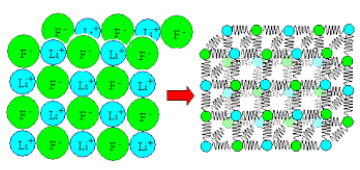


Crystal Binding



Physics
UCF

2/10/2017 Unit #4 Crystal Binding

Outlines

1. Crystals of inert gases
2. Ionic crystals
3. Covalent crystals
4. Metals
5. Hydrogen bonds
6. Atomic radii

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Inside a crystal such as quartz, there consists billion of atoms that bind together to form a solid. The force that binds atoms/ions together is dominated by the electrostatic force. Other forces such as magnetic force or gravitational force are negligible. There are five different types of bonding in solid: (They are all electrostatic in nature)

Types of Bonding
Molecular
Ionic
Covalent
Metallic
Hydrogen-bonded

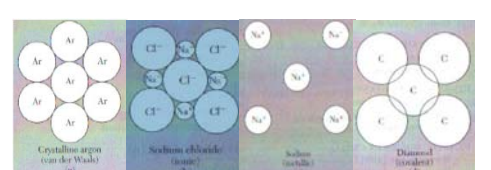
The distinction between different type of bindings is not very rigid. In real crystals, mixed binding is possible.

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First we will define two quantities related to crystal binding.

Cohesive energy is the energy required to change solid into neutral atoms.

Lattice energy is used in ionic crystal and is defined as the energy required to separate ionic crystal's component ions into free ions.

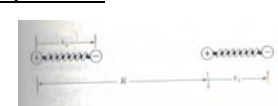


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Crystal of inert gases

For inert gas, the atom has closed outer shell. The interaction between inert gas atoms is very weak. This weak interaction is caused by **Induced dipole interaction**. Historically we call this type of potential **Lennard-Jones potential**, or **6-12 potential**, and the interaction itself, **van der Waals-London interaction**.

1D induced dipole model



$$H_o = \frac{P_1^2}{2m} + \frac{1}{2}Cx_1^2 + \frac{P_2^2}{2m} + \frac{1}{2}Cx_2^2 \quad \text{unperturbed}$$

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The Coulomb interactions between charges is treated as a perturbation to H_o .

$$H_1 = \frac{e^2}{R} + \frac{e^2}{R+x_1-x_2} - \frac{e^2}{R+x_1} - \frac{e^2}{R-x_2}$$

$$= \frac{e^2}{R} \left[1 + \left(1 + \frac{x_1}{R} - \frac{x_2}{R}\right)^{-1} - \left(1 + \frac{x_1}{R}\right)^{-1} - \left(1 - \frac{x_2}{R}\right)^{-1} \right]$$

Since $R \gg x_1, R \gg x_2$ and $(1 + \epsilon)^{-1} = 1 - \epsilon + \epsilon^2 + \dots$

$$H_1 = -\frac{2e^2x_1x_2}{R^3}$$

$$H_{total} = \frac{P_1^2}{2m} + \frac{P_2^2}{2m} + \frac{1}{2}Cx_1^2 + \frac{1}{2}Cx_2^2 - \frac{2e^2x_1x_2}{R^3} \quad \text{Eq. (1)}$$

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The previous equation can be solved by normal mode transformation

$$\text{Let } \begin{aligned} x_1 &\equiv \frac{1}{\sqrt{2}}(x_s + x_a) & x_2 &\equiv \frac{1}{\sqrt{2}}(x_s - x_a) \\ P_1 &\equiv \frac{1}{\sqrt{2}}(P_s + P_a) & P_2 &\equiv \frac{1}{\sqrt{2}}(P_s - P_a) \end{aligned} \quad \text{Eq. (2)}$$

This is a standard method to solve two coupled oscillator problem. It converts the coupled SH oscillator problem in the previous page into a two independent SHO

$$H_{total} = \left[\frac{P_s^2}{2m} + \frac{1}{2} \left(C - \frac{2e^2}{R^3} \right) x_s^2 \right] + \left[\frac{P_a^2}{2m} + \frac{1}{2} \left(C + \frac{2e^2}{R^3} \right) x_a^2 \right]$$

This is two independent simple harmonic oscillators. For SHO, $\omega = \sqrt{(k/m)}$,

