

Module 4 : Solid State Chemistry

Lecture 16 : Lattices and Unit Cells

Objectives

In this Lecture you will learn the following

- Definition of a lattice and a unit cell
- Classification and characterization of different lattices
- Some examples of different lattices.
- Estimates of lattice energies.

16.1 Introduction

Solids may be classified into different types such as crystalline, amorphous, glassy and so on. At low temperatures and high pressures, most substances condense into a solid state. The formation of a solid is a consequence of a variety of intermolecular forces such as ionic, covalent as well as non-covalent (such as van der Waals forces). In this lecture we will classify crystalline solids into various types of lattice structures and give examples of each type. We will also estimate lattice energies of ionic crystals.

The variety and beauty of patterns in crystals is due to the presence of repeating units. The repeating units extend periodically in three dimensional space giving a space filling structure. The structurally repeating unit may be a group of one or more atoms, molecules or ions. If each one of these units is represented by a point, a space filling pattern can be obtained by regularly repeating this unit in three dimensions. This space filling pattern is called a space lattice or a crystal lattice or a Bravais lattice. Bravais showed in 1875 that there can be only 14 distinct lattices in three dimensions. Each point of a Bravais lattice can be associated with a unit cell, which is an imaginary parallelepiped (i.e., a figure with parallel sides) that contains one unit of the translationally repeating pattern.

The fourteen Bravais lattices can be grouped into seven crystal systems by using the symmetry properties of unit cells, as well as by the relations between the sides and angles of the unit cell. Consider two unit cells as shown below.

Figure 16.1 Unit cells. Sides are a, b and c and the angles are α (between b and c in the bc plane), β (in the ac plane, between a and c) and γ (between a and b in the ab plane). (a) cubic unit cell, (b) non-cubic unit cell

In a cubic crystal system (formed from cubic unit cells placed at the lattice points) there are four C_3 axes placed in a tetrahedral arrangement. In Fig 16.1(a) the line joining the points 3 and 5, for example is a C_3 axis. What this means is that if the unit cell/crystal is rotated by 120° , 240° and 360° (three angles, multiples of 120°), we get an arrangement which is indistinguishable from the original arrangement. Having only a C_1 axis is as good as having no symmetry at all because every object has a C_1 axis of symmetry, i.e., if you rotate it with respect to any axis by 360° , you will recover the original arrangement. A triclinic crystal has no symmetry or has only a C_1 symmetry axis

The symmetry elements of the seven crystal systems are given in Table 16.1

Table 16.1 Essential symmetries of the seven crystal systems.

| Sr no | System | Symmetries |
|-------|--------------|--|
| 1 | Cubic | four C_3 axes tetrahedrally arranged |
| 2 | Hexagonal | one C_6 axes |
| 3 | Tetragonal | one C_4 axes |
| 4 | Rhombohedral | one C_3 axes |
| 5 | Orthorhombic | three perpendicular C_2 axes |
| 6 | Monoclinic | one C_2 axes |
| 7 | Triclinic | none ! or only C_1 axes |

The seven cubic systems can also be classified in terms of the relations between their unit cell parameters a, b, c and α , β and γ . These relations are shown in Table 16.2

The parameters characterizing the seven crystal systems are given in Table 16.2

Table 16.2 Seven crystal systems or Bravais unit cells

| Sr no | Type/category cubic | Edge lengths | Internal angles |
|-------|---------------------|-------------------|---|
| 1 | Cubic | $a = b = c$ | $\alpha = \beta = \gamma = 90^\circ$ |
| 2 | Hexagonal | $a = b \neq c$ | $\alpha = \beta = 90^\circ, \gamma = 120^\circ$ |
| 3 | Tetragonal | $a = b \neq c$ | $\alpha = \beta = \gamma = 90^\circ$ |
| 4 | Rhombohedral | $a = b = c$ | $\alpha = \beta = \gamma \neq 90^\circ$ |
| 5 | Orthorhombic | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90^\circ$ |
| 6 | Monoclinic | $a \neq b \neq c$ | $\alpha = \beta = 90^\circ, \neq \gamma$ |
| 7 | Triclinic | $a \neq b \neq c$ | $\alpha \neq \beta \neq \gamma \neq 90^\circ$ |

The cubic unit cell can be further categorized as simple cubic, face centered cubic and body centered cubic. The fourteen Bravais lattices are shown in fig 16.2

Figure 16.2 The 14 Bravais lattices

In the following table (16.3), we list some common substances which are found in the 14 Bravais lattices. How a given substance chooses to be found in a given lattice type is determined by the sizes of the constituent particles and the detailed interactions between them.

