

I. INTRODUCTION

A crystal is a solid composed of atoms or other microscopic particles arranged in an orderly repetitive array. That is about the shortest definition of a crystal. It may not be a complete definition, yet it is a true description.

The three general types of solids—amorphous, polycrystalline and single crystal—are distinguished by the size of ordered regions within the materials. Order in amorphous solids is limited to a few molecular distances. In polycrystalline materials, the solid is made-up of grains which are highly ordered crystalline regions of irregular size and orientation. Single crystals have long-range order. Many important properties of materials are found to depend on the structure of crystals and on the electron states within the crystals. At the beginning of the study of crystals it was their external form which was related to the physical properties. In this way only a limited success was achieved. Towards the middle of the last century a deeper understanding developed regarding the correlation of the structure of crystals and mechanical, thermal, electrical and magnetic properties of solids. This is primarily due to the advances in the band theory of electron states and in the theory of bonding in solids. This knowledge has led to the development of newer and better materials for electrical, electronic and structural engineering. The study of crystal physics aims to interpret the macroscopic properties in terms of properties of the microscopic particles of which the solid is composed. The study of the geometric form and other physical properties of crystalline solids by using x-rays, electron beams and neutron beams constitutes the science of crystallography or crystal physics.

II. LATTICE POINTS AND SPACE LATTICE

The atomic arrangement in a crystal is called crystal structure. In a perfect crystal there is a regular arrangement of atoms. This periodicity in the arrangement generally varies in different directions. It is very convenient to imagine points in space about which these atoms are located. Such points in space are called *lattice points* and the totality of such points forms a *crystal lattice* or *space lattice*. If all the atoms at the lattice points are identical, the lattice is called a *Bravais lattice*. The

the three-dimensional space lattice may be defined as a finite array of points in three-dimensions in which every point has identical environment as any other point in the array.

Let us now consider the case of a two-dimensional array of points as shown in Fig. 4.1. It is obvious from the figure that environment about any two points is the same and hence it represents a *space lattice*. This is explained as follows:

We choose any arbitrary point as origin and consider the position vectors \vec{r}_1 and \vec{r}_2 of any two lattice points by joining them to O as shown in Fig. 4.1. If the difference \vec{T} of the two vectors \vec{r}_1 and \vec{r}_2 satisfies the following relation

$$\vec{T} = n_1\vec{a} + n_2\vec{b}$$

where n_1 and n_2 are integers and \vec{a} and \vec{b} are fundamental *translation vectors* characteristic of the array, then the array of points is a two-dimensional lattice.

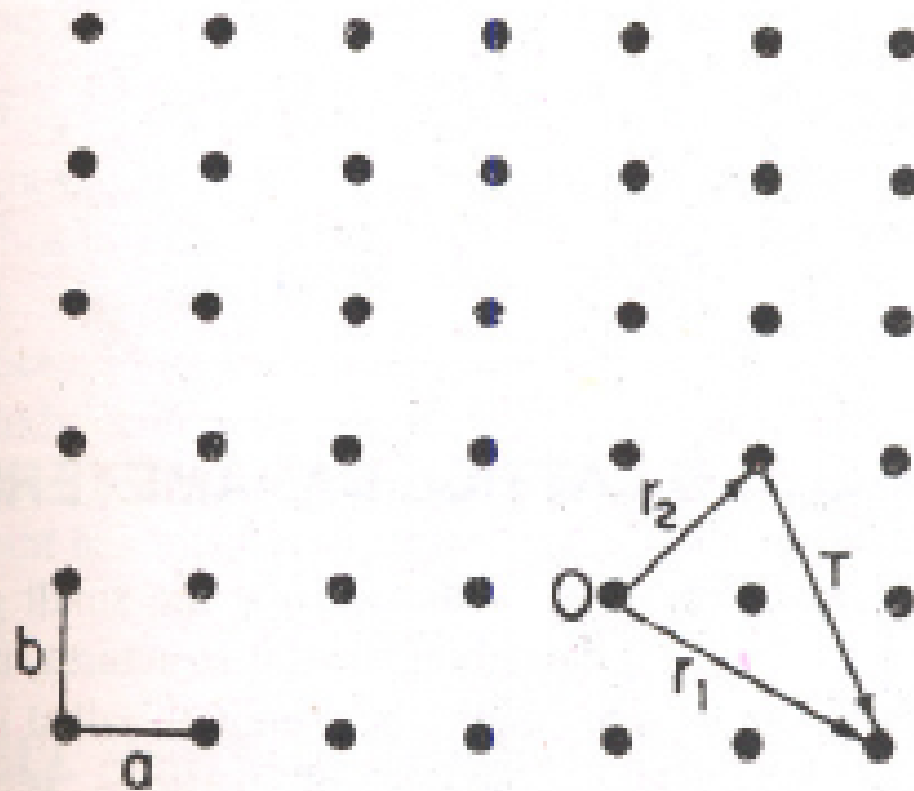


Fig. 4.1 Two-dimensional array of points.

