CHAPTER 7

The Crystalline Solid State
Solid-state chemistry uses the same principles for bonding as those for molecules. **The differences from molecular bonding come from the magnitude of the “molecules” in the solid state.** In many cases, a macroscopic crystal can reasonably be described as a single molecule, with molecular orbitals extending throughout.
The above description leads to significant differences in the molecular orbitals & behavior of solids compared with those of small molecules.

There are two major classifications of solid materials: *crystals* & *amorphous materials*. 
Crystalline Solids
A crystal is a solid in which the constituent atoms, molecules, or ions are *packed in a regularly ordered, repeating pattern* extending in all three spatial dimensions.

Amorphous Solids
An amorphous solid is a solid in which there is no long-range order of the positions of the atoms.
7-1 Formulas and structures

Crystalline solids have atoms, ions, or molecules packed in regular geometric arrays, with the structural unit called the **unit cell**.

![Diagram of unit cells](image)

**CaF₂**

**ZrO₂**

How many atoms are in one unit cell?
Unit Cell

- The unit cell is a tiny box containing one or more motifs (組態), a spatial arrangement of atoms.
- The unit cell stacked in three-dimensional space describes the bulk arrangement of atoms of the crystal.
- The *lengths* of the edges of a unit cell & the *angles* between them are called the *lattice parameters*. The *symmetry* properties of the crystal are embodied in its *space group* (v.s. point group).
What is Lattice Point?

- **Lattice**: An infinite array of *lattice points* in space, in which each point has identical surroundings to all others.

- **Lattice point**: Each lattice point represents a group of atoms.
Crystal System

- A crystal system (7) is a category of space groups, which characterize symmetry of structures with translational symmetry in three directions.
Seven Crystal Systems

**Cubic**

\[ a = b = c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

**Tetragonal**

\[ a = b \neq c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

**Hexagonal**

\[ a = b \neq c \]
\[ \alpha = \beta = 90^\circ \]
\[ \gamma = 120^\circ \]

The full hexagonal prism is shown, although the unit cell is just the part outlined in solid lines.
FIGURE 7-1 The Seven Crystal Classes and Fourteen Bravais Lattices. The points shown are not necessarily individual atoms, but are included to show the necessary symmetry.
In **body-centered cube (bcc)**, the positions of atoms are frequently described in **lattice points**, expressed as fractions of the unit cell dimensions, i.e., \((0,0,0)\), \((1/2, 1/2, 1/2)\). *The other atoms can be generated by moving these two atoms in each direction in increments of one cell length.*
Cubic: The most basic crystal structure is the simple cube, called the primitive cubic structure, with atoms at the eight corners.

Body-Centered Cubic (bcc): If another sphere is added in the center of the simple cubic structure, the result is called bcc.
How many lattice points are in one unit cell?

Cubic

\[ a = b = c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

Tetragonal

\[ a = b \neq c \]
\[ \alpha = \beta = \gamma = 90^\circ \]
Close Packing

There are two regular lattices that achieve this highest average density. They are called face-centered cubic (fcc) & hexagonal close-packed (hcp), based on their symmetry.

Many minerals have close-packing structures.
Where are the Td & Oh holes?

**ccp (fcc)**

- **A-B-C**

**hcp**

- **A-B-A**

**Td**

- Two close-packed layers, A and B. Octahedral holes can be seen extending through both layers surrounded by three atoms in each layer. Tetrahedral holes are under each atom of the second layer and over each atom of the bottom layer. Each is made up of three atoms from one layer and one from the other.

**Oh**

- A single close-packed layer, A, with the hexagonal packing outlined.
A-B-A

A-B-C
Figure 7.3
Hexagonal Close Packing. (a) The hexagonal prism with the unit cell outlined in bold. (b) Two layers of an hcp unit cell. The parallelogram is the base of the unit cell. The third layer is identical to the first. (c) Location of the atom in the second layer.
FIGURE 7-4 Cubic Close Packing. (a) Two layers of a ccp (or fcc) cell. The atom in the center of the triangle in the first layer and the six atoms connected by the triangle form half the unit cell. The other half, in the third and fourth layers, is identical, but with the direction of the triangle reversed. (b) Two views of the unit cell, with the close-packed layers marked in the first.

