

Introduction into defect studies in ceramic materials(I)

Structure, Defects and Physical Properties

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Contents

- **Structure of Ceramic.**

Discuss the idealized structure of crystalline, as the first level in hierarchy of structure to be explored in subsequent part.

Objectives:

1. To develop a systematic understanding of why particular crystal structure form, and how they may be predicted. Well-known ionic structure and their important derivatives are described, with an emphasis on viewing even complex structures from the basis of a few simple structure types.
2. To illustrate important relationships between the atomic arrangements of crystalline and the physical properties of ceramics, using examples with particular technological relevance.

- **Defects in Ceramics.**

Isolated charged defects in crystals are able to interact with one another. In the solid-state analogy, the perfect crystal may be regarded as a neutral medium into which the charged defects are dissolved. There is fruitful similarity between solution-chemical interactions and solid-state defect interactions, which has resulted in the development of the field known as Defect Chemistry, which provides immensely useful tools for understanding the properties of crystals containing point defects.

Close-Packed Lattices

A majority of ceramic compounds crystallize in structures based on close packing of at least one of the atomic constituents.

Two simple close-packed lattices:

Face-centered cubic (FCC) and hexagonal close packed (HCP)

It is generally the larger of the ions (usually the anion) that forms the close-packed structure, with the smaller ion or ions occupying the interstices.

Large ion in ceramics is:

oxygen, halogen, nitrogen, sulfur;

high atomic number cation, such as zirconium, uranium;

cation with the sizes of cation close to anion's in some structure such as perovskite.

Close-Packed Lattices

1. FCC and HCP Lattices

These structures may be quite familiar. I will especially emphasize the location and number density of interstitial sites available to cations.

The fig.1.1 below shows one of the close-packed planes used to form an FCC or HCP lattice.

This layer is called "A" layer. The FCC and HCP lattice are obtained by stacking like layers on top of the first layer.

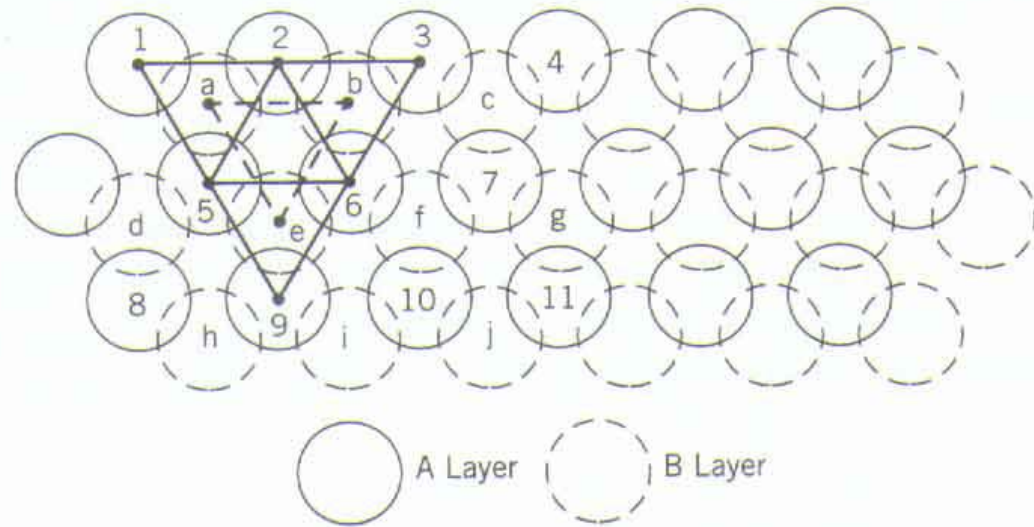


Fig. 1.2 Close-packing of two atomic layers.

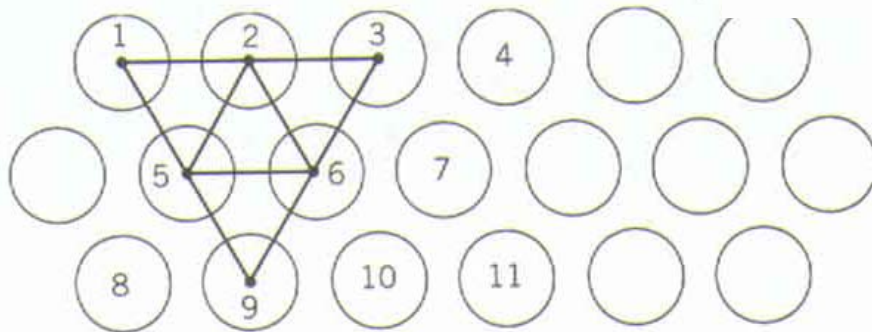


Fig. 1.1 Hexagonal close-packed layer of atoms.

