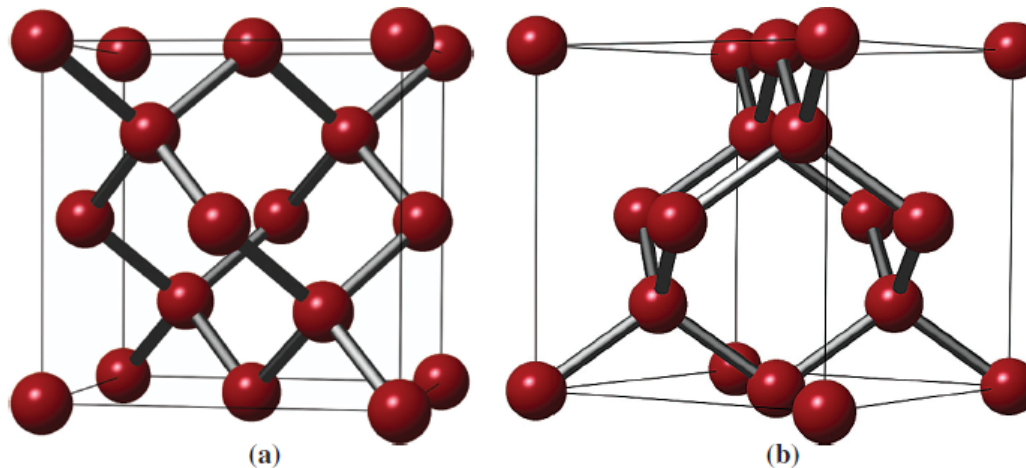
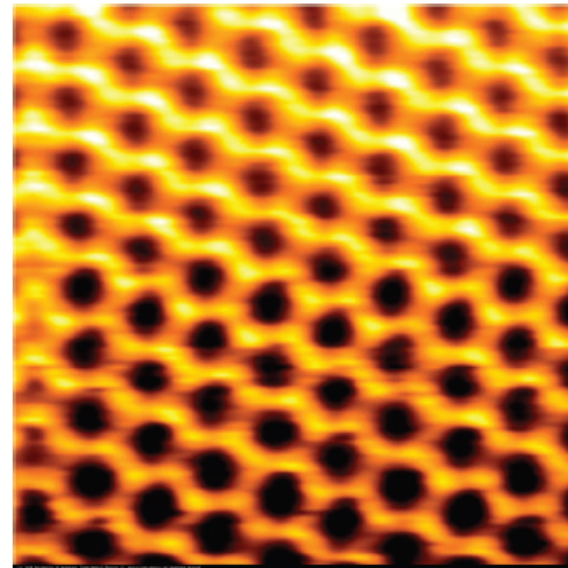
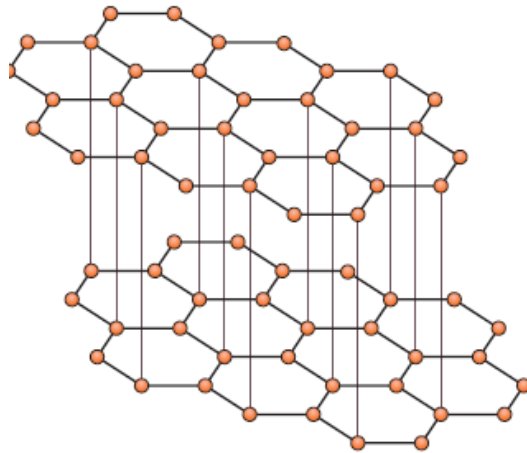


Figure 2-21 The structure of diamond. (a) The repeat unit of the diamond crystal, also known as the unit cell of diamond. (b) The same image as (a) rotated by 45° around a vertical axis.

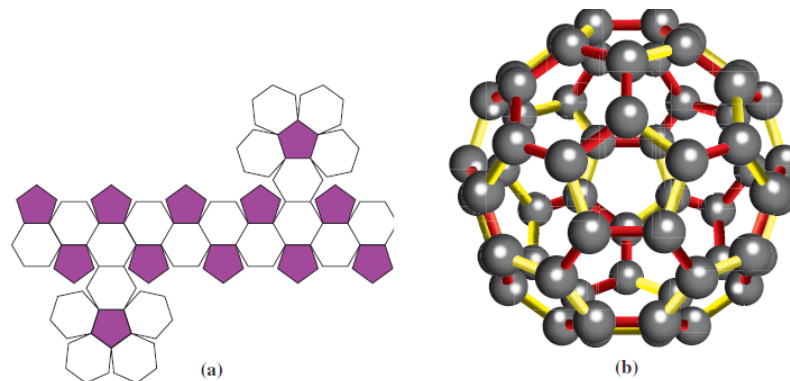
2-7 The Many Forms of Carbon

- In graphite, carbon is arranged in layers with each carbon atom having 3 covalent bonds. Its properties are:
 - High melting point, lower density than diamond
 - Electrical conductor



