Chapter 2

Crystal Structure

Until the discovery of the quasicrystalline state in 1984, solids were generally classified according to their structure as amorphous and crystalline. In amorphous structures, the range over which translational and orientational correlations in atomic positions decay to zero is finite. Hence the atomic structure is random. The window glass has an amorphous, vitreous, structure. Glass is in fact a supercooled liquid in which the viscosity is too large to permit atomic rearrangement towards a more ordered form. An amorphous solid yet exhibits a considerable degree of short-range order (SRO) in its nearest-neighbor bonds, but not the long-range order (LRO) of a periodic atomic lattice. Namely, crystals are characterized by the presence of both SRO and LRO.

Quasicrystals, also called quasiperiodic crystals, are a relatively new ordering state of condensed matter. For their discovery, Shechtman received the Nobel Prize for Chemistry in 2011. Shechtman and coworkers observed electron diffraction patterns typical of icosahedral point-group symmetry from a rapidly solidified Al₆Mn alloy. The existence of a diffraction pattern indicates LRO in atomic positions, but the presence of the fivefold-symmetry axes, forbidden in crystalline solids, represents the paradox presented by quasicrystals.

This paradox can very simply be transformed to a tiling problem in 2DIM, namely it can be reduced to the question how to completely cover a surface with fivefold-symmetric tiles. M. Gardner proposed several possibilities upon which the so-called Penrose tiles become popular. Penrose tilings have many amazing properties: There are infinitely many Penrose tilings, i.e., there are infinitely many distinct tilings admitted by oblate and prolate rhombi. Not only are Penrose tilings aperiodic, they have no translational symmetry. Any finite region of a Penrose tiling occurs infinitely many times in that tiling. In fact, any finite region that occurs in a Penrose tiling appears infinitely many times in every Penrose tiling. Yet, no part of the tiling repeats itself in the sense of crystallography.

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thick and thin rhombi, as shown in Fig. 2.1, can be obtained by projecting a 5DIM cubic structure onto a 2DIM plane cutting through 5DIM space at an irrational angle.

The translational order in quasicrystals is quasiperiodic rather than periodic, but imposing LRO which makes possible the existence of diffraction patterns. These patterns consist of a set of Bragg peaks which densely fill the reciprocal space without a minimum spacing between peaks due to missing periodicity.

One year after Shechtman et al. introduced icosahedral quasicrystals Bender-sky\textsuperscript{4} discovered decagonal quasicrystals. In this class of quasicrystals the atomic distribution is quasiperiodic within planes, while the planes are stacked periodically along the tenfold-symmetry axis. Hence, they are 2DIM quasicrystals and represent an intermediate state between crystalline and quasicrystalline materials.

Quasicrystals are all binary, ternary, or quaternary alloys whose great majority is Al based. The origin of the existence of stable quasicrystal phases remains in question. No proven explanation clarifies why a material favors crystallographically forbidden rotational symmetries and translational quasiperiodicity when at nearby chemical compositions it forms more conventional crystal structures. Besides their extraordinary structures and symmetries, quasicrystals possess unusual physical properties.

Before we investigate the crystalline state, let us review different types of bonds that hold atoms together in a solid.


2.1 Chemical Bonding

All of the mechanisms which cause bonding between atoms derive from electrical attraction and repulsion. The different strengths and different types of bond are determined by the particular electronic structures of the atoms involved. The weak van-der-Waals bond provides a universal weak attraction between closely spaced atoms and its influence is overridden when the conditions necessary for ionic, covalent, or metallic bonding are also present.

The energy gained by forming a stable bonding arrangement compared to isolated atoms is known as the cohesive energy, and ranges in value from 0.1 eV/atom for solids which is typical only to the weak van-der-Waals bond to 7 eV/atom or more in some covalent and ionic compounds and some metals. The cohesive energy constitutes the reduction in potential energy of the bonded system compared to separate atoms minus the additional kinetic energy which the Heisenberg uncertainty principle tells us must result from localization of the nuclei and outer shell electrons.