Stacking is achieved by putting the atoms of next layer in the depressions between three atoms in the A layer. Fig.1.2 shows how this B layer of close-packed atoms positioned with respect to the A layer.

Close-Packed Lattices

1. FCC and HCP Lattices

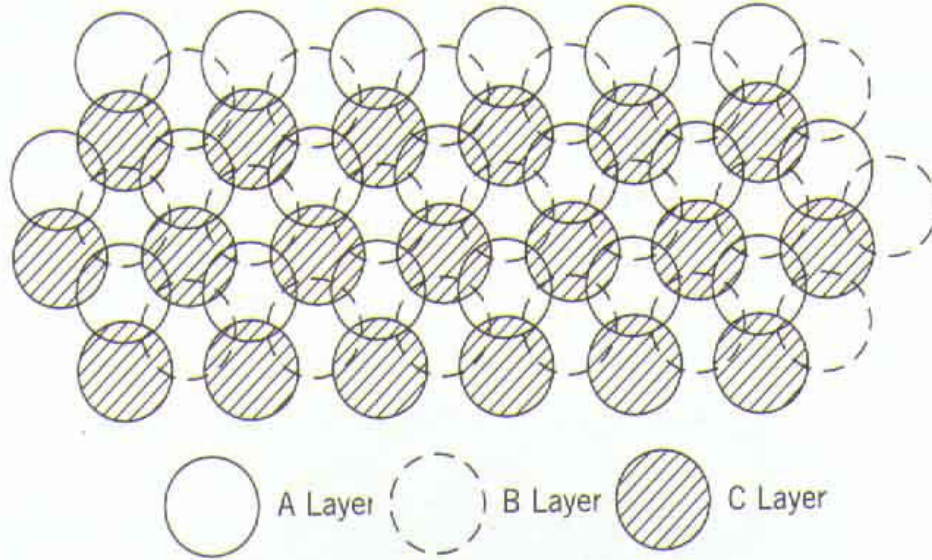


Fig. 1.3 A-B-C close-packing of the FCC structure

out that these positions do not lie directly over atoms in either the A or B layer, and so we denote it as a "C" layer.

The HCP lattice is formed by stacking another A layer directly above the A-B layer sequence shown in Fig. 1.2. Fig. 1.5 shows this arrangement.

Continued stacking of close-packed layers on top of the B-layer generates the FCC and HCP lattice.

The FCC lattice is formed when a third layer is stacked with its atoms in the triangular arrays of atoms in the B layer that have their apex downward in the orientation of Fig. 1.3. It turns

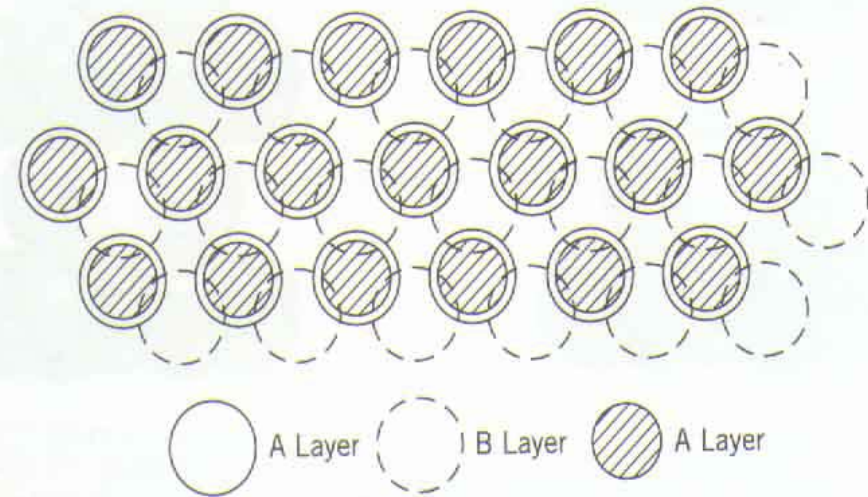


Fig. 1.5 A-B-A close-packing of the HCP structure.

Close-Packed Lattices

2. Location and Density of Interstitial Sites

Sites between close-packed layer.