Table 16.3 Common substances in seven crystal systems.

| | | |
|---|-------|--|
| 1 | Cubic | Metal like Ni, Ag, Au, Cu, Al; Na ⁺ ions in NaCl lattice [FCC] one form of Fe, V, Cr, Mo, W; CsCl, taking Cs ⁺ and Cl ⁻ together [BCC], - |
|---|-------|--|

| | | | |
|---|--------------|---|----------|
| | | Polonium, Cl^- lattice in a CsCl lattice [simple cubic] | α |
| 2 | Hexagonal | Metallic Be, SiO_2 , Mg_2SiO_4 , corundum, quartz, ruby | |
| 3 | Orthorhombic | Epsom salts, ancylite, sulphur, pyrite, Hg(II)chloride | |
| 4 | Tetragonal | Zircon, Tellurium oxide, PbTiO_3 | |
| 5 | Triclinic | Pentahydrate form of Cu (II) sulphate, serandite, feldspar, n- alkanes, lysozyme crystals grown at pH 4.5 | |
| 6 | Mono clinic | Gypsum, sulphur, jadite, nephrite, $\text{K}_3\text{Fe}(\text{CN})_6$ Hg(II) chloride, potassium chlorate | |
| 7 | Rhombohedral | La cerite, dolomite, calcite, ruby, MgCO_3 | |
| | | | |

16.2 Ionic lattices and Lattice Energies.

We have studied in Module 2 the details regarding intermolecular interactions. In Fig 16.3, the total interaction is shown as a sum of the attractive (Coulombic) and repulsive interactions.

Figure 16.3 Interaction energy between a positive ion and a negative ion as a function of interionic distance r .

The repulsive term is dominated by exchange interactions(see lecture 10). The above form is for a pair of ions. When ion pairs are stable at a distance r_0 , why are lattices formed at all? To see why, consider a one dimensional chain of sodium and chloride ions as shown in fig 16.4.

Figure 16.4 A one dimensional sodium chloride lattice.

Let the central sodium ion be at $r = 0$. The other sodium ions, will be at $\pm 2r_0$, $\pm 4r_0$, $\pm 6r_0$, and so on and the chlorides at $\pm r_0$, $\pm 3r_0$, $\pm 5r_0$ and so on. The total Coulombic interaction for this central ion is

$$U_{\text{ionic}} = -2e^2/r_0 [(1-1/2) + (1/3 - 1/4) + (1/5 - 1/6) + \dots] \quad (16.1)$$

In each parentheses, the first term is the attraction due to Cl^- and the second term is the repulsion due to the next neighbour Na^+ . Note that each term in parentheses is positive and the sum of the series is found to be

$$U_{\text{ionic}} = -2 / r_0; \quad (16.2)$$

This arrangement is more stable than a single pair of Na^+ and Cl^- . This is the reason why lattices of ions or other objects are stabler than pairs, triplets or quartets. In three dimensions, the summation such as eq (16.1) leads to a value of Coulombic energy given by

$$U_{\text{Coulombic}} = - Me^2 / r_0, \quad (16.3)$$

where r_0 is the shortest distance between the + and the - ions and M is called the Madelung constant. The values of M for various lattices is given in Table 16.4.

| Molecule | Lattice | M | M/n _f | Coordination Number |
|----------|------------------|--------|------------------|---------------------|
| NaCl | Rock salt | 1.7476 | 0.8738 | 6 |
| CsCl | Calcium chloride | 1.7627 | 0.8813 | 8 |
| | | | | |

| | | | | |
|------------------|----------|-------|-------|---|
| ZnS | Wurtzite | 1.641 | 0.820 | 4 |
| TiO ₂ | Rutile | 2.408 | 0.803 | 4 |

In the Table n_f is the number of ions per molecular formula unit (e.g., n_f for CaCl₂ is 3) and the coordination number is the average number of neighbours around an ion. Madelung constants are in the range 1.5 to 2.5 and the total Coulomb energy for N ion pairs is given by

$$U_{\text{Coul}} = -NM z_+ z_- e^2 / r_0, \quad (16.4)$$

where z_+ and z_- are the magnitudes of charges on the ions.