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Substitute Eq. (2) into Eq. (1), we obtain

$$\begin{aligned} H_{Total} &= \frac{1}{2} \frac{(P_s^2 + P_a^2 + 2P_s P_a)}{2m} + \frac{1}{2} \frac{(P_s^2 + P_a^2 - 2P_s P_a)}{2m} \\ &+ \frac{1}{2} C(x_s^2 + x_a^2 + 2x_s x_a) + \frac{1}{2} C(x_s^2 + x_a^2 - 2x_s x_a) \\ &- \frac{2e^2 \frac{1}{2} (x_s^2 - x_a^2)}{R^3} \\ H_{Total} &= \frac{P_s^2}{2m} + \frac{P_a^2}{2m} + \frac{1}{2} C(x_s^2 + x_a^2) - \frac{e^2 x_s^2}{R^3} + \frac{e^2 x_a^2}{R^3} \\ &= \frac{P_s^2}{2m} + \frac{1}{2} \left(C - \frac{2e^2}{R^3} \right) x_s^2 + \frac{P_a^2}{2m} + \frac{1}{2} \left(C + \frac{2e^2}{R^3} \right) x_a^2 \end{aligned}$$

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$$\omega_s = \sqrt{\frac{C - \frac{2e^2}{R^3}}{m}} \quad \text{and} \quad \omega_a = \sqrt{\frac{C + \frac{2e^2}{R^3}}{m}}$$

For convenience, we write ω_s as ω_- and ω_a as ω_+ , and we assume $C \gg \frac{2e^2}{R^3}$, and let $\omega_o = \sqrt{C/m}$

$$\rightarrow \omega_{\pm} \cong \omega_o \left[1 \pm \frac{1}{2} \left(\frac{2e^2}{CR^3} \right) - \frac{1}{8} \left(\frac{2e^2}{CR^3} \right)^2 \pm \dots \right]$$

So the zero point energy of the coupled system is lower than the unperturbed system by

$$\Delta U = 2 \cdot \frac{1}{2} \hbar \omega_o - \frac{1}{2} \hbar (\omega_+ + \omega_-) \propto \frac{1}{R^6}$$

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Another approach is to start with dipole interaction, the E field produced by a dipole is given by

$$\vec{E} = \frac{1}{4\pi\epsilon_o r^3} [3(\vec{p} \cdot \hat{r})\hat{r} - \vec{p}] \quad \text{3.104 of Griffiths}$$

This field will produce a dipole at position 2,

$$\vec{p}_2 = \alpha \vec{E} = \frac{\alpha}{R^3} [3(\vec{p} \cdot \hat{R})\hat{R} - \vec{p}_1]$$

The energy of this dipole \vec{p}_2 in electric field \vec{E} is

$$U(R) = -\vec{p}_2 \cdot \vec{E} = -\frac{\alpha}{R^6} [3(\vec{p}_1 \cdot \hat{R})^2 + \vec{p}_1^2]$$

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Repulsive interaction

The repulsive interaction between atoms mainly comes from the Pauli exclusion principle. Namely two electrons can not have all their quantum numbers the same. So when brought together, electrons have to be promoted to a higher energy level. We found that Lennard-Jones potential fit experimental data quite well.

$$U(R) = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right]$$

The ϵ and σ can be calculated from virial coefficient and viscosity data. Other form of repulsive potential can also be used, for example

$$\lambda e^{-\left(\frac{R}{\rho} \right)}$$

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Equilibrium lattice constant

If we ignore the quantum zero point energy and assume $T=0$ then the total energy of the inert gas solid can be expressed

$$U_{total} = \frac{1}{2} N(4\epsilon) \left[\sum_j \left(\frac{\sigma}{p_{ij}R} \right)^{12} - \sum_j \left(\frac{\sigma}{p_{ij}R} \right)^6 \right]$$

Here

N is the total # of atoms in the solid,
 $N/2$ is the # of pair potential,
 The two summations are dimensionalless quantities, they only depend on geometry of the system.

For fcc lattice in 3D

$$\sum_j P_{ij}^{-6} = 14.45392, \quad \sum_j P_{ij}^{-12} = 12.1388$$

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There are two competing interactions in the Lennard-Jones potential.

$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$

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The equilibrium position of the lattice constant will be at the minimum energy position, using eq. on page 12,

$$\frac{dU}{dR_{R_0}} = 0 \Rightarrow 12(12.13) \frac{\sigma^{12}}{R_0^{13}} - 6(14.45) \frac{\sigma^6}{R_0^7} = 0$$

$$\Rightarrow \left(\frac{\sigma}{R_0}\right)^6 = 0.59563 \Rightarrow \frac{\sigma}{R_0} = 0.917$$

$R_0 = 1.09\sigma$

The above result agree well with some observed values.

	Ne	Ar	Kr	Xe
R_0/σ	1.14	1.11	1.10	1.09

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Cohesive energy

Cohesive energy is the energy to break up solid into individual free atoms, (assume fcc structure)

$$U_{tot} = 2N\epsilon \left[12.13 \left(\frac{\sigma}{R}\right)^{12} - 14.45 \left(\frac{\sigma}{R}\right)^6 \right]$$

At equilibrium, $R = R_0$

$$U_{tot}(R_0) = -(2.15)(4N\epsilon)$$

Ionic Crystals

Ionic crystals are made up of positive and negative ions. The electronic configuration of ions in an ionic crystal have closed electronic shell, like inert gas solid but they carry charges. The binding of ionic solid is mostly due to electro-statics force.