- Two principle types of interstitial sites, tetrahedral and octahedral, exist between layers of close-packed ions.
- tetrahedral and octahedral are the most common locations for cations in ceramic structures.
- Each site is defined by a local coordination polyhedron formed between any two adjoining close-packed layers.
- These sites do not depend on the configuration of the third layer
- FCC and HCP lattices have the same number density of octahedral and tetrahedral sites.

Close-Packed Lattices

2. Location and Density of Interstitial Sites

Interstitial sites between two close-packed layers

A single octahedral site is defined by the six oxygen atoms labeled 3, 6, 7, and b, c, f; i.e., three of these atoms are in the A layer and the others in the B layer.

There are two different types of tetrahedral sites. One group of tetrahedral sites is defined by having three A-layer atoms and one B-layer atom (1, 2, 5 and a). The other group is defined by having three B-layer atoms and one A-layer atom (e, h, i and 9).

Each of interstitial sites form a hexagonal array.

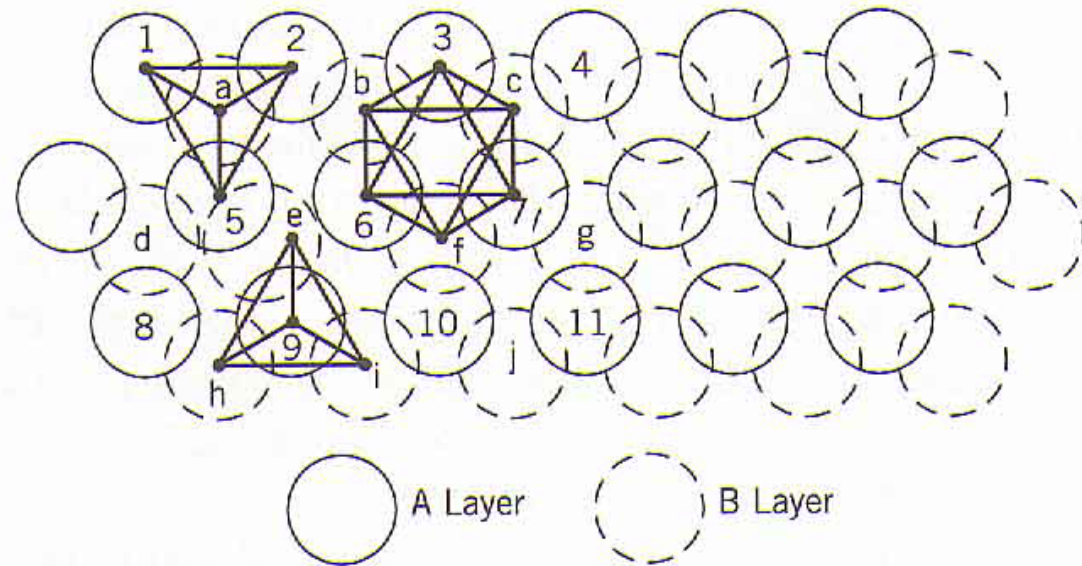


Fig. 1.7 Octahedral (3-6-7-b-c-f) and tetrahedral (1-2-5-a and e-h-i-9) interstices between two close-packed layers of atoms.

Note that the geometric centers and direction of polyhedral site.

Close-Packed Lattices

3. Three-Dimensional Arrangements of Interstitial Sites

Let's now examine the position of these sites with respect to the conventional depiction of the FCC and HCP unit cells. One of the octahedral sites is at the cube center, and one is at halfway along each edge at symmetrically equivalent positions. So, the FCC unit cell contains a total of four octahedral sites. The ratio of octahedral sites to atoms is therefore 1:1.

Fig.1.8b shows the location of the tetrahedral sites in FCC structure. One is inside each corner in the FCC structure, coordinated by the corner atom and the three closest face atoms. There are eight of these sites in each unit cell containing four atoms, the ratio of tetrahedral sites to atoms is 2:1.