Layer 1

Layer 2

(a)
FIGURE 7-5 Tetrahedral and Octahedral Holes in Close-packed Layers. (a) Tetrahedral holes are under each x and at each point where an atom of the first layer appears in the triangle between three atoms in the second layer. (b) An octahedral hole is outlined, surrounded by three atoms in each layer.
Metallic Crystals

Except for the antinides (銅系元素), most metals crystallize in body-centered cubic (bcc), cubic close-packed (ccp), & hexagonal close-packed (hcp) structures, with approximately equal numbers of each type. Changing pressure or temperature will change many metallic crystals.

![Periodic Table of Metal Structures](image)
• **Metal**: metal bond is non-directional (malleable)

• **Non-metal**: covalent bond is directional (brittle)
FIGURE 7-6 The Structure of Diamond. (a) Subdivision of the unit cell, with atoms in alternating smaller cubes. (b) The tetrahedral coordination of carbon is shown for the four interior atoms.
7-1-2 Structures of binary compounds

If the larger ions (usually the anions) are in close-packed structures, ions of the opposite charge occupy these holes, depending primarily on two factors:

1. **The relative sizes of the atoms or ions** \((r_+/r_-)\). Small cations (Td or Oh holes), somewhat larger cations (Oh holes), even larger cations (structural change).

2. **The relative numbers of cations & anions.**
Both in fcc

**FIGURE 7-7** Sodium Chloride and Cesium Chloride Unit Cells.

**Both in simple cubic:**

CsCl $\rightarrow$ NaCl (469 °C)
FIGURE 7-8 ZnS Crystal Structures. (a) Zinc blende. (b, c) Wurtzite.

(a) Zinc blende (the same structure results if the Zn and S positions are reversed)

Both in fcc
(c) One sulfide layer and one zinc layer of wurtzite. The third layer contains sulfide ions, directly above the zinc ions. The fourth layer is zinc ions, directly above the sulfides of the first layer.
FIGURE 7-9 Fluorite and Antifluorite Crystal Structures. (a) Fluorite shown as Ca$^{2+}$ in a cubic close-packed lattice, each surrounded by eight F$^{-}$ in the tetrahedral holes. (b) Fluorite shown as F$^{-}$ in a simple cubic array, with Ca$^{2+}$ in alternate body centers. Solid lines enclose the cubes containing Ca$^{2+}$ ions. If the positive and negative ion positions are reversed, as in Li$_2$O, the structure is known as antifluorite.
FIGURE 7-9 Fluorite and Antifluorite Crystal Structures. (a) Fluorite shown as Ca$^{2+}$ in a cubic close-packed lattice, each surrounded by eight F$^-$ in the tetrahedral holes. (b) Fluorite shown as F$^-$ in a simple cubic array, with Ca$^{2+}$ in alternate body centers. Solid lines enclose the cubes containing Ca$^{2+}$ ions. If the positive and negative ion positions are reversed, as in Li$_2$O, the structure is known as antifluorite.

〇 Calcium  ● Fluoride
**FIGURE 7-10** NiAs Crystal Structure.

**FIGURE 7-11** Rutile (TiO$_2$) Crystal Structure. The figure shows two unit cells of rutile. The heavy line across the middle shows the edge shared between two TiO$_6$ octahedra.
7-1-3 More complex compounds

It is possible to form many compounds by substitution of one ion for another in part of the locations in a lattice. *If the charges & ionic sizes are the same, there may be a wide range of possibilities.*
If the charges or sizes differ, the structure must change, sometimes *balancing charge by leaving vacancies & frequently adjusting the lattice to accommodate larger or smaller ions*. When the anions are complex & nonspherical, the crystal structure must accommodate the shape by distortions, & large cations may require increased coordination numbers.
More Complex Compounds

FIGURE 7-12 Structures of Calcium Carbonate, CaCO₃. (a) Calcite. (b) Two views of aragonite.
7-1-4 Radius ratio rule

- A simple, but at best approximate, approach to predicting coordination numbers uses the radius ratio, $r_+/r_-$ (treating the ions as hard spheres).