In covalent bonding the angular placement of bonds is very important, while in some other types of bonding a premium is placed upon securing the largest possible coordination number (= number of nearest neighbors). Such factors are clearly important in controlling the most favorable 3DIM structure. For some solids, two or more quite different structures would result in nearly the same energy, and a change in temperature or hydrostatic pressure can then provoke a change from one allotropic form of the solid to another.

2.1.1 The van-der-Waals Bond

Van-der-Waals bonding occurs universally between closely spaced atoms, but is important only when the conditions for stronger bonding mechanisms fail. It is a weak bond, with a typical strength of 0.2 eV/atom, and occurs between neutral atoms and between molecules. The weak attractive forces between molecules in a gas lead to an equation of state which represents the properties of real gases.

A neutral atom has zero permanent electric dipole moment, as do many molecules; yet such atoms and molecules are attracted to others by electrical forces. The zero-point motion, which is a consequence of the Heisenberg uncertainty principle, gives any neutral atom a fluctuating dipole moment whose amplitude and orientation vary rapidly. The field induced by a dipole falls off as the cube of the distance. Thus if the nuclei of two atoms are separated by a distance $r$, the instantaneous dipole of each atom creates an instantaneous field proportional to $r^{-3}$ at the other. The potential energy of the coupling between the dipoles which is attractive is then $E_{\text{att}} = -Ar^{-6}$.

$E_{\text{att}}$ would reach 10 eV if $r$ could be as small as 1 Å. However, a spacing this small is impossible because of overlap repulsion. As the interatomic distance decreases, the attractive tendency begins to be offset by a repulsive mechanism when the
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Figure 2.2: Sum of the attractive and repulsive terms give the total potential energy in a stable van-der-Waals bond at an internuclear distance of \( r_o \). From JSB.

electron clouds of the atoms begin to overlap. This can be understood in terms of the Pauli exclusion principle, that two or more electrons may not occupy the same quantum state.

The variation of repulsive energy with interatomic spacing can be simulated in terms of a characteristic length \( \rho \). The total energy can be written as

\[
E = -Ar^{-6} + Be^{-r/\rho}
\]

which is shown in Fig. 2.2. The strength of the bond formed and the equilibrium distance \( r_o \) between the atoms so bonded depend on the magnitudes of the parameters \( A, B, \) and \( \rho \). Since the characteristic length \( \rho \) is small compared to the interatomic spacing, the equilibrium arrangement of minimum \( E \) occurs with the repulsive term making a rather small reduction in the binding energy.

There are no restrictions on bond angles, and solids bound by van-der-Waals forces tend to form in the (close-packed) crystal structures for which an atom has the largest possible number of nearest neighbors. This is the case, for example, in the crystals of the inert gases Ne, Ar, Kr, and Xe, all face-centered-cubic (fcc) structures, in which each atom has twelve nearest neighbors. The rapid decrease of van-der-Waals attraction with distance makes atoms beyond the nearest neighbors of very little importance.

Besides the solid inert gases, crystals of many saturated organic compounds and also for solid \( \text{H}_2, \text{N}_2, \text{O}_2, \text{F}_2, \text{Cl}_2, \text{Br}_2, \) and \( \text{I}_2 \) are examples of solids which are bound solely by van-der-Waals forces. This group of solids have low melting and boiling points. They are electrical insulators and are transparent for visible to far ultraviolet light.
2.1.2 The Covalent Bond

The covalent bond is an electron-pair bond in which two atoms share two electrons. The result of this sharing is that the electron charge density is high in the region between the two atoms. An atom is limited in the number of covalent bonds it can make depending on how much the number of outer electrons differs from a closed-shell configuration, and there is a marked directionality in the bonding. Thus carbon can be involved in four bonds at tetrahedral angles (109.5°), and the characteristic tetrahedral arrangement is seen in crystalline diamond. Other examples of characteristic angles between adjacent covalent bonds are 105° in plastic sulphur and 102.6° in tellurium.