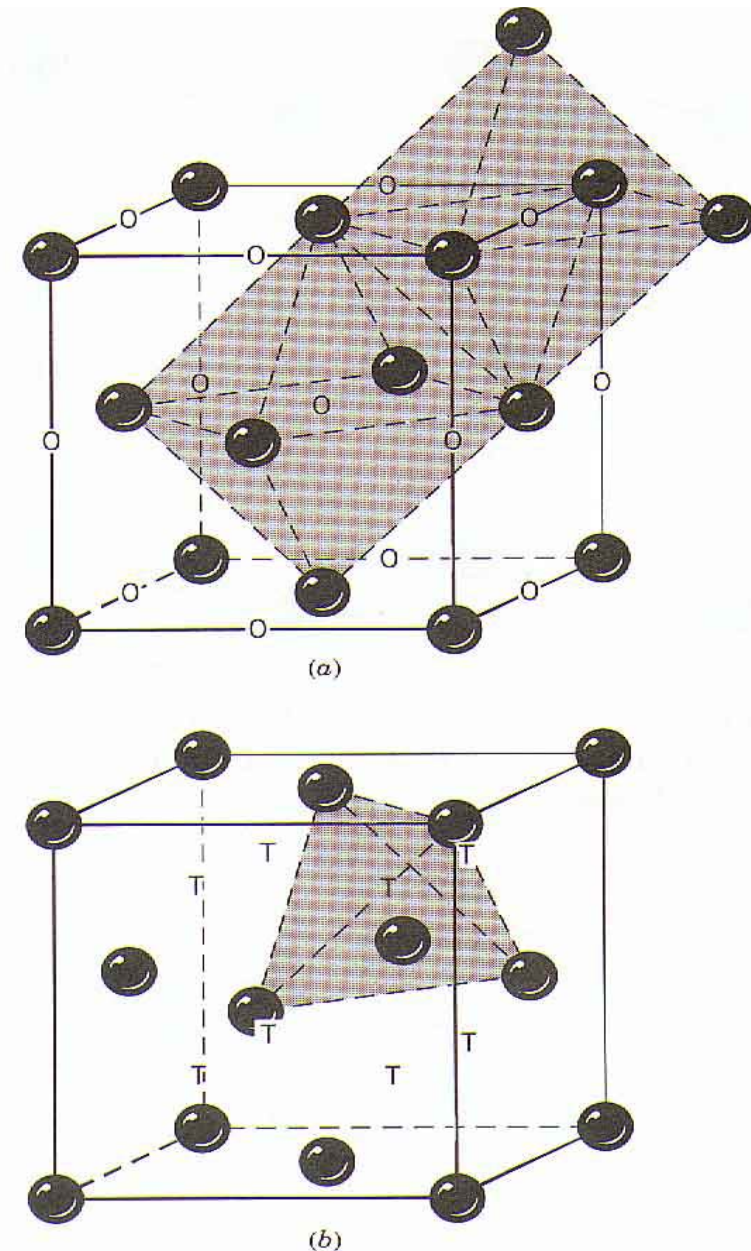


Fig. 1.8 (a) Octahedral sites (O) in FCC. The body-centered site and one edge site are outlined. (b) Tetrahedral sites (T) in FCC. There is one within each corner, and together they form a simple cubic array.

Close-Packed Lattices

2.2. Three-Dimensional Arrangements of Interstitial Sites

We already deduced that the density of octahedral and tetrahedral sites is the same in FCC and HCP. In HCP unit cell, there are two tetrahedral sites contained entirely within the cell above and below the body atom, and two on each vertical edge of the cell. The total number is therefore four tetrahedral sites per unit cell. Since this cell contains just two atoms, the ratio of tetrahedral sites to atoms is 2:1.

There are two octahedral sites per unit cell, situated within the unit cell, so, the ratio of octahedral sites to atoms is 1:1.