For three dimensional lattice:

$$\vec{T} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$$

Hence it should be remembered that a crystal lattice refers to the geometry of a set of points in space whereas the structure of crystal refers to the actual ordering of its constituent ions, atoms, molecules in the space.

III. THE BASIS AND CRYSTAL STRUCTURE

For a lattice to represent a crystal structure, we associate every lattice point with one or more atoms (i.e., a unit assembly of atoms or molecules identical in composition) called the *basis* or the *pattern*. When the basis is repeated with correct periodicity in all directions, it gives the actual crystal structure. The crystal structure is real, while the lattice is imaginary. Thus,

lattice + basis = crystal structure

Fig. 4.2 shows the basis or pattern representing each lattice point. It is observed from the figure that a basis consists of three different atoms. It can also be observed that the basis is identical in composition, arrangement and orientation. In crystalline solids like copper and sodium, the basis is a single atom, in NaCl and CsCl, the basis is diatomic whereas in crystals like CaF_2 , the basis is triatomic.

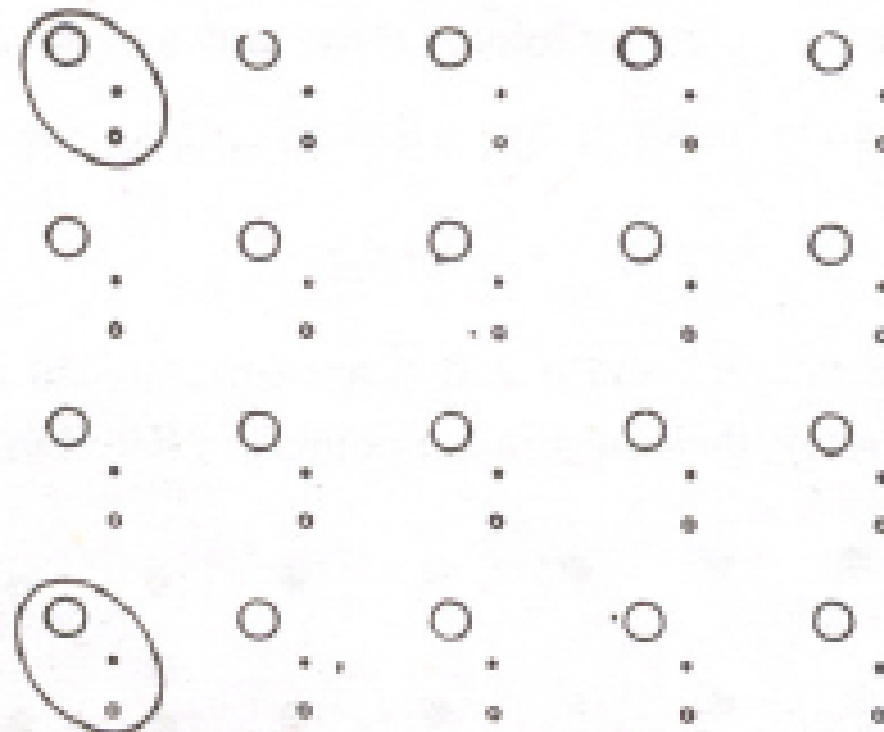


Fig. 4.2 Basis or pattern.

