Discussion Questions

- Discuss the crystal structures of NaCl, CaF\(_2\), zinc-blende, and Li\(_3\)Bi in relation to the cubic close packing of spheres.
- Describe the features of NiAs structure.
- What are the features of wurtzite structure?

Inorganic Solids

Inorganic solids can be divided into salts, metals, molecular solids, and covalent solids.

Salts are by-products in neutralization reactions of acids and bases, and these ionic solids, are composed of cations and anions. For example, NaCl, BaCl\(_2\), AlCl\(_3\), CsI, FeCl\(_2\), FeCl\(_3\), PtCl\(_2\), CuSO\(_4\), AgNO\(_3\), NaClO\(_4\), NaClO\(_3\), NaClO\(_2\), Ca(ClO)\(_2\), (NH\(_4\))\(_3\)PO\(_4\), ZrSiO\(_4\), Mg\(_2\)SiO\(_4\) and Be\(_3\)Al\(_2\)Si\(_6\)O\(_{18}\). Some of these salts contain monoatomic ions, and some polyatomic ions.

Binary solids consist of two elements, and they are usually carbides, silicide, nitride, phosphide, arsenide, oxides, sulfide, and halides. These solids are involved in many technological industries. Some of these are ionic compounds, but when the electronegativity differences between the two elements are small, covalent bonds between different atoms are strong.

Metals include elemental metals (such as Cu, Au, K, Fe, Ni, Rh, and Pt) and alloys. Alloys are composed of two or more elements. They are produced by melting the mixture of ingredients. Some alloys such as brass (copper zinc) and bronze (copper tin) were used in ancient times, because they were harder than copper. Today, steel, magnesium, aluminium, titanium, and zirconium alloys are very important in new technology, because of their high strength to weight ratio.

Molecular solids include those of non-metals such as I\(_2\), P\(_4\), S\(_8\), As, Se, CaC\(_2\) and solids of O\(_2\), N\(_2\) and ice. Graphite consists of layers packed together via van der Waals forces (intermolecular forces).

Some inorganic solids consist of atoms bonded by strong chemical bonds. These are called covalent solids. Every atom in crystals of diamond, silicon, germanium, and non-metallic tin is bonded to four neighbouring atoms via strong covalent bonds. Elements of this group are typical semiconductors. Every silicon atom in quartz, empirical formula SiO\(_2\), is bonded to four oxygen atoms, and every oxygen atom is bonded to two silicon atoms. Thus, quartz is also a covalent solid.

Dr. S. J. Heyes has made up some impressive and extensive lecture notes on these subjects. He has a total of 4 lectures on these topics, each has about 20 printed pages. His lecture 1 is mainly on the close packing model, which we have covered in Solids and Metals.

Dr. Heyes lecture 2 discusses some common structure types: rock salt, fluorite, zinc-blende (sphalerite), nickel arsenide (NiAs), wurtzite, cadmium iodide (CdI\(_2\), CsCl, and MoS\(_2\). Each of these is a typical model for a number of structures.

Dr. Heyes lecture 3 deals with some theories related to radius ratio. Since we have other topics to cover, we are not going to spend much time on these topics.

Dr. Heyes lecture 4 gives extensive description on rutile and perovskite structures together with other oxides. Structure of
diamond, sphalerite, crystobalite, and silicate minerals are discussed in terms of connectivity (a topological approach to structures.)

These lecture notes covers the topics very well. Some problems are given here to guide your study.

**Crystal structures of NaCl, CaF$_2$, zinc-blende, and Li$_3$Bi**

The cubic closest packing (ccp) or face-centered cubic packing (fcc) of spheres used as models for crystal structures not only enable us to visualize the metal structures, this model correlate the structures of NaCl, CaF$_2$, zinc-blende, and Li$_3$Bi structures very well. Each of these is a structure type common to many other compounds.

In this diagram, the ccp packing is shown in the center. When Cl$^-$ ions form an array of ccp packing, and the octahedral sites occupied by Na$^+$ ions, we have the NaCl structure. Of course, in this case, the sodium ions are smaller than the chloride ions even though they have the same number of electrons. The smaller size is due to a positive charge on the sodium ion.

The radii for Ca$^{2+}$ and F$^-$ ions are 99 and 71 pm respectively. Thus, it is fair to consider the larger Ca$^{2+}$ ions forming a close packed array, with the F$^-$ ions filling all the tetrahedral sites. Since there are twice as many tetrahedral sites, the stoichiometry is CaF$_2$. In this structure, the ratio of anion radius to cation radius is 0.71, and the calcium ions have a coordination number 8 according to the radius ratio rules. Thus, the calcium ions are pushed far apart in terms of packing, reducing their repulsion. Using the sphere packing geometry helps us to recognize the arrangement of the ions in space.

The material used for fission nuclear reactor is a uranium oxide, UO$_2$, and it has the same structure as CaF$_2$. The uranium cations are larger than the oxygen anions.

In an anti-fluorite structure, the anions occupy the Ca$^{2+}$ position whereas the cations occupy the F$^-$ positions. An example of antifluorite structure is Mg$_2$Sn, in which Sn is surrounded by 8 a Mg cube with Sn-Mg distances of 293 pm, and the Mg is surrounded by 4 Sn in a tetrahedral fashion. Heyes mentioned Na$_2$O as having an anti-fluorite structure.

The zinc-blende structure can be viewed as a ccp array of S atoms with Zn occupying half of the tetrahedral sites, resulting in a ZnS stoichiometry. In this compound, there is considerable Zn-S covalent bonding, and the structure is actually
very similar to that of diamond. Yet, since the Zn-S bonding is weak, zinc-blende is much softer. Note however, that the covalent radii of zinc and sulfur are 133 and 103 respectively.