For Octahedral Holes

\[
\frac{r_{\text{cation}}}{r_{\text{anion}}} = \begin{cases} 
0.225 & \text{tetrahedral} \\
0.414 & \text{octahedral} \\
0.73 & \text{cubic}
\end{cases}
\]

\[
d = 2R_{\text{anion}} + 2r_{\text{cation}} \\
\text{also } d = \sqrt{(2R_{\text{anion}})^2 + (2R_{\text{anion}})^2}
\]

Therefore: $r_{\text{cation}}/r_{\text{anion}} = 0.414$

- Stable when $r_{\text{cation}}/r_{\text{anion}} < $ ideal
- Stable when $r_{\text{cation}}/r_{\text{anion}} = $ ideal
- Unstable when $r_{\text{cation}}/r_{\text{anion}} > $ ideal
<table>
<thead>
<tr>
<th>Radius Ratio Limiting Values</th>
<th>Coordination Number</th>
<th>Geometry</th>
<th>Ionic Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.414</td>
<td>4</td>
<td>Tetrahedral</td>
<td>ZnS</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Square planar</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Octahedral</td>
<td>NaCl, TiO₂ (rutile)</td>
</tr>
<tr>
<td>0.732</td>
<td>8</td>
<td>Cubic</td>
<td>CsCl, CaF₂ (fluorite)</td>
</tr>
<tr>
<td>1.00</td>
<td>12</td>
<td>Cubooctahedron</td>
<td>No ionic examples, but many metals are 12-coordinate</td>
</tr>
</tbody>
</table>
One study reported that the actual structure matches the predicted structure in about two-thirds of cases, with a higher fraction correct at $CN=8$ & a lower fraction correct at $CN=4$ (actually, ions are not hard spheres).
7-2 Thermodynamics of ionic crystal formation

Born-Haber Cycle

\[
\begin{align*}
\text{Li}(s) & \longrightarrow \text{Li}(g) \quad \Delta H_{\text{sub}} = 161 \text{ kJ/mol} \quad \text{Sublimation} \quad (1) \\
\frac{1}{2} \text{F}_2(g) & \longrightarrow \text{F}(g) \quad \Delta H_{\text{dis}} = 79 \text{ kJ/mol} \quad \text{Dissociation} \quad (2) \\
\text{Li}(g) & \longrightarrow \text{Li}^+(g) + e^- \quad \Delta H_{\text{ion}} = 531 \text{ kJ/mol} \quad \text{Ionization energy} \quad (3) \\
\text{F}(g) + e^- & \longrightarrow \text{F}^-(g) \quad \Delta H_{\text{ion}} = -328 \text{ kJ/mol} \quad \text{Electron affinity} \quad (4) \\
\text{Li}^+(g) + \text{F}^-(g) & \longrightarrow \text{LiF}(s) \quad \Delta H_{\text{xtal}} = -1239 \text{ kJ/mol} \quad \text{Lattice enthalpy} \quad (5) \\
\text{Li}(s) + \frac{1}{2} \text{F}_2(g) & \longrightarrow \text{LiF}(s) \quad \Delta H_{\text{form}} = -796 \text{ kJ/mol} \quad \text{Formation} \quad (6)
\end{align*}
\]
7-2-1 Lattice energy and Madelung constant

\[ \Delta U = \left( \frac{Z_i Z_j}{r_0} \right) \left( \frac{e^2}{4 \pi \varepsilon_0} \right) \]

- \( Z_i Z_j \) = ionic charges in electron units
- \( r_0 \) = distance between ion centers
- \( e \) = electronic charge = 1.6x10\(^{-19}\) C
- \( 4 \pi \varepsilon_0 \) = permittivity of a vacuum = 1.1x10\(^{-10}\) C\(^2\)J\(^{-1}\)m\(^{-1}\)
- \( e^2/4 \pi \varepsilon_0 \) = 2.307x10\(^{-28}\) Jm

When consider all neighbor (attractive) interactions:
\[ \Delta U = \left( N M Z^+ Z^- / r_0 \right) \left( \frac{e^2}{4 \pi \varepsilon_0} \right) \]