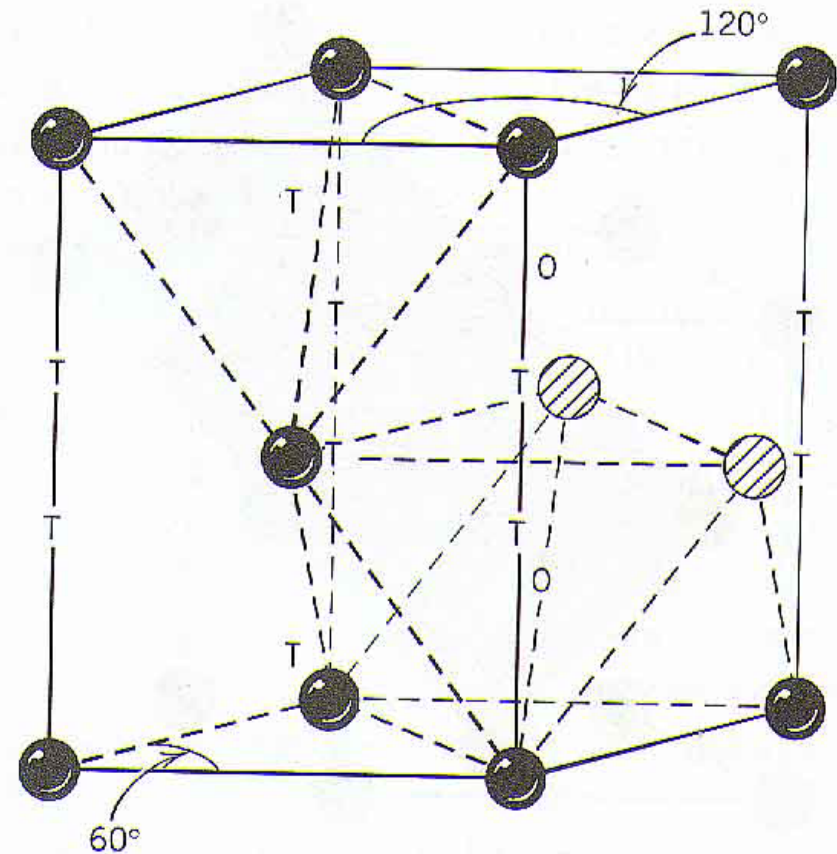


Fig. 1.9 Location of tetrahedral sites (T) and octahedral sites (O) in HCP. Dotted lines show one of each type.

Stability of ionic crystal structures

• The Madelung Constant

Between two ions of charge $Z_i e$ and $Z_j e$, the interaction energy has the form:

$$E = \frac{Z_i Z_j e^2}{4 \pi \epsilon_0 R_{ij}} + \frac{B_{ij}}{R_{ij}^n}$$

There exists an equilibrium separation R_0 at which the total energy is a minimum, which we will denote as E_0 . Consider a crystal composed of N such molecules. The interaction energy of the crystal is obtained by summing the interaction of each of $2N$ ions with every other ion in the crystal. It is:

$$E_c = N \sum_j \left[\frac{Z_i Z_j e^2}{4 \pi \epsilon_0 R_{ij}} + \frac{B_{ij}}{R_{ij}^n} \right]$$

For a compound of formula "MX" in which the cation valence is Z_c and the anion valence is Z_a , upon writing the separation between ions as $R_{ij} = x_{ij} R_0$, where R_0 is the minimum possible separation, we have

$$E_c = N \left[\alpha \frac{Z_c Z_a e^2}{4 \pi \epsilon_0 R_0} + \frac{C}{R_0^n} \right]$$

Stability of ionic crystal structures

- **The Madelung Constant**

In the relation α is the summation of the electrostatic interactions, given by:

$$\alpha = - \sum_i \frac{(z_i / |z_i|)(z_j / |z_j|)}{X_{ij}}$$

α is termed the Madelung Constant, and represents the electrostatic energy of the crystal relative to the energy of the same number of isolated molecules. The sum of short-range repulsive interactions is given by the term C :

$$C = \sum_i \frac{B_{ij}}{X_{ij}^n}$$

The Madelung Constant is a measure of the magnitude of the electrostatic stabilization and for stable crystals has a value greater than unity.

Table 1.1 Madelung Constants for Some Common Ionic Crystal Structures

Structure Type	α
Rocksalt	1.748
Cesium Chloride	1.763
Zincblende	1.638
Wurtzite	1.641
Fluorite	2.519
Corundum	4.040

Stability of ionic crystal structures

- **Pauling's Rules**

The Madelung constant α gives the electrostatic energy of particular structure, but does not by itself allow us to predict structures.

In any structure with a large fraction of ionic bonding character, minimum electrostatic energy is achieved when cation-anion attractions are maximized and like-ion electrostatic repulsion is minimized. That is, cations prefer to be surrounded by the maximum number of anions as first nearest neighbors, and vice versa. At the same time, however, cations prefer to maintain maximum separation from the other cations that are their second nearest neighbors.

Often, the larger of the ions will form a FCC or HCP array, the interstices are occupied by the oppositely charged ion in an orderly way. However, any such arrangement must conform to the need for local charge neutrality, which when extended over the entire crystal maintains the stoichiometry or cation/anion ratio of the compound.

Pauling's rules are a set of five general statements, given as follows in approximate order of decreasing influence, which allow us to understand how known ionic structures satisfy the preceding requirements. Conversely, we may use them to predict the structure in which a compound is likely to crystallize.

Stability of ionic crystal structures

- **Pauling's Rules**

Pauling's rules are based on the geometric stability of packing for ions of different sizes, combined with simple electrostatic stability arguments.