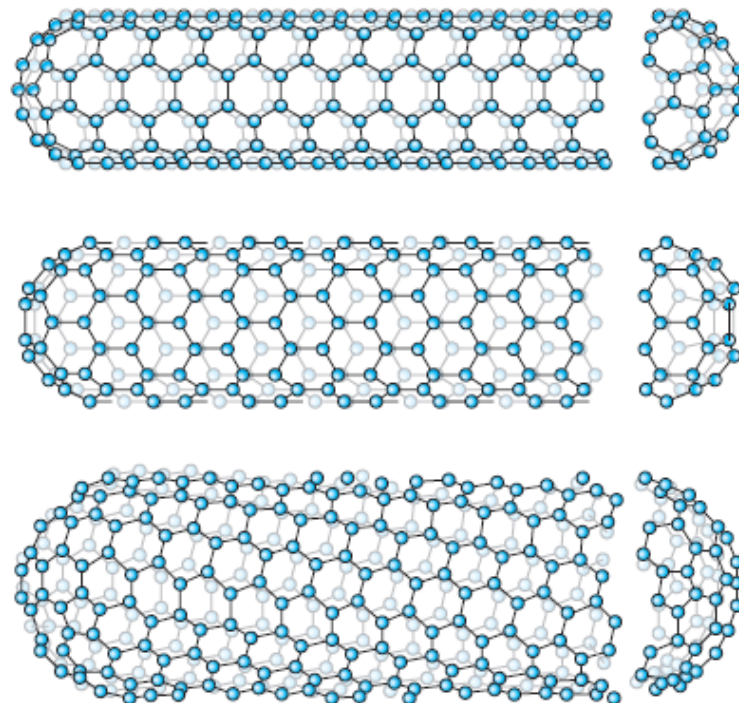
2-7 The Many Forms of Carbon

- Graphene is a single graphite sheet. In addition to graphite properties, it is transparent and a good thermal conductor.
- Buckminsterfullerene is another allotrope containing 60 carbon atoms. It can enclose other atoms and has interesting magnetic/electronic properties.



2-7 The Many Forms of Carbon

- Carbon nanotubes can be envisioned as rolled-up graphite sheets with fullerene ends. Research is focused on developing microscopy, nanoelectronics, and composite materials applications for nanotubes.



Summary

- Like composition, material structure has profound influence on material properties.
- Material structure can be understood at various levels such as atomic, long- & short-range atomic arrangements, nano-, micro-, and macro-structure.
- Engineers need to understand materials on micro- and macro-structures. Emerging technologies such as MEMS and nanotechnology require understanding atomic and nanoscale structure.

Summary

- The atom's electronic structure is described by 4 quantum numbers and determines the nature of atomic bonding and hence material properties.
- Atomic bonding is partly determined by valence electron interactions. Bond types include metallic, covalent, ionic, van der Waals. Engineered materials often have mixed bonding.
- A metallic bond forms when low electronegativity atoms donate valence electrons to a "sea" of electrons.

Summary

- Metallic bonds are relatively strong, non-directional. Consequently, most metals are ductile, good heat/electrical conductors. They reflect visible light and have a high Young's modulus.
- Covalent bonds form when valence electrons are shared between 2 atoms. These strong bonds are found in polymeric, ceramic, plastic, and semiconductor materials.

Summary

- Covalent bonded materials are good electrical insulators. Inorganic covalent materials have high strength and hardness, and limited ductility. Organic covalent materials have lower strength and high ductility.
- Ionic bonding found in ceramics occurs when a valence electron is donated from an electropositive to an electronegative atom. This creates cations (+) and anions (-).

Summary

- Ionically bonded materials are strong and hard but brittle. They have high melting points and are insulators. In some cases, the microstructure can be tailored to achieve significant conductivity.
- Van der Waals bonds are formed when atoms/groups of atoms have nonsymmetrical electric charge, causing bonding by electrostatic attraction. The charge asymmetry results from induced or permanent dipoles.

Summary

- Binding energy is related to bond strength and is high in ionically & covalently bonded materials. High binding energy materials have high melting points, high modulus of elasticity, and low coefficient of thermal expansion.
- Not all properties depend on microstructures. One example is modulus of elasticity.
- Pure carbon exists as several allotropes (e.g., diamond, graphite, nanotubes, buckminsterfullerene) with dramatically different properties due to differences in atomic structures.