\( N \) = Avogadro’s number
\( M \) = Madelung constant

The sum of all these geometric factors carried out until the interactions become infinitesimal is called the Madelung constant.
### TABLE 7-2
Madelung Constants

<table>
<thead>
<tr>
<th>Crystal Structure</th>
<th>Madelung Constant, $M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>1.74756</td>
</tr>
<tr>
<td>CsCl</td>
<td>1.76267</td>
</tr>
<tr>
<td>ZnS (zinc blende)</td>
<td>1.63805</td>
</tr>
<tr>
<td>ZnS (wurtzite)</td>
<td>1.64132</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>2.51939</td>
</tr>
<tr>
<td>TiO$_2$ (rutile)</td>
<td>2.3850</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (corundum)</td>
<td>4.040</td>
</tr>
</tbody>
</table>

**Source:** D. Quane, *J. Chem. Educ.*, 1970, 47, 396, has described this definition and several others, which include all or part of the charge ($Z$) in the constant. Caution is needed when using this constant because of the different possible definitions.
Corrections of Madelung Constant

Repulsion between close neighbors is a more complex function, frequently involving an inverse sixth- to twelfth-power dependence on the distance.

*The Born-Mayer equation:*

\[
U = \frac{\text{NMZ}_+ Z_-}{r_o} \left[ \frac{e^2}{4\pi \varepsilon_o} \right] \left( 1 - \frac{\rho}{r_o} \right)
\]

For simple compounds, \( \rho = 30 \text{ pm} \) works well.
7-2-2 Solubility, ion size (large-large and small-small), and HSAB

\[ \text{AgCl}(s) \rightarrow \text{Ag}^+(g) + \text{Cl}^-(g) \quad \Delta H = 917 \text{ kJ/mol} \quad \text{−Lattice enthalpy} \]
\[ \text{Ag}^+(g) + \text{H}_2\text{O} \rightarrow \text{Ag}^+(aq) \quad \Delta H = -475 \text{ kJ/mol} \quad \text{Solvation} \]
\[ \text{Cl}^-(g) + \text{H}_2\text{O} \rightarrow \text{Cl}^-(aq) \quad \Delta H = -369 \text{ kJ/mol} \quad \text{Solvation} \]

\[ \text{AgCl}(s) + \text{H}_2\text{O} \rightarrow \text{Ag}^+(aq) + \text{Cl}^-(aq) \quad \Delta H = 73 \text{ kJ/mol} \quad \text{Dissolution} \]
Many factors are involved in the thermodynamics of solubility, including ionic size & charge, the hardness or softness of the ions (HSAB), the crystal structure of the solid, & electronic structure of each ions.

Small ions have strong electrostatic attraction for each other & for water molecules, whereas large ions have weaker attraction for each other & for water molecules, but can accommodate more water molecules around each ion.
The above factors work together to make compounds formed of two large ions (soft) or of two small ions (hard) less soluble than compounds containing one large ion and one small ion, particularly when they have the same charge magnitude.
\[ \text{LiI}(s) + \text{CsF}(s) \rightarrow \text{CsI}(s) + \text{LiF}(s) \ (\text{HSAB}) \]

\[ \Delta H = -590 - 1025 - (-745) - (-724) = -146 \text{ kJ/mol} \]

**Only consider the lattice energies, & ignore the hydration energies (all the same).**
When molecular orbitals are formed from two atoms, each type of atomic orbital gives rise to two molecular orbitals. When \( n \) atoms are used, the same approach results in \( n \) molecular orbitals. In the case of solids, \( n \) is very large (similar to Avogadro’s number).
Because the number of atoms (solids) is large, the number of orbitals & energy levels with closely spaced energies is also large. The result is a band of orbitals of similar energy, rather than the discrete energy levels of small molecules. These bands then contain the electrons from the atoms.
FIGURE 7-13 Band Structure of Insulators and Conductors. (a) Insulator. (b) Metal with no voltage applied. (c) Metal with electrons excited by applied voltage.

