

STRUCTURE: Bonding

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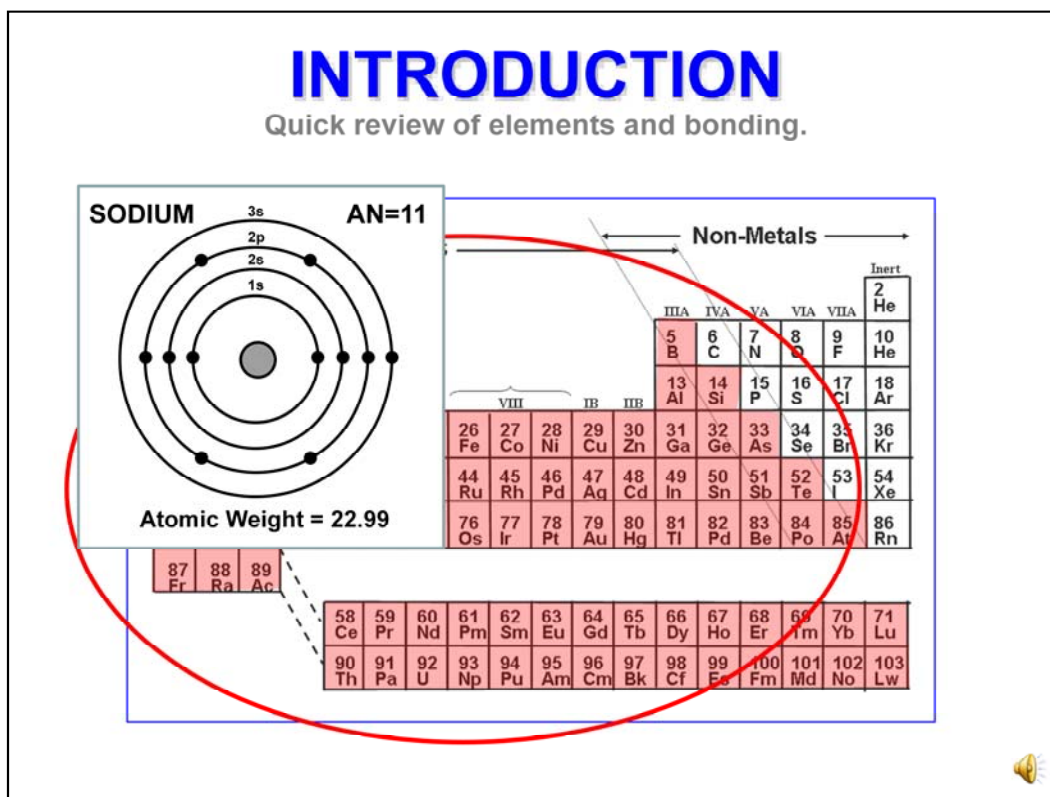
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Welcome to the first of a series of modules that discuss the structure of materials.

INTRODUCTION

Quick review of elements and bonding.



The following comments are an over-simplified but practical review of atomic physics.

[CLICK] Elements, in the simplest atomic model, are envisioned as composed of a core of neutrons (no charge) and protons (positive charges), with electrons in various energy shells surrounding the nucleus. The atomic number of an element is the number of protons (e.g., Na = 11). The practical atomic weight is the average of the sum of the number of neutrons and protons. Isotopes may contain additional neutrons and so the average atomic weight for any particular sample may not be an integer (Na = 22.99 gms/mole).

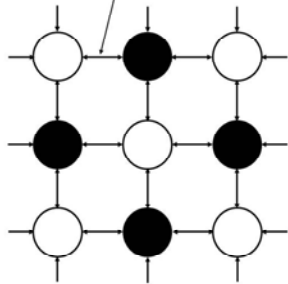
[CLICK] Most of the periodic table involves metallic elements. Moving from the left to right and down in the periodic table represents atoms with more and more electrons in outer (valence) shells and more and more energy levels (or shells). The heaviest elements are not presented in this table.

PRIMARY BONDING

Types.