IV. UNIT CELLS AND LATTICE PARAMETERS

The atomic order in crystalline solids indicates that the small groups of atoms form a repetitive pattern. Thus, in describing crystal structures, it is often convenient to subdivide the structure into small repeat entities called *unit cells*, i.e., in every crystal some fundamental grouping of particles is repeated. Such fundamental grouping of particles is called a *unit cell*. Unit cells for most crystals are parallelepiped or cubes having three sets of parallel faces. A unit cell is chosen to represent the symmetry of the crystal structure, wherein all the atom positions in the crystal may be generated by translations of the unit cell through integral distances along each of its edges. Thus, the unit cell is the basic structural unit or *building block* of the crystal structure by virtue of its geometry and atomic positions within. Furthermore, more than a single unit cell may be chosen for a particular crystal structure; however, we generally use the unit cell having the highest geometrical symmetry. Unit cells may also be regarded as the '*building blocks*' that make up the crystal, each one indistinguishable from the next. Fig. 4.3, shows a unit cell of a three-dimensional crystal lattice. A space lattice is a regular distribution of points in space, in such a manner that every point has identical surroundings. The lattice is made-up of a repetition of unit cells, and a unit cell can be completely described by the three vectors \vec{a} , \vec{b} , \vec{c} when the length of the vectors and the angles between them (α , β , γ) are specified. Taking any lattice point as the origin, all other points on the lattice can be obtained by a repeated operation of the lattice vectors \vec{a} , \vec{b} , \vec{c} . These lattice vectors and the above said

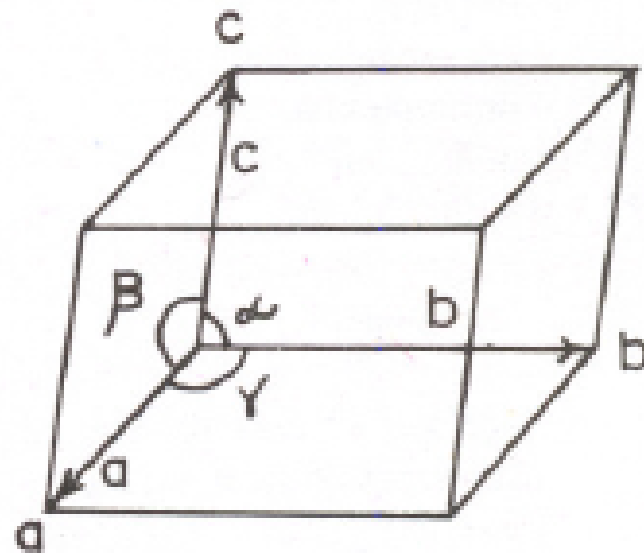


Fig. 4.3 Lattice parameters of a unit cell.

interfacial angles constitute the *lattice parameters* of the unit cell. It is thus obvious that if the values of these intercepts and interfacial angles are known, we can easily determine the form and actual size of the unit cell.

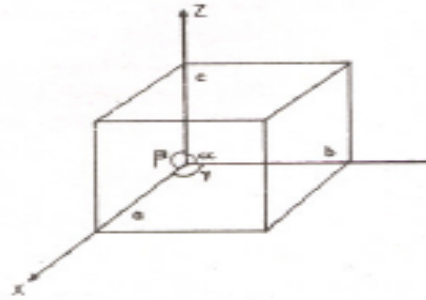
The vectors \vec{a} , \vec{b} , \vec{c} may or may not be equal. Also, the angles, α , β , and γ may or may not be right-angles. Based on these conditions, there are seven different crystal systems. Thus in a cubic system, $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$. If atoms are existing only at the corners of the unit cells, the seven crystal systems will yield seven types of lattices. More space lattices can be constructed by placing atoms (or particles) at the body centres of unit cells or at the centres of the faces. Bravais showed that the total number of different space lattice types (obeying the condition that every point has identical surroundings) is only fourteen. Hence the term '*Bravais Lattice*'.

V. UNIT CELL VERSUS PRIMITIVE CELL

In the literature, references to *unit cells* and *primitive cells* are often made. Primitive cell may be defined as a geometrical shape which, when repeated indefinitely in three dimensions, will fill all space and is the equivalent of one lattice point i.e., the unit cell that contains one lattice point only at the corners is known as *primitive cell*. The unit cell differs from the primitive cell in that it is not restricted to being the equivalent of one lattice point. In some cases, the two coincide. Thus, unit cells may be primitive cells, but all the primitive cells need not be unit cells.

VI. CRYSTAL SYSTEMS

There are thirty two classes of crystal systems based on the geometrical considerations (i.e., symmetry and internal structure). But, it is a common practice to divide all the crystal systems into seven groups or basic systems. These seven basic crystal systems are distinguished from one another by the angles between the three axes and the intercepts of the faces along them. The basic crystal systems are:



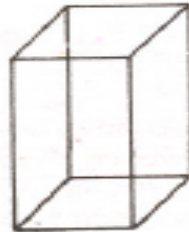
- cubic (Isometric)
- tetragonal
- orthorhombic
- monoclinic
- triclinic
- trigonal (rhombohedral)
- hexagonal

We shall now discuss all the above-mentioned seven types of the basic crystal systems one by one.