With partly filled orbitals
In those with *partly filled orbitals*, the valence band-conduction band distinction is *blurred* & very little change is required to move some electrons to higher energy levels within the band. *As a result, they are then free to move throughout the crystal, as are the holes (electron vacancies) left behind in the occupied portion of the band.*
Density of States (DOS)

The concentration of energy levels within bands is described as the density of states, \( N(E) \), actually determined for a small increment of energy \( dE \).

Density of State vs Energy

**FIGURE 7-14** Energy Bands and Density of States. (a) An insulator, with a filled valence band. (b) A metal, with a partly filled valence band and a separate empty band. (c) A metal with overlapping bands caused by similar energies of the initial atomic orbitals.
**Conductor:**

**Metals:** the conductance decreases with increasing temperature, *because the increasing vibrational motion of the atoms interferes with the motion of the electrons* & increases the resistance to electron flow.

High conductance (low resistance) in general, & decreasing conductance with increasing temperature, are characteristics of metals.
Semiconductor: At very low temperatures, they are insulators (Si, Ge), but the conduction band is very near the valence band in energy (near \(2eV\) or less).

At higher temperatures, when a potential is placed across the crystal, a few electrons can jump into the higher conduction band (the electrons can be free to move through the crystal). When the temperature is further raised, more electrons are excited into the upper band & conductance increases (resistance decreases).
**Intrinsic semiconductors**: It means the pure materials have semiconductive properties.

**Doped semiconductors**: They are not semiconductors in the pure state, but they can be modified by adding a small amount of another element with energy levels close to those of the host.
Doping can be thought of as replacing a few atoms of the original element with atoms having either more or fewer electrons. If the added materials has more electrons in the valence shell than the host material (P/Si), the result is an **n-type semiconductor** (n for negative, adding electrons); **vice versa**, a **p-type semiconductor** (Al/Si).
n-type semiconductors (As/Si)

5e, +e
(raising HOMO)

p-type semiconductors (Ga/Si)

3e, +hole
(lowering LUMO)
**Intrinsic Semiconductor**

**n-type semiconductor**

**p-type semiconductor**

**FIGURE 7-15** Semiconductor Bands at 0 K and at Room temperature. (a) Intrinsic semiconductor. (b) n-type semiconductor. (c) p-type semiconductor.
# Band Gaps of Semiconductors

<table>
<thead>
<tr>
<th>Material</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Elemental</strong></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>1.11</td>
</tr>
<tr>
<td>Ge</td>
<td>2.2</td>
</tr>
<tr>
<td><strong>Group 13–15 Compounds</strong></td>
<td></td>
</tr>
<tr>
<td>GaP</td>
<td>2.25</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.42</td>
</tr>
<tr>
<td>InSb</td>
<td>0.17</td>
</tr>
<tr>
<td><strong>Group 12–16 Compounds</strong></td>
<td></td>
</tr>
<tr>
<td>CdS</td>
<td>2.40</td>
</tr>
<tr>
<td>ZnTe</td>
<td>2.26</td>
</tr>
</tbody>
</table>
In an intrinsic semiconductor, the **Fermi level** ($E_F$), the energy at which an electron is equally likely to be in each of the two levels, is near the middle of the band gap.
Addition of an \textit{n-type dopant raises the Fermi level} to an energy near the middle of the band gap between the new band & the conduction band of the host.

Addition of a \textit{p-type dopant lowers the Fermi level} to a point near the middle of the band gap between the new conduction band & the valence band of the host.
Layers of intrinsic, n-type & p-type semiconductors together with insulating materials are used to create the integrated circuits (IC) that are so essential to the electronics industry. Controlling the voltage applied to the junctions between the different layers controls conductance through the device.
**7-3-2 Quantum Dots**

*Quantum confinement effect*: smaller particles (semiconductors) showing a discrete energy level structure rather than a continuum. Nanoparticles showing this effect that have diameters smaller than approximately 10 nm are often called *quantum dots*; because of their size, they behave differently than bulk solids.
The energy-level spacings of QDs are related to their size; experiments have shown that the difference in energy between the VB & CB increases as the particle size gets smaller, & the bulk semi-conductor become more like a single molecule. Consequently, for smaller particles, more energy is needed for excitation & similarly, more energy is emitted as electrons return to the VB.
Relationship between PL energy & particle size

**FIGURE 7.19**
The conductivity of some metals changes abruptly near liquid helium temperature (frequently below 10 K), called \textit{superconductors}.