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The electron density distribution of NaCl crystal measured by X-ray scattering.

The lattice energy is 7.9 eV. The cohesive energy is $7.9 - 5.14 + 3.61 = 6.4$ eV.

The binding energy of ionic crystals is called the Madelung energy.

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Madelung Energy

In ionic crystal, the attractive potential is the Coulomb potential ($\propto \frac{1}{r}$), so this is a long range interaction.

Let U_{ij} be the interaction energy between ion i and ion j , we define the total interaction energy for ion i as U_i

$$U_i = \sum_j' U_{ij}$$

The summation is over all ions except itself. Each interaction energy can be written as

$$U_{ij} = \lambda e \left(\frac{r_{ij}}{\rho}\right) \pm \frac{q^2}{r_{ij}} \quad (\text{cgs unit})$$

The exponential term represents the short-range repulsive interaction, it only applies to the 1st nearest neighbor.

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In a regular lattice, we introduce quantities, p_{ij}

$$r_{ij} = p_{ij}R$$

Where R is nearest neighbor distance.

$$U_{ij} = \lambda \exp\left(-\frac{R}{\rho}\right) - \frac{q^2}{R} \quad (\text{nearest neighbor})$$

$$\pm \frac{1}{p_{ij}} \frac{q^2}{R} \quad (\text{otherwise})$$

The total energy of the system is

$$U_{total} = NU_i = N \left(z\lambda e \frac{R}{\rho} - \frac{\alpha q^2}{R} \right)$$

Where z is the # of nearest neighbors and

$$\alpha = \sum_j' \frac{(\pm)}{p_{ij}} \equiv \text{Madelung constant}$$

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To find the equilibrium lattice constant,

$$\left. \frac{dU}{dR} \right|_{R_0} = 0 \Rightarrow -\frac{Nz\lambda}{\rho} \exp(-R_0/\rho) + N \frac{\alpha q^2}{R_0^2} = 0$$

$$\Rightarrow R_0^2 \cdot \exp(-R_0/\rho) = \frac{\rho \alpha q^2}{z\lambda}$$

We can solve the above equation to find R_0 .

At $R = R_0$

$$U_{tot}(R_0) = N \left(z\lambda e^{-R_0/\rho} - \frac{\alpha q^2}{R_0} \right)$$

$$= -\frac{N\alpha q^2}{R_0} \left(1 - \frac{\rho}{R_0} \right)$$

The term $-\frac{N\alpha q^2}{R_0}$ is the Madelung energy.

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Both α and $\sum_j' D_{ij}^{-6}$ on page 11 converge, but for different reasons. The α converges because of the alternating signs, while the 6-potential terms converge because of the 6th power. The p_{ij} terms are pure geometric quantities.

Evaluation of the Madelung constant

1-D chain

... - + - + - + - + - + - + - + ...

$$\alpha = 2 \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \frac{1}{6} + \dots \right]$$

$$= 2[\ln 2] = 1.38629$$

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As dimension increases to 2 and 3, the summation becomes more and more difficult. The series will not converge unless the successive terms are carefully chosen from the positive and negative terms, so they nicely cancel each other out.

- + - + - $\alpha(a) = 4 \cdot \frac{1}{2} - 4 \cdot \frac{1}{4} + \frac{1}{\sqrt{2}}$
 = 1.2929

+ - + - + $\alpha(2a) = 4 \cdot 1 - 4 \cdot 1 \cdot \frac{1}{\sqrt{2}} - 4 \cdot \frac{1}{2} \cdot \frac{1}{2}$
 + $8 \cdot \frac{1}{2} \cdot \frac{1}{\sqrt{5}} - 4 \cdot \frac{1}{4} \cdot \frac{1}{\sqrt{8}}$
 = 1.6069

+ - + - + $\alpha(3a) = 1.6135$
 $\alpha(4a) = 1.6145$
 $\alpha(5a) = 1.6149$

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Covalent bonding

Covalent bond is very different from von der Waals bonding or ionic bonding mentioned before. For example, in NaCl (ionic solid), the electronic configuration of the Na⁺ ion is similar to Na atom. Covalent bonding on the other hand, has a large overlap of the electron wave function. In another word, the electronic configuration of individual atom changed significantly to form covalent bond. For example, individual carbon atom has 1S², 2S²2P² configuration, but in diamond, the outer electron configuration is SP³.

Covalent bonding is important, because Si, Ge and diamond all have covalent bonding. Covalent bonded solids usually have high melting temperatures, and the bonding is very directional.

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Here we will use a hydrogen molecular ion as an example. When dealing with covalent bond, we need to use some basic QM. We will start with a quantitative picture first.