These geometric arguments treat ions as hard spheres, which is clearly an oversimplification. However, while ionic radii do vary from compound to compound, they tend to vary most strongly with the valence state of the ion and the number of nearest-neighbor ions of the opposite charge.

We will consider an ionic radius to be constant for a particular valence state and a nearest-neighbor coordination number. This is a useful approximation supported by empirical observations of the interatomic spacings in a wide variety of oxides and halides.

In general, ion size increases as valence decreases (as electrons are added) and also increases as the number of nearest neighbors increases. These trends can be seen in Table 1.2.

Rule 1

Pauling's first rule states that each cation will be coordinated by a polyhedron of anions, the number of ions¹³ is determined by the relative sizes of the cation and anion.

Table 1.2 Ionic Crystal Radii (nm)

Coordination Number = 6

Ag ¹⁺	Al ³⁺	As ⁵⁺	Au ¹⁺	B ³⁺	Ba ²⁺	Be ²⁺	Bi ³⁺	Bi ⁵⁺	Br ¹⁻	C ⁴⁺	Ca ²⁺	Cd ²⁺
0.115	0.054	0.046	0.137	0.027	0.135	0.045	0.103	0.076	0.196	0.016	0.100	0.095
Ce ⁴⁺	Cl ¹⁻	Co ²⁺	Co ³⁺	Cr ²⁺	Cr ³⁺	Cr ⁴⁺	Cs ¹⁺	Cu ¹⁺	Cu ²⁺	Cu ³⁺	Dy ³⁺	Er ³⁺
0.087	0.181	0.075	0.055	0.080	0.062	0.055	0.167	0.077	0.073	0.054	0.091	0.089
Eu ³⁺	F ¹⁻	Fe ²⁺	Fe ³⁺	Ga ³⁺	Gd ³⁺	Ge ⁴⁺	Hf ⁴⁺	Hg ²⁺	Ho ³⁺	I ¹⁻	In ³⁺	K ¹⁺
0.095	0.133	0.078	0.065	0.062	0.094	0.053	0.071	0.102	0.090	0.220	0.080	0.138
La ³⁺	Li ¹⁺	Mg ²⁺	Mn ²⁺	Mn ⁴⁺	Mo ³⁺	Mo ⁴⁺	Mo ⁶⁺	N ⁵⁺	Na ¹⁺	Nb ⁵⁺	Nd ³⁺	Ni ²⁺
0.103	0.076	0.072	0.083	0.053	0.069	0.065	0.059	0.013	0.102	0.064	0.098	0.069
Ni ³⁺	O ²⁻	OH ⁻	P ⁵⁺	Pb ²⁺	Pb ⁴⁺	Rb ¹⁺	Ru ⁴⁺	S ²⁻	S ⁶⁺	Sb ³⁺	Sb ⁵⁺	Sc ³⁺
0.056	0.140	0.137	0.038	0.119	0.078	0.152	0.062	0.184	0.029	0.076	0.060	0.075
Se ²⁻	Se ⁶⁺	Si ⁴⁺	Sm ³⁺	Sn ⁴⁺	Sr ²⁺	Ta ⁵⁺	Te ²⁻	Te ⁶⁺	Th ⁴⁺	Ti ²⁺	Ti ³⁺	Ti ⁴⁺
0.198	0.042	0.040	0.096	0.069	0.118	0.064	0.221	0.056	0.094	0.086	0.067	0.061
Tl ¹⁺	Tl ³⁺	U ⁴⁺	U ⁵⁺	U ⁶⁺	V ²⁺	V ⁵⁺	W ⁴⁺	W ⁶⁺	Y ³⁺	Yb ³⁺	Zn ²⁺	Zr ⁴⁺
0.150	0.089	0.089	0.076	0.073	0.079	0.054	0.066	0.060	0.090	0.087	0.074	0.072