The hydrogen molecule, H₂, serves as a simple example of the covalent bond. Two isolated hydrogen atoms have separate 1s states for their respective electrons. When they are brought together, the interaction between the atoms splits the 1s state into two states of differing energy, as sketched in Fig. 2.3. When the two nuclei are very close together, the total energy is increased for both kinds of states by internuclear electrostatic repulsion; but for the 1s state marked σ_g, which has an symmetric orbital wave-function, the energy is lowered, i.e., there is an attractive tendency, for a moderate spacing.

![Figure 2.3: Variation of energy with r for the neutral hydrogen molecule. The bonding (σ_g) and antibonding (σ_u) orbitals, accommodate two electrons with antiparallel and parallel spins, respectively. g and u represent gerade and ungerade which stand for even and odd. From JSB.](image)

This symmetric σ_g solution requires that the electron charge density $-e\psi^2$ be concentrated in the region between the two nuclei. The requirement of the Pauli principle that total wave functions combine in an antisymmetric manner is satisfied if the σ_g 1s state is occupied by two electrons with antiparallel spins.
The alternative $\sigma_u$ state would have to be occupied by two electrons with parallel spins in order to conform with the Pauli principle, but as observed in Fig. 2.3, this state is an antibonding (repulsive) one at all distances. This is unimportant for $\text{H}_2$, since the $\sigma_g$ state can accommodate the only two electrons in the system and a strong bond results.

Some of the classes of covalently bonded materials are: 1. Most bonds within organic compounds. 2. Bonds between pairs of halogen atoms (and between pairs of atoms of hydrogen, nitrogen, or oxygen) in the solid and fluid forms of these media. 3. Elements of Group VI (such as the spiral chains of tellurium), Group V (such as in the crinkled hexagons of arsenic), and Group IV (such as diamond, Si, Ge, $\alpha$-Sn). 4. Compounds obeying the $8 - N$ rule (such as InSb) when the horizontal separation in the Periodic Table is not too large.

It is often found that valence-bonded solids can crystallize in several different structures for almost the same cohesive energy. The energetically most favored structure can be displaced from its prime position by a change of temperature or pressure, resulting in the situation known as *allotropy* or *polymorphism*. Thus ZnS can exist either in a cubic form (*zinc blende*) or as a hexagonal structure (*wurtzite*). The coordination of nearest neighbors is the same for zinc blende and wurtzite; it is the arrangement of second-nearest neighbors which creates a very slight energy difference between the two structures.

Allotropic conversion is provided by tin, which is stable as a gray semimetal ($\alpha$-Sn) below 17°C, crystallizing in the diamond lattice with four tetrahedrally-located bonds. Temperatures above 17°C (or application of pressure even below that temperature), cause a conversion to a much more dense white metallic form ($\beta$-Sn) with a tetragonal structure in which each atom has six nearest neighbors. Covalently bonded materials are hard and have high melting points. They are electrical insulators or SC’s. They absorb light above a characteristic threshold.

### 2.1.3 Covalent–van-der-Waals Structures

This combination of bonding mechanisms is found in materials such as solid hydrogen, in which each pair of atoms is internally covalently bonded and van-der-Waals bonds create a “molecular crystal”. The same principles apply to most organic solids.

An example of another kind of covalent-residual bonding is provided by tellurium, in which successive atoms in each spiral chain are covalently bonded. The forces between chains are much weaker and are probably little more than van-der-Waals attraction. Consequently, tellurium has a low structural strength and is anisotropic in all its mechanical, thermal, and electronic properties.