(empty) antibonding molecular orbital

combine out-of-phase

1s atomic orbital hydrogen atom A

1s atomic orbital hydrogen atom B

(full) bonding molecular orbital

the hydrogen molecule resulting from the combination of the two hydrogen atoms

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(a) Wave functions combined for σ_{1s}

(b) Bonding probability density

(c) Wave functions combined for σ_{1s}^*

(d) Antibonding probability density

The negative sign has nothing to do with charge, it is the sign of wavefunction.

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We assume the wavefunction of the molecular ion is very close to H atom 1s orbit, where N is normalization constant. Now we define two new wavefunction for the molecule:

$$\psi_{\pm}(\vec{r}) = N[\psi_a(\vec{r}) \pm \psi_b(\vec{r} - \vec{R})] \quad (1)$$

Now apply the normalization condition

$$\int |\psi_{\pm}|^2 d^3r = 1$$

$$\Rightarrow |\psi_{\pm}|^2 = N^2[\psi_a^2(\vec{r}) + \psi_b^2(\vec{r} - \vec{R}) \pm 2\psi_a\psi_b]$$

Let $\int \psi_a\psi_b d^3r = \Delta$ be the overlap integral,

$$\Rightarrow N^2(2 \pm 2\Delta) = 1 \Rightarrow N = \frac{1}{\sqrt{2(1 \pm \Delta)}} \quad (2)$$

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We substitute eq.(2) back into eq.(1):

$$\psi_+(\vec{r}) = \frac{\psi_a + \psi_b}{\sqrt{2(1 + \Delta)}} \quad \psi_-(\vec{r}) = \frac{\psi_a - \psi_b}{\sqrt{2(1 - \Delta)}}$$

The energy of the electron that have these wave-function is given by

$$E_{\pm} = \langle \psi_{\pm} | \mathcal{H} | \psi_{\pm} \rangle$$

Let

$$H_{11} = \langle \psi_a | \mathcal{H} | \psi_a \rangle = H_{22} = \langle \psi_b | \mathcal{H} | \psi_b \rangle$$

$$\beta = \langle \psi_a | \mathcal{H} | \psi_b \rangle = \langle \psi_b | \mathcal{H} | \psi_a \rangle$$

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Bonding State with energy E_+

$$\Rightarrow E_+ = \frac{1}{2(1 + \Delta)} [H_{11} + 2\beta + H_{22}] = \frac{H_{11} + \beta}{1 + \Delta}$$

Anti-bonding state with energy E_-

$$\Rightarrow E_- = \frac{1}{2(1 - \Delta)} [H_{11} - 2\beta + H_{22}] = \frac{H_{11} - \beta}{1 - \Delta}$$

Since both H_{11} and β are negative numbers and $1 \gg \Delta$, so E_+ is a lower energy than E_- which explains the energy levels on page 22.

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Metallic bonding

If you look at periodic table, you notice that two thirds of elements crystallize as metals.

Periodic Table of Elements

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

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Basic properties of metals

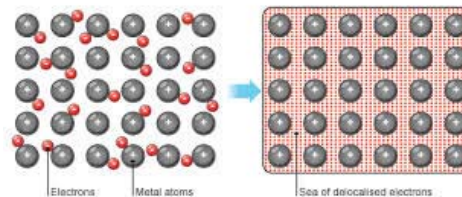
1. Excellent electrical conductivities
2. Excellent thermal conductivities
3. Relatively more ductile than covalent bonding
4. Typical structures are fcc, hcp, or bcc
5. Usually more closely packed
6. Usually has more near neighbors

Drude model was a reasonable model for metals. However it has limitation as mentioned in Unit#1.

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We can think of metal as positive ions embedded in the negative electron sea. The binding usually are weak. Therefore they are usually ductile.

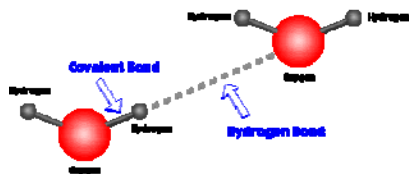


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Hydrogen-bonded crystals

When one hydrogen atom is attracted by two other atoms, we call the bond a hydrogen bond.

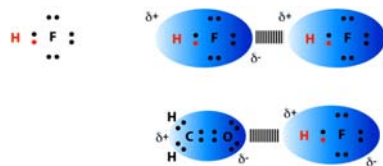


Hydrogen bond is weak, but plays an important role in biology. The bond between hydrogen atom in solid hydrogen is not hydrogen bond.

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Two more examples of hydrogen bond. As can be seen, the hydrogen atom kind of sits between two F atoms, formed covalent bond with one F and hydrogen bond with another F. The hydrogen bond is kind of like ionic bond but much weaker. Hydrogen bond is extremely important in the biological process.



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