In eq (16.4) we have taken into account only the attractive interaction between ions. The repulsive interactions may be expressed as Be^{-r/r_0} (exponential form) or Cr^{-n} (power law repulsion). The values of B or C and n are to be determined for each lattice.

Taking the second form for the repulsive term, the total ionic lattice energy is

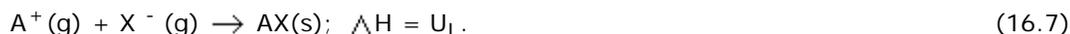
$$U_L = -Me^2 / r + C / r^n \quad (16.5)$$

At equilibrium when $r = r_0$, $dU_L / dr = 0$ and we get

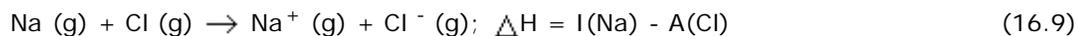
$$C = Me^2 r_0^{n-1} / n \text{ and}$$

$$U_L = - Me^2 / r_0 [1-1/n]. \quad (16.6)$$

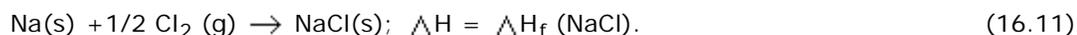
The lattice energy U_L is the energy for the process of forming the solid from the ions:



This is not an easy quantity that can be determined experimentally. We shall now illustrate how to obtain U_L through a thermodynamic cycle (known as the Born Haber cycle) in the case of the NaCl lattice. We start with the normal forms of atoms at room temperature Na(s) and Cl₂(g), obtain their gaseous forms Na(g) and Cl(g), through vaporization [ΔH_v (Na)] and dissociation for Cl₂] ionize the gaseous atoms and then condense the ions into the ionic lattice. These steps can be expressed as in equations (16.8) to (16.11).



The resultant of the above three steps is



Eq (16.11) gives the enthalpy of formation of NaCl. This is identical to the sum of equations (16.8), (16.9) and (16.10) by the first law of thermodynamics (energy and enthalpy changes are independent of path. Summing eq (16.8) to (16.10) we get

$$\Delta H_f (\text{NaCl}) = \Delta H_v (\text{Na}) + 1/2 D (\text{Cl}_2) + I (\text{Na}) - A (\text{Cl}) + U_L \quad (16.12)$$

Here I is the ionization energy of Na ($\text{Na} \rightarrow \text{Na}^+ + e^-$) and $A (\text{Cl})$ is the electron affinity of Cl^- (i.e., the energy change for the process $\text{Cl}^- \rightarrow \text{Cl} + e^-$). By taking all the quantities in kcal/mol units, we have,

$$\Delta H_f (\text{NaCl}) = 24.14 + 28.56 + 118.4 - 83.4 + U_L \quad (16.13)$$

i) Lattice energy for an exponential repulsion form

ii) Calculations of U_L

Heat of formation of NaCl can be easily found from calorimetric measurements. A knowledge of this heat of formation allows us to calculate the lattice energy. We can also calculate the lattice energy by a knowledge of ionic sizes, the value of r_0 and the value of the Madelung constant. If the calculated value of the lattice energy matches with the value calculated from the Born Haber cycle, it gives us an indication that the form of the interionic potentials and the sizes of ions that we have used are quite good. We thus have a method to test our theories of intermolecular forces with experimental results.