Similarly, in graphite (Fig. 1.11) carbon atoms are arranged in hexagons in each layer, so that three of the four outer shell electrons from each atom are used in valence bonds within the layer. The fourth electron is free. The interlayer spacing
is large, with essentially only van-der-Waals attraction. Thus the planes can slide over each other very easily, the property which makes graphite useful as a "solid lubricant." The same considerations are valid in the layered compound MoS$_2$.

### 2.1.4 The Ionic Bond

An ionic crystal is made up of positive and negative ions arranged so that the Coulomb repulsion between ions of the same sign is more than compensated for by the Coulomb attraction of ions of opposite sign. Thus, the main contribution to the binding energy of ionic crystals is electrostatic and called the *Madelung energy*. The alkali halides such as NaCl are typical members of the class of ionic solids; NaCl crystallizes as Na$^+$Cl$^-$. Electron transfer from Na to Cl occurs to such a major extent because the ionization potential $I_e$ of the alkali metal is small (work $eI_e$ must be done to convert Na into the cation Na$^+$ with a closed electronic shell configuration), whereas the electron affinity $E_a$ of the halogen is large. (Energy $E_a$ is provided when Cl receives an electron and becomes the anion Cl$^-$, also with a closed shell configuration.)

![Figure 2.4: The energy of a Na$^+$Cl$^-$ molecule as a function of internuclear spacing $r$. From JSB.](image)

When a Na$^+$ ion and a Cl$^-$ ion approach each other in the absence of any other atoms, the attractive Coulomb energy at internuclear separation $r$ is $E_{\text{Coul}} = -e^2/(4\pi\epsilon_0 r)$ since the closed-shell electronic charge distributions are spherically symmetrical. The approach distance is limited by repulsion when the closed-shell electron clouds of anion and cation overlap, in consequence of the Pauli principle. The energy associated with repulsion varies rapidly with separation, as noted in
connection with van-der-Waals bonding; two approximate ways of describing it are 
\[ E_{\text{rep}} = A r^{-n} \] with \( n \approx 12 \) or \[ E_{\text{rep}} = B e^{-r/\rho} \]. The stable bond length between 
Na\(^+\) and Cl\(^-\) will be the value for which the total energy is a minimum. Figure 2.4 
shows this minimum at around 2.7 Å.

Materials with ionic bonding often dissociate upon heating. They are electrical 
insulators at low temperatures, while ionic conduction is observed at high temper-
atures. They absorb light above an intrinsic photon energy.

### 2.1.5 The Hydrogen Bond

A hydrogen atom, having one electron, can be covalently bonded to only one atom. 
However, the hydrogen atom can involve itself in an additional electrostatic bond 
with a second atom of highly electronegative character, such as fluorine, oxygen, 
or to a smaller extent with nitrogen. This second bond permits a hydrogen bond 
between two atoms or structures. The hydrogen bond is found with strengths 
varying from 0.1 to 0.5 eV per bond.

Hydrogen bonds connect the H\(_2\)O molecules in ordinary ice, a structure similar 
to wurtzite in which there is a spacing of 2.76 Å between the oxygen atoms of 
adjacent molecules. This is much more than twice the “ordinary” O-H spacing of 
0.96 Å for an isolated water molecule. The molecules in ice can flip into a variety 
of arrangements, the equilibrium one depending on pressure and temperature, and 
numerous high pressure allotrophic modifications of ice are known. Materials ex-
hibiting hydrogen bonding are electrical insulators and optically transparent. They 
are easily polarizable.

### 2.1.6 The Metallic Bond

Metallic structures have typically large internuclear spacings and prefer lattice ar-
rangements in which each atom has many nearest neighbors. In many metals only 
one electron per atom is involved in bonding. So, in a metallic solid we have a 
widely spaced array of positively charged ion cores with a superposed electron gas 
to give macroscopic charge neutrality. The wave functions of the electrons compris-
ing this gas overlap strongly and are therefore delocalized. The electrons which are 
used for binding have different energies; the average energy per binding electron 
is smaller than that of an isolated atom. Incomplete inner shells and correlation 
effects within the electron gas also contribute to binding.