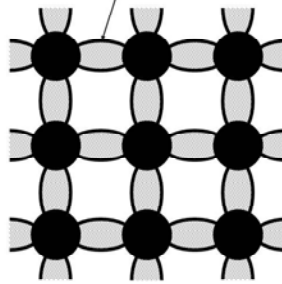
IONIC BONDING

(Strong) Attractive Forces Between Positive and Negative Ions



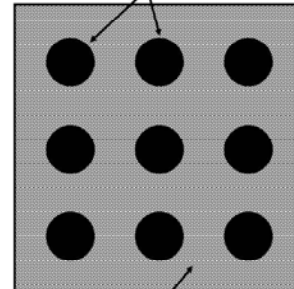
COVALENT BONDING

Shared Valence Electrons



METALLIC BONDING

(Positive) Metal ion



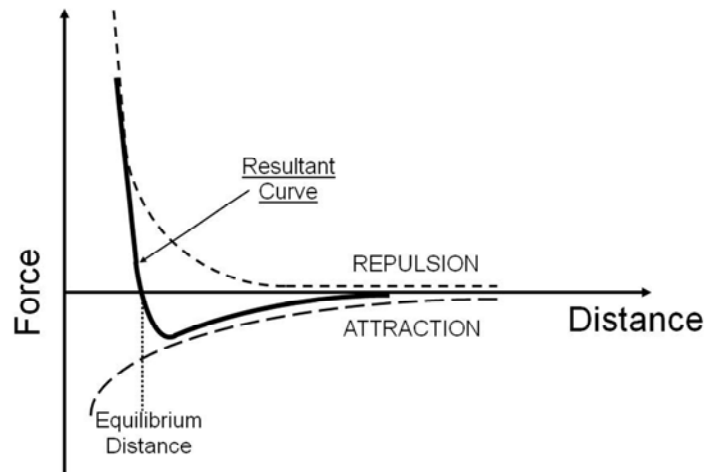
(Negative) Electron Cloud



Primary bonding determines the major structure of a liquid or solid. Bonding patterns are attempts to create completely-filled outer electron shells. Adjacent atoms accomplish this with ionic (i.e., exchange of electrons), covalent (i.e., sharing of electrons), or metallic bonding (i.e., sharing electrons over the entire group of atoms). You are most likely familiar with ionic and covalent bonding, but metallic bonding may be new for you.

PRIMARY BONDING

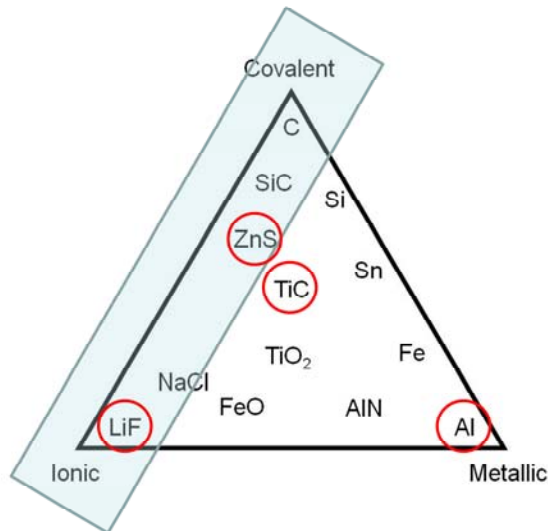
Formation of bonds.



As atoms are brought close together they attempt to bond with each other. The atomic nucleus of one is attracted to the electron cloud of neighboring atom. However, the nucleus of one repels the nucleus of the other. Therefore, there are forces of **ATTRACTION** and **REPULSION** at work determining the equilibrium distance for atoms that bond together. The solid curve in the figure shows the **NET** force versus distance. If you try to push the atoms much closer together the force rises rapidly. If you try to stretch the atoms apart the force rises much more slowly. This is also why atoms being compressed mechanically are very strong and atoms being pulled in tension are much weaker. See – you already know something now about mechanical properties.

BONDING CHARACTER

Mixed bonding character is the rule rather than the exception.



Most solids have bonding patterns that are not exclusively one type of bonding or another but rather mixtures. This can be represented as shown in the figure as a triangular field with pure bonding of each type at each of the corners. Examples are positioned in the field that demonstrate materials with mixed bonding character. **[CLICK]** ZnS or zinc sulfide has about 60% covalent character, about 30% ionic character, and about 10% metallic character. **[CLICK]** TiC or titanium carbide has about equal amounts of all bonding characters. **[CLICK]** LiF or lithium fluoride is highly ionic. **[CLICK]** Al or aluminum is highly metallic.

Quite often the most complex materials to sort out are those with dominant mixtures of ionic and covalent character. **[CLICK]** There is a relatively simple method of sorting this out developed by Linus Pauling, based on the electronegativity of the elements involved. We will demonstrate this next.

Theory of Electronegativity

Distinguishing the degree of ionic-covalent bonding character.

