Chapter #3:
Crystal Binding

Lecture 2: Types of Crystals based on Atomic Bonds

3.3 Types of Crystals (Atomic Bonds)

1. Ionic Bond
2. Covalent Bond
3. Molecular Bond (Van der Waals Bond)
4. Metallic Bond
5. Hydrogen Bond

✓ In the previous lecture, we introduced the concept of the interatomic potential and showed that atoms form a stable crystal because the total energy has a minimum.
We also defined the cohesive (binding) energy as the energy required to separate atoms from this equilibrium state.

Different physical mechanisms between atoms produce different types of bonds — and therefore different crystal properties.

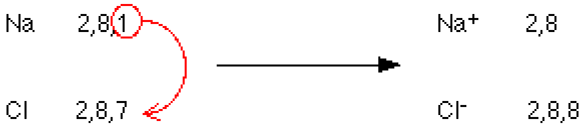
1. Ionic Bond

Ionic bonding arises between positive and negative ions due to the electrostatic interaction between oppositely charged ions (Coulomb attraction).

Example-1: Sodium Chloride (NaCl)

One or more atoms lose electrons and other atoms gain them in order to produce a noble gas electron configuration; the bond thus formed is called an ionic bond.

$$Na \; + \; Cl \longrightarrow Na^+ \; + \; Cl^-$$



Example-2: Lithium Fluoride (LiF)

Ionic Bonding and Cohesive Energy (Alkali Halides)

Strong electrostatic interactions between positive and negative ions provide cohesive energy in alkali-halide crystals (Group I–VII compounds).

Dominant Bonding:

➡ **Ionic bonding**

$Li + F \rightarrow Li^+ + F^-$

1) Ionization of Lithium:
   $Li \rightarrow Li^+ + e^-$
   First ionization energy = 5.39 eV
2) Electron attachment to Fluorine:
   $F + e^- \rightarrow F^-$
   Electron affinity = 3.40 eV

Net energy change:
$\Delta E = 5.39 - 3.40 = 1.99$ eV
Energy should be supplied.
This indicates that ion formation alone requires energy, and the crystal's stability arises from strong Coulomb attraction between Li^+ and F^- ions.

I- Calculating the total interaction energy

The total interaction energy between ion i and ion j is:

$$U = \frac{1}{2}\sum\left[\frac{1}{4\pi\varepsilon_0}\frac{q_iq_j}{r_{ij}} - \frac{A}{r_{ij}^n}\right]$$

- The first term represents electrostatic interaction (long-range Coulomb attraction)

- The second term represents short-range nuclear repulsion (short-range repulsion due to overlapping electron clouds (Pauli exclusion principle)).

- r_i is the position of ion i carrying charge q_i.

- r_j is the position of ion j carrying charge q_j.

- The prime on Σ indicates summation over all ions except i = j.
- $r_{ij} = |\vec{r_i} - \vec{r_j}|$
- The factor 1/2 avoids double-counting.

II- Madelung Energy

Madelung (German physicist: **Erwin Madelung)** realized that an ion does not interact only with its nearest neighbors, but with the entire crystal lattice. The total contribution of all these interactions is summarized by a number called the Madelung constant.

The electrostatic energy between one ion and all other ions in the crystal is called the Madelung energy.

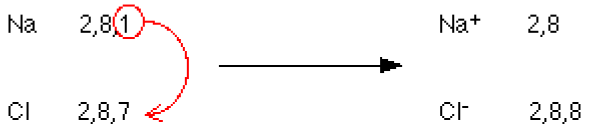
$$U = -\alpha \frac{q^2}{4\pi\varepsilon_0 a}$$

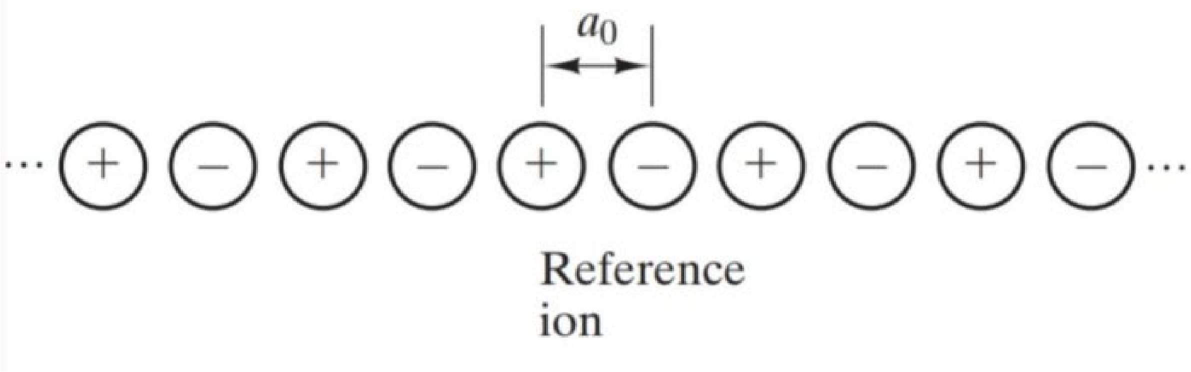
Where:

- α = Madelung constant (depends on structure)
- q = ionic charge
- a = nearest-neighbor distance

The Madelung constant accounts for the interaction with all ions in the crystal lattice.