Coordination Number = 4

Ag ¹⁺	Al ³⁺	As ⁵⁺	B ³⁺	Be ²⁺	C ⁴⁺	Cd ²⁺	Co ²⁺	Cr ⁴⁺	Cu ¹⁺	Cu ²⁺	F ¹⁻	Fe ²⁺
0.100	0.039	0.034	0.011	0.027	0.015	0.078	0.058	0.041	0.060	0.057	0.131	0.063
Fe ³⁺	Ga ³⁺	Ge ⁴⁺	Hg ²⁺	In ³⁺	Li ¹⁺	Mg ²⁺	Mn ²⁺	Mn ⁴⁺	Na ¹⁺	Nb ⁵⁺	Ni ²⁺	O ²⁻
0.049	0.047	0.039	0.096	0.062	0.059	0.057	0.066	0.039	0.099	0.048	0.055	0.138
OH ⁻	P ⁵⁺	Pb ²⁺	S ⁶⁺	Se ⁶⁺	Sn ⁴⁺	Si ⁴⁺	Ti ⁴⁺	V ⁵⁺	W ⁶⁺	Zn ²⁺		
0.135	0.017	0.098	0.012	0.028	0.055	0.026	0.042	0.036	0.042	0.060		

Coordination Number = 8

Bi ³⁺	Ce ⁴⁺	Ca ²⁺	Ba ²⁺	Dy ³⁺	Gd ³⁺	Hf ⁴⁺
0.117	0.097	0.112	0.142	0.103	0.105	0.083
Ho ³⁺	In ³⁺	Na ¹⁺	Nd ³⁺	O ²⁻	Pb ²⁺	Rb ¹⁺
0.102	0.092	0.118	0.111	0.142	0.129	0.161
Sr ²⁺	Th ⁴⁺	U ⁴⁺	Y ³⁺	Zr ⁴⁺		
0.126	0.105	0.100	0.102	0.084		

Coordination Number = 12

Ba ²⁺	Ca ²⁺	La ³⁺	Pb ²⁺
0.161	0.134	0.136	0.149
Sr ²⁺			
0.144			

Source: R. D. Shannon, *Acta Crystallographica*, A32, 751 (1976).

Stability of ionic crystal structures

- **Pauling's Rules**

Rule 1

When anions form a regular polyhedron, there is a single characteristic size for the interstice if the anions are in contact. For instance, the largest sphere that can fit in the tetrahedral and octahedral interstices of the FCC and HCP arrays when all atoms are touching can be calculated to be 0.225 and 0.414 times the radius of the close-packed atom.

A stable configuration is obtained when the cation is as large or slightly larger than this characteristic dimension, as depicted in Fig.1.11.

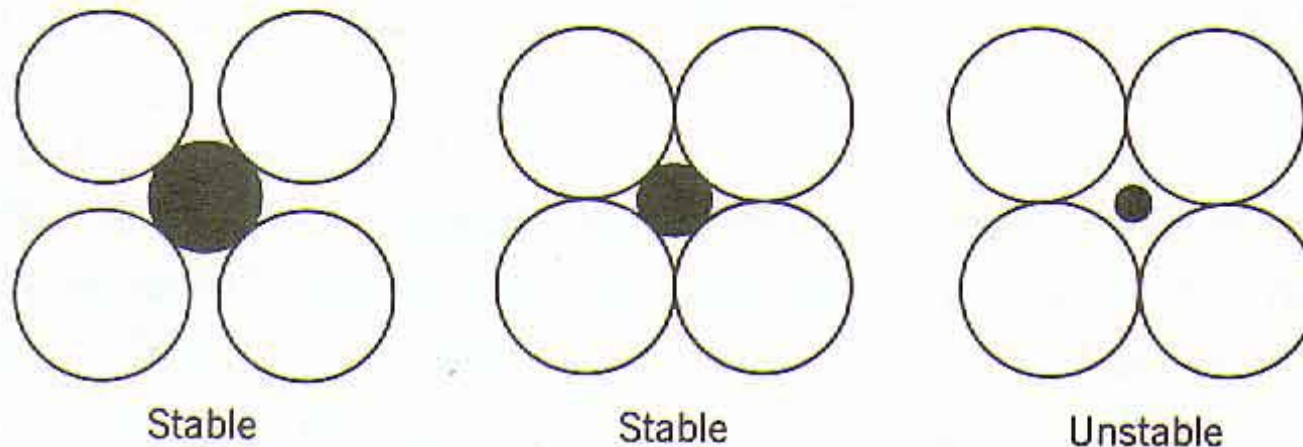


Fig. 1.11 Stable and unstable coordination configurations.

