Skills to Develop

- To construct a model for the tetrahedral and octahedral holes of closest packing.
- To calculate geometric properties of the model.
- Apply these properties to interpret crystal chemistry.

Tetrahedral and Octahedral Sites in Closest Packing

Tetrahedral and octahedral sites in closest packing can be occupied by other atoms or ions in crystal structures of salts and alloys. Thus, recognizing their existence and their geometrical constraints helps the study and interpretation of crystal chemistry. The packing of spheres and the formation of tetrahedral and octahedral sites or holes are shown below.

Whenever you put four (4) spheres together touching each other, you've got a tetrahedral arrangement of spheres. The space in the center is called a tetrahedral site. The octahedral site is formed by six spheres. These sites are also called holes in some literature, and they are shown in the diagrams above.

Example 1

What is the radius of the largest sphere that can be placed in a tetrahedral hole without pushing the spheres apart?

**Suggestion for Solution**

To solve a problem of this type, we need to construct a model for the analysis. The following statement explicitly tells you how to construct such a model.
Use the diagram shown here as a starting point, and construct a tetrahedral arrangement by placing four spheres of radius $R$ at alternate corners of a cube. Once complete, work out the following:

- What is the length of the face diagonal $fd$ of this cube in terms of $R$?
  Since the spheres are in contact at the centre of each cube face, $fd = 2R$.

- What is the length of the edge for such a cube, in terms of $R$?
  Cube edge length $a = \sqrt{2}R$.

- What is the length of the body diagonal $bd$ of the cube in $R$?
  $bd = \sqrt{6}R$.

- Is the center of the cube also the center of the tetrahedral hole?
  Yes, but do you know why?

- Let the radius of the tetrahedral hole be $r$. Express $bd$ in terms of $R$ and $r$.
  If you put a small ball there, it will be in contact with all four spheres. Thus,

  $bd = 2(R + r)$

  $r = \frac{2.45R}{2} - R$

  $= 0.225R$

- What is the radius ratio of tetrahedral holes to the spheres?
  $\frac{r}{R} = 0.225$

Example 2

What is the radius of the largest sphere that can be placed in an octahedral hole without pushing the spheres apart?

Solution

The octahedral hole is located at the center of any four spheres that form a square. If we represent the radius of a ball fitting in the octahedral holes by $r$, and the radius of the sphere as $R$, then we have the relationship:

$r + R = \left(\sqrt{2}\right) \left(2R\right)$

$\frac{r}{R} \leq \sqrt{2} - 1$

$= 0.414$

The implication:

Pure geometric consideration shows that only small balls fit in the tetrahedral holes of packed spheres. However, if the radii of cations are smaller than $0.225R$, the structure of having ions in the tetrahedral site is unstable. The anions may be pushed apart slightly to reduce the repulsion by fitting a cation in the tetrahedral site.
For ionic crystal structure consideration, the cations are usually smaller than anions. Cations fitting into the tetrahedral sites cannot be smaller than 0.225 R. Usually, most ions are slightly larger than 0.225 R, but smaller than 0.414 R. In such cases, the cation coordination is tetrahedral, and a typical structure is \(\ce{ZnS}\), although covalent bonding is also involved in \(\ce{ZnS}\). The animated diagram is a model of \(\ce{ZnS}\) structure.

When the cation radii are greater than or equal to 0.414 R, but less than 0.732 R, the cations occupy the octahedral sites. Sodium chloride is one such structure, and it serves as an important structure type.

If the cations are large such that \(r \geq 0.732\) R, the cation will have a cubic coordination of 8. The structure is typified by \(\ce{CsCl}\).

The above discussion is summarized below:

| \(r/R\) | 0.225 | between | 0.414 | between | 0.732 | <
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<tbody>
<tr>
<td>Coordination &amp; number</td>
<td>tetrahedral 4</td>
<td>octahedral 8</td>
<td>cubic 8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Typical structure</td>
<td>(\ce{ZnS})</td>
<td>(\ce{NaCl})</td>
<td>(\ce{CsCl})</td>
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**Discussion**

What is the radius of the largest sphere that can be placed in an octahedral hole without pushing the spheres apart? (Answer: 0.731)

Example 3

**Is there a structure in which all the tetrahedral sites are occupied by a different type of atoms or ions?**

**Solution**
The outline of a unit cell for \(\ce{PuO2}\) is shown here, and all the tetrahedral sites are occupied by small \(\ce{O^2-}\) ions.
Actually, the crystal structure of $\text{UO}_2$ has the same structure as $\text{PuO}_2$. A common salt $\text{CaF}_2$ also has the same structure, but the fluoride ions are by no means small compared to the calcium ions. However, the $\text{Pu}^{4+}$ and $\text{U}^{4+}$ ions are large compared to the oxygen ions.

**Questions**

1. **In the $\text{NaCl}$ structure, which ion is larger?**

   Hint: The chloride ion is larger.

   **Discussion**
   Usually anions are larger than cations if they have similar electronic configurations. In this case, the $\text{Na}^+$ and $\text{Cl}^-$ ions have electronic configurations of $\text{Ne}$ and $\text{Ar}$ respectively. We already know that $\text{Ar}$ is larger than $\text{Ne}$.

2. **The ionic radii of $\text{Na}^+$ and $\text{Cl}^-$ ions are 91 and 181 pm respectively. Calculate the radii ratio of cation to anions.**

   Hint: $91/181 = 0.5$

   **Discussion**
   Since the ratio of 0.5 is between 0.414 and 0.732, the sodium ion prefers an octahedral coordination.

3. **The ionic radii of $\text{K}^+$ and $\text{I}^-$ ions are 133 and 220 pm respectively. What type of structure should $\text{KI}$ have?**

   Hint: The ratio = $133/220 = 0.605$; the $\text{NaCl}$ structure type prevails.

   **Discussion**
   Structure of $\text{KI}$ is indeed $\text{NaCl}$ type, with $a = 706$ pm. The data agree with the ionic radii of the ions: $706 = 2 (133 + 220)$.

4. **The ionic radii of $\text{Cs}^+$ and $\text{Cl}^-$ ions are 167 and 181 pm respectively. What type of coordination should $\text{CsCl}$ have?**

   Hint: The ratio = $167/181 = 0.923$; $\text{Cs}^+$ ion has cubic coordination.

   **Discussion**
   The $\text{CsCl}$ structure is an important type of structure. The diagram shows a unit cell of the $\text{CsCl}$ structure.

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