\textit{Superconductivity}, an effect discovered by Kammerling Onnes in 1911 \textbf{while studying mercury at liquid helium temperature}. 
In this state, the metals offer no resistance to the flow of electrons, & currents started in a loop will continue to flow indefinitely without significant change (superconducting magnets in NMR).

**perfect diamagnetism**

**FIGURE 7-19** Temperature Dependence of Resistivity in Semiconductors, Metals, and Superconductors.
7-4-1 Low-temperature superconducting alloys

*Nb-Ti alloys*, one of the most common superconducting materials, which can be formed into wire & handled with relative ease.
**Type I superconductors (one Tc)**

They have the additional property of expelling all magnetic flux when cooled below the critical temp, $T_c$. This is called the *Meissner effect.* It prevails until the magnetic field reaches a critical value, $H_c$, at which point the applied field destroys the superconductivity. As in the temp dependence, the change between superconducting & normal conduction is abrupt rather than gradual ($T_c = 23.3$ K for Nb$_3$Ge).
Type II superconductors (two $T_{c1} < T_{c2}$)

$T_{c2} < T$: display normal conductance behavior

$T_{c1} < T < T_{c2}$: they allow partial penetration by the magnetic field (a mixture of superconducting & normal regions)

$T < T_{c1}$: superconductors (exclude the magnetic field completely)
A major goal of superconductor research is a material that is *superconducting at higher temp*, to remove the need for liquid helium & nitrogen for cooling.

Images of magnetically levitated trains (磁浮列車) on test tracks in Japan.
7-4-2 The theory of superconductivity (Cooper pairs)

BCS (Bardeen, Cooper, & Schrieffer) theory postulated that electrons travel through the material in pair in spite of their mutual electrostatic repulsion, as long as the two have opposite spins (Cooper pairs).
The formation of these *Cooper pairs* is assisted by small vibrations of the atoms in the lattice; as one electron moves past, the nearest positively charged atoms are drawn very slightly toward it. *This increases the positively charge density, which attracts the second electron.* This effect then continues through the crystal, in a manner somewhat analogous to *a sports crowd doing the waves* (波浪舞).
The attraction between the two electrons is small, & they change partners frequently, but the overall effect is that the lattice helps them on their way rather than interfering, as is the case with metallic conductivity. If the temperature rises above $T_c$, the thermal motion of the atoms is sufficient to overcome the slight attraction between the electrons & the superconductivity ceases.
In 1986, Bednorz and Müller discovered that the ceramic oxide La$_2$CuO$_4$ was superconducting above 30 K when doped with Ba, Se, or Ca to form compounds such as La$_{2-x}$Sr$_x$CuO$_4$. This opened many more possibilities for the use of superconductivity.
In 1987, $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Type II) was discovered to have an even higher $T_c$, 93 K. (MK Wu & CW Chu)

The present record is a critical temperature of 164 K for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8-\delta}$ under pressure. (in 1994, CW Chu)

Difficulties: ceramics are brittle & cannot be drawn into wire, making fabrication a problem.
The structures of all high-temp superconductors are related, most with copper oxide planes & chains, as shown in Figure 21.

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Intercalation of $C_{60}$ with alkali (A) & alkaline-earth metals (A’) can be achieved
(1) by reaction of the metal vapor & solid $C_{60}$ or,
(2) by the heterogeneous reaction of the metal & $C_{60}$ dissolved in hot toluene.

$\Rightarrow A_x C_{60}$ or $A’_x C_{60}$ ($x = 0$ up to 6)

$\Rightarrow$ high chemical reactivity toward oxygen & moisture.
C_{60} (fcc; a=14.1 Å), two vacant tetrahedral sites & one vacant octahedral site per molecule are available for occupancy of small electron donors. Molecular orbital calculations show that t_{1u} & t_{1g} LUMO levels are low-lying, such that C_{60} behave as acceptor.
While increasing reduction with alkaline metal atoms, the conductivity or superconductivity of $A_xC_{60}$ increases to a maximum for $x \sim 3$ & then decreases again. Further reduction yields nonsuperconducting phases.