16.3 Problems

- 16.1 Identify the four C_3 axes of the cubic unit cell in Fig 16.1 (a). One of them is the line joining the points 3 and 5. How many C_2 axis does a cubic unit cell have? In the same manner (by labeling the corners or additional points by numbers) identify the C_2 axis in monoclinic and orthorhombic lattices, the C_3 axis in a rhombohedral lattice, the C_4 axis in a tetragonal lattice and the C_6 axis in a hexagonal lattice. Can you show that the four C_3 axes in the cubic lattice are in a tetrahedral arrangement relative to each other?
- 16.2 Give an example for each one of the fourteen Bravais Lattices (other than the examples given in Table (16.3))
- 16.3 Parallelograms can be repeated periodically (by repeatedly translating through the edge lengths a and b) to fill up the whole of two dimensional space. Satisfy yourself that a regular pentagon can not be repeated (by using translations and rotations) so as to fill the whole of a 2-dimensional space. Can you fill up a two dimensional space using triangles?
- 16.4 Distinguish between a lattice and a unit cell.
- 16.5 Why do substances exist in different allotropic forms at different temperatures? e.g., monoclinic and rhombohedral forms of sulphur.
- 16.6 For the repulsive potential of the form B / r^n , we have derived the equation for Lattice energy $U_L = -N_A M z_1 z_2 e^2 r_0^{-1} (1 - 1/n)$ where N_A is the Avogadro number, M the Madelung constant and r_0 the closest cation - anion separation. If the repulsive potential has the form Ce^{-r/r_0} , what is the expression for the Lattice energy?
- 16.7 For NaCl , $r_0 = 2.8 \times 10^{-10}$ m. The value of n in the repulsive form B/r^n can be estimated from the close shell configuration of the ions. For close shells like He, $n = 5$; Ne, $n = 7$; Ar, $n = 9$; Kr, $n = 10$; Xe, $n = 11$. If the cations and anions have different closed shells, as in NaCl . The average value of n over the two closed shells is used. If the cations and anions have different closed shells is used. If the average is a fraction, (as in the case of NaCl again), the larger value of n (of the two) can be used. Estimate the lattice energy of NaCl from the Born Lande equation and compare that with the value of U_L obtained from the Born Haber cycle given in Example 1.
- 16.8 The alkaline earth oxides of group II - A (MgO , CaO ,...) have the NaCl crystal structure (ie, two interpenetrating FCC Lattices of anions and cations). Using the value of the nearest neighbour separation (r_0) for the oxides given below (in pm = 10^{-12} m), calculate their lattice energies (using Born Lande eq) MgO (210pm), CaO (240pm), SrO (257pm), BaO (276pm).
- 16.9 Why are the lattice energies of the above oxides greater than those of the corresponding chlorides?

16.10 Using the energy data given below (in kJ/mol) calculate the electron affinity of fluorine

$$H_{\text{dissociation}}(\text{F}_2) = 160, H_f(\text{NaF}) = -571, 1E(\text{Na}) = 494$$

$$H_{\text{vaporization}}(\text{Na}) = 101, U_L(\text{NaF}) = -894$$

16.11 To extend the Born Haber cycle to bivalent oxides MO, where M is divalent metal ion, we need the second ionization potential ($M^+ \rightarrow M^{2+} + e^-$) and the second electron affinity ($O^{2-} \rightarrow O^-$). Calculate the heat of formation of MO (solid) using the following data (in kJ/mol).

$$H_{\text{dissociation}}(\text{O}_2) = 309, H_{\text{vaporization}}(\text{M}) = 309$$

$$\text{First 1.E of M } (M \rightarrow M^+ + e^-) = 900, \text{ second 1.E of M} = 1760$$

$$\text{First electron affinity of O } (O + e^- \rightarrow O^-) = 142$$

$$\text{Second electron affinity of O} = -879$$

$$\text{Madelung constant} = 1.747, \text{ Born exponent } n = 8$$

$$r_0(\text{M-O}) = 1.75 \times 10^{-10} \text{ m}$$

16.12 To calculate the heat of formation of gaseous MO, we can use the Born Haber cycle except that, instead of Lattice energy $M^{2+} + O^{2-} \rightarrow \text{MO}(\text{lattice})$, we have the gas phase energy for $M^{2+} + O^{2-} \rightarrow \text{MO}(\text{g})$. We can use the Born Lande formula for the above process without the factor of Madelung constant. The calculation reveals that MO(solid) is a more stable than MO(gas). can you rationalize this fact? can use the Born Land formation.

Recap

In this Lecture you would have learnt the following

Summary

In this lecture you have been introduced to lattices and unit cells. The fourteen Bravais lattices were characterized in terms of the unit cell parameters a, b, c, α, β and γ (edge lengths and interplanar angles).

The symmetry properties of the unit cells and examples of various space filling lattice systems were given. The lattice energy of ionic crystals was calculated using the interionic forces by the introduction of the Madelung constant. The value of the Madelung constant is a characteristic of each lattice type and arises out of the summation of the Coulombic energies between the infinite sites of the lattice. The Born-Haber cycle was also described which gives an experimental method for determining the lattice energies using the first law of thermodynamics.