Example-3: 1D NaCl Crystal





Consider a reference ion:

- Nearest neighbors → opposite charge → **attraction (−)**
- Next neighbors → same charge → **repulsion (+)**
- Next → opposite → **attraction (−)**

Using the Taylor series of the logarithm:

$\ln(1 + x) = \Sigma\ [\ (-1)^{n+1}\ x^n / n\ ]$ for $|x| \leq 1$

The Madelung energy becomes:

For a linear chain:

$$U = -\frac{q^2}{4\pi\varepsilon_0 a_0} 2[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots]$$

For a linear chain:

$$1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots = \ln 2$$

Using the known series:

$$\ln(1 + x) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{x^n}{n} \text{ for } |x| \leq 1,\ x \neq -1$$

Where the + sign is taken for the like charges and the - sign for the unlike charges

$$U = -\frac{q^2}{4\pi\varepsilon_0 a} 2 \ln 2$$

where $\alpha = 2 \ln 2$ is the Madelung constant in 1D.

Why is the Energy Negative?

$U<0$

This means:

- ✔ Attraction dominates
- ✔ The crystal is energetically stable

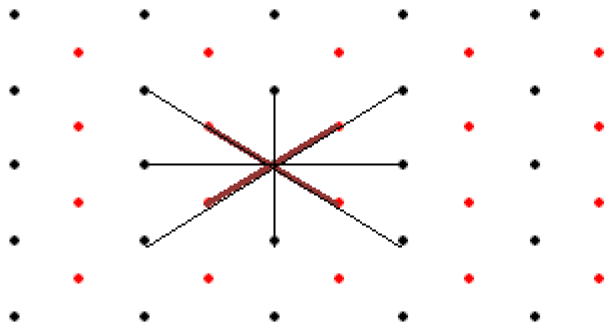
== > The Madelung energy measures how strongly an ion is bound to the entire crystal due to electrostatic interactions.

Key observation:

Larger Madelung constant → stronger binding → more stable structure

Example-4: 2D NaCl Crystal

For a 2D lattice, the electrostatic expansion is:



$^{st}1$ $\quad U_A = \dfrac{q^2}{4\pi\varepsilon_0}[-\dfrac{1}{a/\sqrt{2}}\text{x}4$

2^{nd} $\quad +\dfrac{1}{a}\text{x}4$

3^{rd} $\quad -\dfrac{1}{\sqrt{2}a}\text{x}4$

$+\ldots\ldots\ldots\ldots]$

$U = (q^2 / 4\pi\, \varepsilon_0\, a)\, [\, -4 + (4/\sqrt{2}) - (4/3) + \ldots\,]$

The more terms included, the more accurate the calculated energy.

Example-5: 3D NaCl Crystal

Think about it.

What is the electrostatic energy (Madelung energy) for NaCl Crystal in 3D?

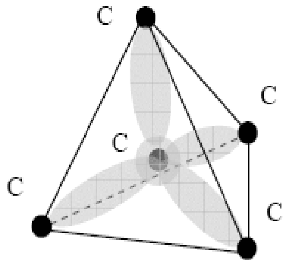
2. Covalent Bond

A **covalent bond** is formed when atoms **share valence electrons** to achieve a stable electronic configuration.

Unlike ionic bonding:

- No charge transfer
- No ions formed
- Electrons are **shared between atoms**

- Occurs mainly between atoms of similar electronegativity (often same type (C, Si, Ge).
- Atoms share electrons to complete outer shells.
- Example: Carbon in diamond forms four bonds.
- Bond strength depends on spin orientation.



◇ Hybridization

In many covalent crystals (e.g., Si, diamond):

sp^3 hybridization

- Orbitals mix to form 4 equivalent bonds
- Bonds point toward the corners of a tetrahedron

👉 This explains the crystal structure.

Please note that:

Hybridization = **Mixing atomic orbitals (like s and p) inside ONE atom**

Example in Silicon:

- 1 s orbital + 3 p orbitals → 4 **sp^3 hybrid orbitals**

Directionality of Covalent Bonds

Covalent bonds are **directional**

This means:

- Bond strength depends on orientation
- Atoms prefer specific angles

Example:

- Tetrahedral angle ≈ 109.5°

Properties of Covalent Crystals

✔ Very strong bonds → high melting point
✔ Directional bonding → rigid structure
✔ Usually poor electrical conductivity
✔ Often **brittle**

Why Are Covalent Crystals Brittle?

Because:

- Bonds are directional
- When structure is deformed → bonds break instead of sliding

Feature	Ionic Bond	Covalent Bond
Mechanism	Charge transfer	Electron sharing
Direction	Non-directional	Directional
Example	NaCl	Si, C
Strength	High	Very high

Exercises

Exercise 1: Determine the dominant type of bonding in the compound GaAs, and explain the reason.

Exercise 2: Discuss the bonding in the graphene structure.