Li 1.5	Be 1.5	B 2.0												C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5												Si 1.5	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.5	Cr 1.5	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.5	Mo 1.8	Tc 1.9	Ru 2.2	Th 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	
Cs 0.7	Ba 0.9	La/Lu 1.15	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	
Fr 0.7	Ra 0.9	Ac 1.1	Th 1.3	Pa 1.5	U 1.7	Np/No 1.3											

The “theory of electronegativity” assigns a relative electronegativity value to all the elements in the periodic table. For any combination of elements, one simply looks up the electronegativities and determines the differences between them. If the difference is greater than or equal to 1.7 units, then the dominant character is ionic.

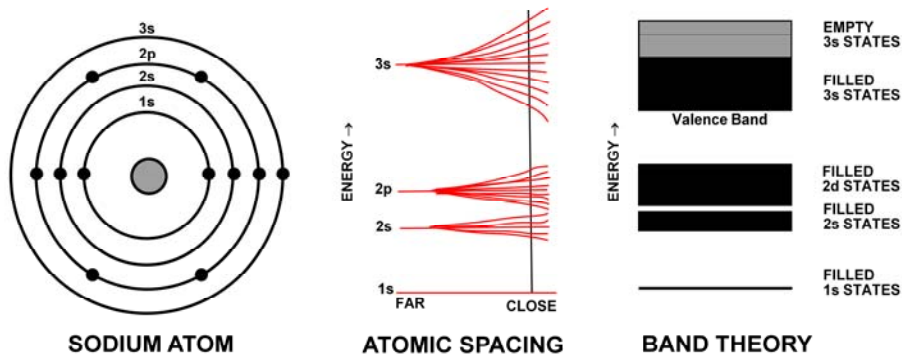
Let’s try out the system.

What type of character is predicted for NaF? **[CLICK]** Na=0.9 and **[CLICK]** F=4.0 so the difference is 3.1, which is far more than 1.7 units, predicting a highly ionic character.

What type of character is predicted for LiCl? **[CLICK]** Li=1.5 and **[CLICK]** Cl=3.0 so the difference is 1.5, which is slightly less than 1.7 units, predicting a covalent character.

BAND STRUCTURE

Energy band types and properties.

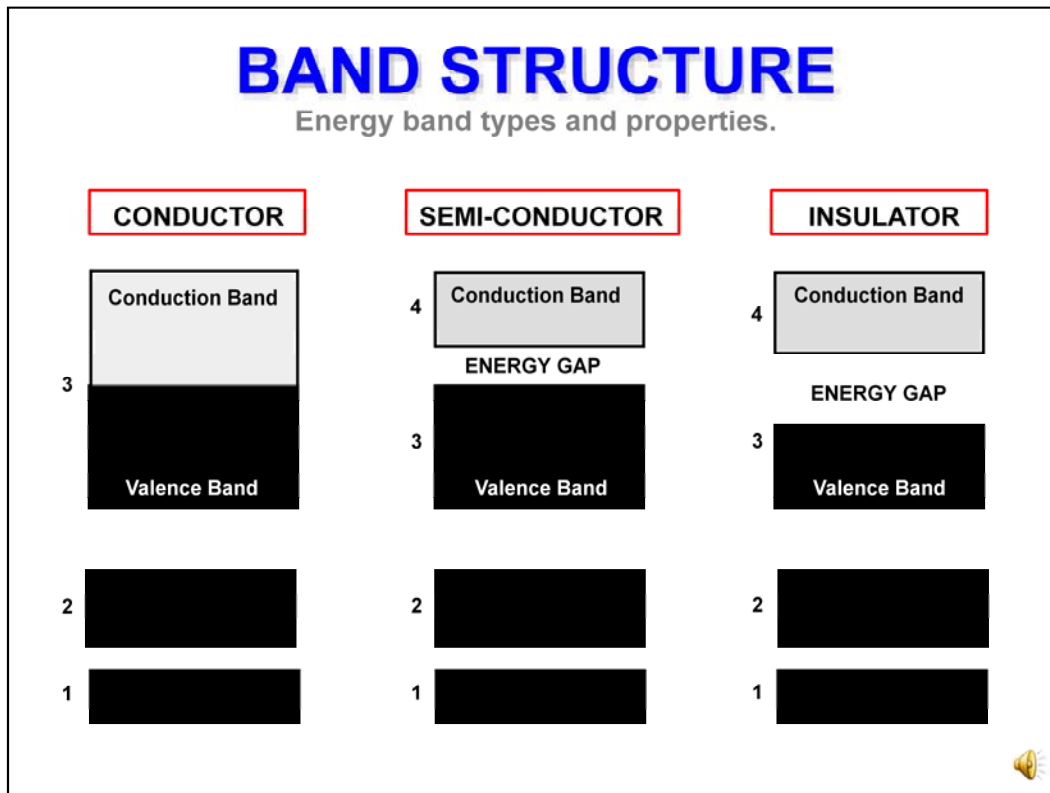


In the simplistic model with which we started, electrons have discrete energy levels. However, as atoms are brought together and bonded, the interactions of the levels create a large number of possible energy levels in the neighborhood of the original level. Instead of having well-separated energy levels, we now have bands of very close energy levels.