(i) Cubic crystal system

$$a = b = c, \alpha = \beta = \gamma = 90^\circ$$

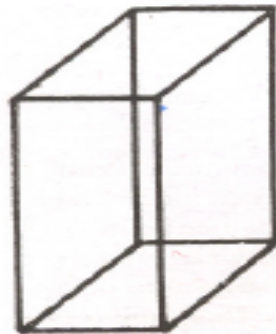
The crystal axes are perpendicular to one another, and the repetitive interval is the same along all the three axes. Cubic lattices may be simple, body-centred or face-centred.



(ii) Tetragonal crystal system

$$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$$

The crystal axes are perpendicular to one another. The repetitive intervals along two axes are the same, but the interval along the third axis is different. Tetragonal lattices may be simple or body-centred.



(iii) Orthorhombic crystal system

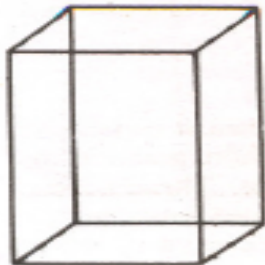
$$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$$

The crystal axes are perpendicular to one another, but the repetitive intervals are different along all the three axes. Orthorhombic lattices may be simple, base centred, body-centred or face-centred.

(iv) Monoclinic crystal system

$$a \neq b \neq c, \alpha = \beta = 90^\circ \neq \gamma$$

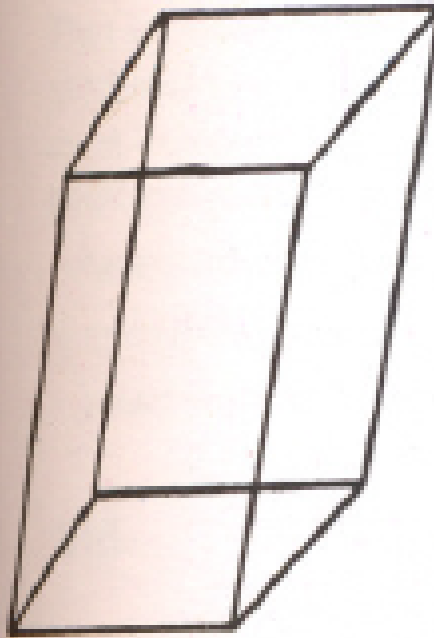
Two of the crystal axes are perpendicular to each other, but the third is obliquely inclined. The repetitive intervals are different along all the three axes. Monoclinic lattices may be simple or base-centred.



(v) *Triclinic crystal system*

$$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$$

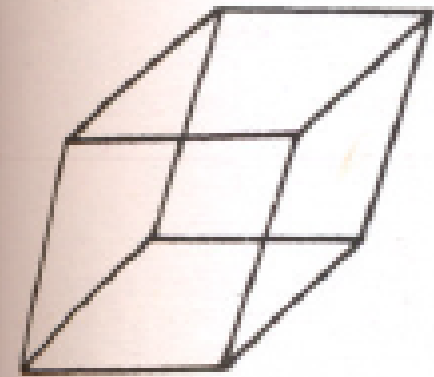
None of the crystal axes is perpendicular to any of the others, and the repetitive intervals are different along all the three axes.



(vi) *Trigonal (sometimes called rhombohedral) crystal system*

$$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$$

The three axes are equal in length and are equally inclined to each other at an angle other than 90° .



(vii) *Hexagonal crystal system*

$$a = b \neq c, \alpha = \beta = \gamma = 90^\circ, \gamma = 120^\circ$$

Two of the crystal axes are 60° apart while the third is perpendicular to both of them. The repetitive intervals are the same along the axes that are 60° apart, but the interval along the third axis is different. The seven systems and their properties are given in Table 4.A.

Table 4. A Seven basis crystal systems with their characteristics

Crystal system	Axial lengths of unit cell (a , b and c)	Interaxial angles (α , β and γ)	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Au, Cu, NaCl
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	TiO_2 , SnO_2 , NiSO ₄
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	KNO ₃ , BaSO ₄ , PbCO ₃
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma$	CaSO ₄ · 2H ₂ O (Gypsum), FeSO ₄ , Na ₂ SO ₄
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	K ₂ Cr ₂ O ₇ , CuSO ₄ · 5H ₂ O
Trigonal	$a = b \neq c$	$\alpha = \beta = \gamma \neq 90^\circ$	As, Sb, Bi, Calcite
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$	SiO ₂ , Zn, Mg, Cd