In summary, there is large spacing between the atoms and large coordination 
number. Metals are conductors for electricity and heat. They are opaque and highly 
reflecting the visible light.\(^5\)

2.2 Symmetry Operations

A *crystal* is an infinite 3D repetition of identical blocks each with the same orientation. These building blocks, called the *basis*, can be an atom, a molecule or a group of atoms or molecules. The basis is located in the *unit cell*, a 3D parallelepiped, which is translated in three directions to fill all the space. This operation is called *translational symmetry* 

\[ T = p\mathbf{a} + q\mathbf{b} + r\mathbf{c} \]  

with the *translation vectors* \( \mathbf{a}, \mathbf{b}, \mathbf{c} \) that lie along three adjacent edges of the unit cell and integers \( p, q, r \). Translational symmetry means that the local arrangement of atoms at the point \( \mathbf{r} \) must be the same at any other point \( \mathbf{r'} = \mathbf{r} + \mathbf{T} \). The set of operations \( \mathbf{T} \) defines a *Bravais lattice*. The points in a Bravais lattice that are closest to a given point are called its *nearest neighbors*. Because of the periodic nature of a Bravais lattice, each point has the same number of nearest neighbors. This number is a property of the lattice, and is called *coordination number*.

The *primitive basis* is the smallest unit cell that is sufficient to characterize the crystal structure. Figure 2.5 displays the conventional cell and the primitive unit cell for the body-centered cubic (bcc) and fcc Bravais lattices. The volume of the conventional cells are \( 4 \times \) and \( 2 \times \) larger than the corresponding primitive unit cells for the fcc and the bcc lattices, respectively.

![Figure 2.5: The conventional (large) and primitive (shaded) unit cells for the a) face-centered and b) body-centered cubic Bravais lattice. The primitive unit cell is defined by the vectors \( \mathbf{a}, \mathbf{b}, \) and \( \mathbf{c} \). From AM.](image)

The most common choice of a primitive cell with the full symmetry of the Bravais lattice is the *Wigner-Seitz cell*. It is a region of space around a lattice point that is closer to that point than to any other lattice point. The Wigner-Seitz unit cell about a lattice point is constructed by drawing planes as bisectors to lines that connect the lattice point with others and taking the smallest polygon thus generated around
the lattice point. Figure 2.6 shows Wigner-Seitz cells for the bcc and fcc Bravais lattices.

![Wigner-Seitz cells for bcc and fcc lattices](image)

Figure 2.6: The Wigner-Seitz cell for the (a) bcc structure is a truncated octahedron and for the (b) fcc structure a rhombic dodecahedron. From AM.

### 2.2.1 Bulk Structure

A lattice is invariant with respect to:
- Translational symmetry
- Reflection at a plane
- Rotation about an axis by $2\pi/n$ with $n = 1, 2, 3, 4, 6$
- Inversion through a point (= rotation by $180^\circ$ + reflection)
- Glide (= reflection + translation)
- Screw (= rotation + translation).

The possible ways in which the symmetry of the basis of atoms can be related to the symmetry of the lattice result in the point groups. Further, there are some plane groups. In total, there are 230 3DIM space groups or structures. There are 14 3DIM Bravais lattices, illustrated in Fig. 2.7. These can further be grouped into seven crystal systems, including triclinic, monoclinic, orthorhombic, tetragonal, cubic, trigonal, and hexagonal. The conventional unit cells for these seven systems arise as a result of progressing distortions of cubic symmetry.