Stability of ionic

Pauling's Rules

Rule 1

We can therefore determine from the cation/anion radius ratio, r_C/r_A , the largest polyhedron for which the cation can completely fill the interstice. This is then the local structural unit most likely to form. These polyhedra and the corresponding limiting radius ratios are shown in Figs.1.12. When the radius ratio is less than this geometrically determined critical value, the next lower coordination becomes preferred. (Remember, that a different effective radius applies when we change coordination number)

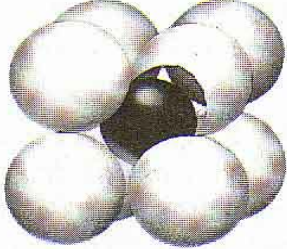
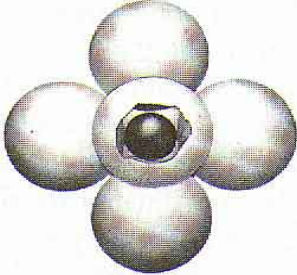
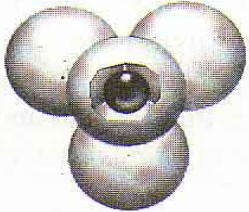
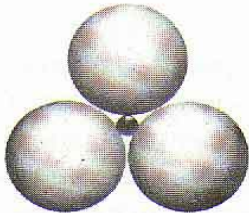

Coordination Number	Disposition of Ions about Central Ion	Range of Cation Radius Ratio Anion Radius	
8	Corners of cube	≥ 0.732	
6	Corners of octahedron	≥ 0.414	
4	Corners of tetrahedron	≥ 0.225	
3	Corners of triangle	≥ 0.155	
2	Linear	≥ 0	

Fig. 1.12 Critical radius ratios for various coordination numbers. The most stable structure is usually the one with the maximum coordination number allowed by the radius ratio.

Stability of ionic crystal structures

- **Pauling's Rules**

Rule 2

The rule ensures that the basic coordination polyhedra are arranged in three dimensions in a way that preserves local charge neutrality. A cation-anion "bond strength" is defined as the valence of the ion divided by its coordination number. Taking the compound MgO as an example, octahedrally coordinated Mg^{2+} will have a bond strength of $2/6$. This is qualitatively a measure of the relative fraction of the $2+$ charge that is being allocated to or shared with each of the coordinating anions. Next, the oxygen anion must be coordinated by sufficient cation to satisfy its $2-$ valence. This is achieved when the sum of the bond strengths reaching the ion equals its valence. This means that in MgO each oxygen atom must be coordinated by six Mg^{2+} ions: $6(2/6)=2$. In multicomponent compounds an anion may be coordinated by more than one type of cation, in which case each cation may have a different bond strength. Still the sum of all bond strength to the anion must equal its valence.

Stability of ionic crystal structures

- **Pauling's Rules**

Rule 3 coordination polyhedra prefer linkages where they share corners rather than edges, and edges rather than faces. This rule is simply based on the fact that cations prefer to maximize their distance from other cations in order to minimize electrostatic repulsion.

Rule 4 This rule states that rule 3 becomes more important when the coordination number is small or the cation valence high. A prime example is SiO_2 , in which SiO_4^{4-} tetrahedra are linked at corners. This also is based on electrostatics; the repulsive energy between a pair of cations is proportional to the charge squared and inversely proportional to their separation.

Rule 5 Simple structures are usually preferred over more complicated arrangements. For example, when several cation of similar size and identical valence are incorporated into a lattice, they frequently occupy the same site but are distributed at random, forming a solid solution or "alloy." As the cations become increasingly dissimilar, a tendency to form an ordered arrangement or "superlattice" may occur. Finally, when the cations are sufficiently different, they may each take on entirely different coordination increasing the complexity of the structure.

Stability of ionic crystal structures

- **Summary**

How can we apply Pauling's rules to deduce the unknown structure of an ionic compound ?

1. If cation is smaller than the anion, as is often the case, we can deduce that FCC or HCP close-packing of the anions will occur.
2. The cation/anion radius ratio helps us to decide which interstitial sites will be occupied; and by far the most common are octahedral and tetrahedral sites.
3. Then, keeping in mind the ratio of interstitial sites to atoms in the FCC and HCP structures, we examine the stoichiometry of the compound. For example, a binary metal oxide MO has a 1:1 cation to anion ratio, so if octahedral coordination (CN=6) is preferable, we can deduce that all of the octahedral sites will be filled since the ratio of octahedral sites to atoms is 1:1. If tetrahedral coordination (CN=4) is preferred, then only one-half of the tetrahedral sites need be filled since the ratio of tetrahedral sites to atoms is 2:1.
4. These sites will tend to be filled in a way that maximizes the cation separation, according to Pauling's third and fourth rules.

Additional Reading

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