Why is this important? Bonding, chemical reactions, and other events involving electrons depend on their abilities to change energy levels. If the levels are far apart then electrons have a very difficult time jumping levels. If they are close together then, electrons can change levels relatively easily.

BAND STRUCTURE

Energy band types and properties.



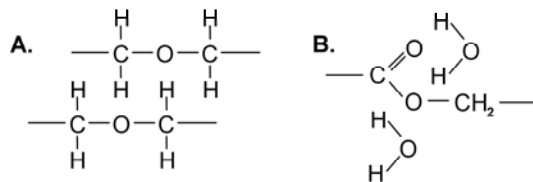
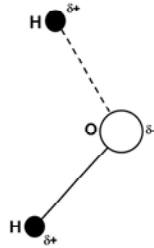
Let's consider just a single event for the present time – that of conducting electricity. For electrons to move through a solid they must jump to a higher energy level. All the electrons in lower energy levels have no energy levels close by that are not already filled by existing electrons and so they can do nothing for all practical purposes. Electrons in the valence band (outer band) may or may not have available levels to which they can jump in energy. You need to look at the band to see what is possible. If the band of energy levels is partially full, then there are most likely lots of close by energy levels. If the band is full, then an electron has to jump to the next band.

[CLICK] CONDUCTORS of electricity have partially filled valence bands. **[CLICK]** INSULATORS have filled valence bands. **[CLICK]** SEMI-CONDUCTORS have filled outer bands but only relatively small gaps to get to the next band. This is called BAND THEORY and is used to explain properties of metals and ceramics. Congratulations you have just successfully completed the hardest content in this course.

The VALENCE BAND is always the outer band containing electrons and may be FULL or PARTIALLY FULL. If it is partially full, there are easy levels for electrons to jump in order to conduct electricity. The valence band is then called the CONDUCTION BAND. If the valence band is full, then electrons must jump to the next band (which is empty) and so that new band is called the conduction band. The big jumps between bands are called ENERGY GAPS.

SECONDARY BONDING

Hydrogen bonding, London dispersion forces, and chelation.



Secondary bonding forces among atoms (intramolecular ones) are significantly weaker than primary bonds (intermolecular ones). Primary bonds typically have strengths of 60-300 kcal/mole while secondary bonds have weak forces of <10 kcal/mole. There are a range of types including hydrogen bonding, London dispersion forces, and others. We will simply focus on 2 types, hydrogen bonding and chelation.

[CLICK] Hydrogen bonding occurs because of local dipoles in hydrogen bonded to other atoms. This is greatest in water. Hydrogen behaves as locally positive and oxygen as locally negative. Hydrogen bonding can occur between complex molecules or between the molecules and their solvents such as water.

CHELATION BONDING

Hydrogen bonding, London dispersion forces, and chelation.



Chelation bonding typically occurs between local dipoles of carboxyls on a covalently-bonded polymer and a divalent or trivalent metal ion among the molecules. The attraction of the locally negative and positive centers is relatively strong – about a third to half of that of a primary bond. This type of bond is used quite often in dentistry to chemically attach dental materials to partly bonded ions along the surfaces of tooth structure. It is often described as a combination of covalent and ionic bonding.

QUICK REVIEW

Review of bonding types.

- Which type of ELEMENT composes most of the periodic table?
METAL
- Which PRIMARY BONDING type is involved with polymer?
COVALENT
- What BONDING CHARACTER is associated with NiTi?
IONIC, COVALENT, but MOSTLY METALLIC.
- How do you characterize a SEMI-CONDUCTOR using band theory?
VALENCE BAND IS FULL, BUT SMALL ENERGY GAP.
- What SECONDARY BONDING type includes ionic and covalent bonding?
CHELATION



Here is a quick review of the concepts from this module.

[CLICK] (1) Which type of ELEMENT composes most of the periodic table?
[CLICK]

[CLICK] (2) Which PRIMARY BONDING type is involved with polymers?
[CLICK]

[CLICK] (3) What bonding character is associated with NiTi?
[CLICK]

[CLICK] (4) How do you characterize a SEMI-CONDUCTOR using band theory?
[CLICK]

[CLICK] (5) What SECONDARY BONDING type includes ionic and covalent bonding?
[CLICK]



THANK YOU



THANK YOU.