The Li₃Bi structure is very interesting in that it may be seen as a result of occupying all the octahedral and tetrahedral sites by Li in the ccp array of Bi atoms. To call this an ionic solid consisting of Li⁺ and Bi³⁻ ions is somewhat drastic, but Bi is in the same group as N, P, As, and Sb.

Example 1

How many Cl⁻ ions surround a Na⁺ ion and what is the geometric description of the coordination around the Na⁺ ion? The ionic radii for Na⁺ and Cl⁻ are 97 and 181 pm (1 pm = 10⁻¹² m) respectively (from Chemistry by Radel and Navidi). What is the cation to anion radius ratio in this structure? In view of this ratio, do the neighbouring chloride ions touch each other?

SOLUTION

There are six Cl⁻ ions surrounding each Na⁺ ion. Such a coordination forms an octahedron.

The cation to anion radius ratio = 97/181 = 0.536. If the cations fit the octahedral holes precisely, the radius ratio would be 0.414. Thus the chloride ions do not touch each other.

DISCUSSION

In a structure, the sites is occupied by slightly larger ions.

Example 2

How many ions of each are contained in the face-centered unit cell of NaCl? The specific gravity of NaCl is 2.165, what is the cell edge length of the unit cell.

SOLUTION

Recall that the unit cells of ccp contains 4 atoms, it is easy to figure out that the unit cell contains 4 each of sodium and chloride ions. If you really need to count them, the break down is given in Inorganic Chemistry by Swaddle (page 80).

The atomic masses for Na and Cl are 23.0 and 35.5 respectively. Assume the cell edge length to be a, then we have

\[
\frac{4 \times (23.0 + 35.5)}{6.023 \times 10^{23} \times a^3} = 2.165 \text{ g/cm}^3
\]

Solving for a gives

\[
a = 5.64 \times 10^{-8} \text{ cm} = 564 \text{ pm}
\]

DISCUSSION

From Example 1, the radii of sodium and chloride ions were given as 97 and 181 pm. \(2 \times (97 + 181) = 556 \text{ pm}\), in reasonable agreement the a evaluated here.
Example 3

In the CaF2 structure, what is the coordination number of Ca2+ ions? What is the geometric arrangement of fluoride ions around calcium ion?

SOLUTION
The coordination number is 8, with 8 fluoride ions around each calcium ion. The 8 fluoride ions form a cube around the calcium ion.

DISCUSSION
The coordination around fluoride ions is tetrahedral, inferred by the filling of tetrahedral sites.

The features of NiAs structure

When the spheres pack in an ABAB... sequence (the hcp packing), the octahedral sites are directly above one another. The NiAs structure can be viewed as the hcp packing of As anions with the Ni ions occupying the octahedral sites.

In the diagram (from Heyes) above, the As ions are represented by small black balls, whereas the Ni ions by larger blue balls. On the left bottom, a layer of As is marked by black balls labelled by 1/4. These fractions represent their elevation along a direction perpendicular to the screen (or paper if you have printed it). Another layer by is up at 3/4 distance. The six As atoms in the center of that portion form an octahedron enclosing a Ni ion in the center (marked by 1/2). In this diagram, the octahedral coordination of only one Ni atom is complete, however, all Ni atoms are surrounded by octahedrons of As atoms. On the other hand, the six Ni atoms around an As atom form a trigonal prism, not an octahedron.

In the NiAs structure, the Ni atoms do not form an ABAB... or hcp array of close packed structure. In fact, the layers of Ni atoms are directly on top of each other. In contrast, for the NaCl structure, the locations of Na+ and Cl- ions are interchangeable. The coordination around both Na+ and Cl- ions are octahedrons.

In the upper left diagram, only the very center Ni is shown being surrounded by a complete octahedron, but several As atoms are shown with trigonal prisms of As around them. On the lower right diagram, the Ni atoms are shown directly on
top of each other, but the (black) As atoms are not directly on top of each other.

Features of wurtzite structure

The wurtzite and zinc-blende (sphalerite) structures are the same from the connectivity point of view. However, in the wurtzite structure, the S or the Zn atoms form a hcp array, with half of the tetrahedral sites occupied by another kind of atoms. This structure is shown below:

There are two layers of tetrahedral site between layers of host atoms. Only one of the two layers of tetrahedral sites are occupied making the structure appear as double layers when viewed from a direction parallel to these layers. The same is true for the sphalerite structures. However, in this diagram, it is clearly shown that the third layer is directly on top of the first layer conforming to the ABAB... sequence.

We can represent the ZnS$_{4/2}$ (formulated this way because the four sulfur atoms are shared between two Zn atoms) tetrahedrons as layers of tetrahedrons. Then the structure can be represented by stacking layers of tetrahedrons using a sequence of ABAB.... If the stacking sequence is ABCABC..., then the structure is that of the zinc-blende (sphalerite).

The bottom diagram is a representation using a hexagonal cell. We have not used this type of notation, and please not to worry about it.

Questions

1. How many F$^-$ ions are there per face centered cubic unit cell in the fluorite structure?
2. What is the structure type of FeO?
3. In the structure of NiAs, what is the coordination of As atoms?
4. What is the major difference between the sphalerite and the wurtzite structures?
Solutions

1. **Hint: eight**
   
   **Skill -**
   
   Knowing the structure enables you to figure out some facts.

2. **Hint: NaCl type**
   
   **Skill -**
   
   Predict structure type based on radius ratio.

3. **Hint: Each As is surrounded by a trigonal prism of Ni atoms.**
   
   **Skill -**
   
   Describe the feature of NiAs structure.

4. **Hint: The packing sequence of ABAB... gives the wurtzite structure.**
   
   **Skill -**
   
   Describe the wurtzite structure, using a diagram if required.

Contributors

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)