Any function defined for a crystal, such as the electron density, is bound to be periodic, repeating itself with the same translation vectors as those that span the lattice. Thus, $f(\vec{r} + \vec{T}) = f(\vec{r})$. Such periodic functions lend themselves easily to Fourier transform. Under certain conditions, it becomes more advantageous to deal with the Fourier components of such systems rather dealing with them in real space. Besides the conventional definition of the Fourier transformation, we can consider a plane wave $e^{i\vec{k}\cdot\vec{r}}$. The set of all wave vectors $\vec{k}$ that yield plane waves with the periodicity of a given Bravais lattice is known as its reciprocal lattice. We can then characterize the reciprocal lattice with a set of $\vec{k}$ satisfying $e^{i\vec{k}\cdot\vec{r}} = 1$. It is appropriate to define primitive vectors $\vec{a}^*$, $\vec{b}^*$, and $\vec{c}^*$ for the reciprocal lattice such
that \( \mathbf{a} \cdot \mathbf{a}^* = \mathbf{b} \cdot \mathbf{b}^* = \mathbf{c} \cdot \mathbf{c}^* = 2\pi \) and \( \mathbf{a} \cdot \mathbf{b}^* = \mathbf{a} \cdot \mathbf{c}^* = \mathbf{c} \cdot \mathbf{b}^* = 0 \). The reciprocal lattice is spanned by the reciprocal lattice vector:

\[
\mathbf{G} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*. \tag{2.3}
\]

We can construct the primitive vectors of reciprocal space such that they obey

\[
\mathbf{a}^* = \frac{2\pi \mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}; \quad \mathbf{b}^* = \frac{2\pi \mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}; \quad \mathbf{c}^* = \frac{2\pi \mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \tag{2.4}
\]

The term in the denominator is numerically equal to the volume of the unit cell in real space. For each \( \mathbf{G} \) in Eq. 2.3, the Fourier transform of the periodic function

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**Figure 2.7:** Conventional unit cells for the fourteen possible 3DIM Bravais lattices. From JSB.
can then be written as

\[ f(G) = \frac{1}{V} \int_{V} \text{d}r f(r) e^{iG \cdot r} \]  

(2.5)

where \( V \) is the cell volume.

The crystallographic directions are fictitious lines linking atoms, ions, or molecules. Similarly, the crystallographic planes are fictitious planes linking nodes of a crystal. Some directions and planes have a higher density of nodes. The behavior of the crystal depends on the fact how dense the planes are. In particular, optical properties, adsorption and reactivity, surface tension, and mechanical properties closely depend on the number of atoms on a plane. For all these reasons, it is important to determine the planes for which we first need a notation system.

A family of lattice planes is determined by three integers \( h, k, \) and \( l \), the Miller indices. They are written \((hkl)\), and each index denotes a plane orthogonal to a direction \((h,k,l)\) in the basis of the reciprocal lattice vectors. By convention, negative integers are written with a bar, as in \( \bar{3} \). The integers are written in lowest terms, i.e., their greatest common divisor should be 1. Miller index \((100)\) represents a plane orthogonal to direction \( h \); index \((010)\) represents a plane orthogonal to direction \( k \), and index \((001)\) represents a plane orthogonal to \( l \). The notation \(\{hkl\}\) denotes the set of all planes that are equivalent to \((hkl)\) by the symmetry of the lattice. The corresponding notation \([hkl]\) denotes a direction in the basis of the direct lattice vectors instead of the reciprocal lattice; and similarly, the notation \(\langle hkl \rangle\) denotes the set of all directions that are equivalent to \([hkl]\) by symmetry.

![Figure 2.8: Three lattice planes and their Miller indices in a simple cubic Bravais lattice. From AM.](image)

The direction \([hkl]\) is not generally normal to the \((hkl)\) plane, except in a cubic lattice. For this case, the lattice vectors are orthogonal and of equal length, similar to the reciprocal lattice. Thus, in this common case, the Miller indices \((hkl)\) and \([hkl]\) both simply denote normals/directions in Cartesian coordinates. For cubic crystals with lattice constant \( a \), the spacing \( d \) between adjacent \((hkl)\) lattice planes is:

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]  

(2.6)