$T_c$ for $A_3C_{60}$ phase is remarkably high, 18 K in $K_3C_{60}$ up to a maximum of 33 K in $RbCs_2C_{60}$. 
7-6 Imperfections in solids

In practice, all crystals have *imperfections* (缺陷). If a substance crystallizes rapidly, it is likely to have many more imperfections, because crystal growth starts at many sites almost simultaneously. Each small *crystallite* (微晶) grows until it runs into its neighbors; the boundaries between these small crystallites are called *grain boundaries* (晶界).
(I) Vacancies & self-interstitials

Vacancies are missing atoms & are the simplest defect (1/10,000).

Self-interstitials are atoms displaced from their normal locations & appear in one of the interstitials in the lattice.

(II) Substitutions

Substitution of one atom for another is a common phenomenon (solid solution).
(III) **Dislocations (差排)**

**Edge dislocations** result when atoms in one layer do not match up precisely with those of the next. As a result, the distances between the dislocated atoms & atoms in adjacent rows are larger than usual, & the angles between atoms are distorted for a number of rows on either side of the dislocation. A **screw dislocation** is one that has part of one layer shifted a fraction of a cell dimension. This kind of dislocation frequently causes a rapidly growing site during crystal growth & forms a helical path, which leads to the name.
In general, dislocations are undesirable in crystals.

(i) **Mechanically**, they can lead to weakness that can cause fracture.

(ii) **Electrically**, they interfere with conduction of electrons & reduce reliability, reproducibility, & efficiency in semiconductor devices.
7-7 Silicates (矽酸鹽)

Quartz (SiO$_2$) is the most common form of silica & contains helical chains of SiO$_4$ tetrahedra, which are chiral, with clockwise or counterclockwise twist. Each full turn of the helix contains three Si atoms & three oxygen atoms, & six of these helices combine to form the overall hexagonal shape.
FIGURE 7-22 Crystal Structure of β-Quartz. (a) Overall structure, showing silicon atoms only.
(b) Three-dimensional representation with both silicon (larger) and oxygen atoms. There are six triangular units surrounding and forming each hexagonal unit. Each triangular unit is helical, with a counterclockwise twist, three silicon atoms and three oxygen atoms per turn. α-Quartz has a similar, but less regular, structure.
Zeolites (aluminosilicates), containing $(\text{Si}, \text{Al})_n\text{O}_{2n}$ frameworks added to maintain charge balance.
Zeolites (aluminosilicates), containing (Si, Al)$_n$O$_{2n}$ frameworks added to maintain charge balance.


- **General Formula:**
  \[
  [M_{x/n}(Al^{III}O_2)]_x \cdot [Si^{IV}O_2]_y \cdot nH_2O
  \]
  where $n =$ charge of M

- **Na$^+$, Ca$^{2+}$, R$_4$N$^+$ or R$_4$P$^+$, ……etc**
**Miller Indices**

Miller indices, \((h k l)\), are a notation system in crystallography for planes & directions in crystal lattices.
**Miller Indices**: A lattice plane can be designated by selecting an arbitrary *lattice point* as the origin & indicating the intercepts of the plane with the three crystallographic axes in units of a, b, & c. This is termed the *Weiss index* of a plane.

The reciprocal of *Weiss index*, the *Miller Index*, is used to describe planes. The *Miller index* is usually used to denote a set of equally spaced parallel planes, including one through the origin.
Using $hkl$ as a general *Miller index* for a set of planes, $h$ gives the number of equal divisions of the $a$ edge, $k$ the divisions of the $b$ edge, & $l$ the divisions of the $c$ edge of the unit cell. The unit cell volume is divided into $h+k+l$ volumes.
The **Miller index** is usually used to denote a set of *equally spaced parallel planes*, including one through the origin.

Miller indices. The [110] form and others as indicated.