

Lecture 2 Crystal Lattices and Miller Indices

Simon Chapter 12 (pp113-125); Kittel Chapter 1 (pp 3-22)

Crystals – Periodic arrays of atoms

It has long been known that crystals are composed of regular periodic arrays of atoms which extend with a repeating structure in 3-dimensions. Crystalline solids are those where the regular periodicity is highly defined, this produces specific electronic (and optical) properties. We know from quantum mechanics that electrons are described by the Schrödinger equation and have wave-like properties. We might imagine that an interaction between the electron wave (wavefunction) and the periodic potential of a crystal might produce some interesting effects. This is the case and is one way of describing energy bands in solids. These are regions of energy where there are no valid solutions to the Schrödinger equation and thus no energy states.

Non-crystalline solids are an important class of solids which have numerous applications today. Non-crystalline solids are generally referred to as amorphous solids (from Greek – without form). An amorphous solid lacks the long-range order that occurs in a crystal. Amorphous solids include glasses, gels, thin films and nanostructures. Glass is amorphous (highly disordered) but can also be considered as a liquid with a very high viscosity. Polycrystalline solids are another important class of solids – see below for more on this.

Mineralogists noticed about 200 years ago that crystals of certain materials exhibited characteristic shapes. This led to the prediction that crystals are ordered structures made up of large numbers of small and identical building blocks by Frenchman René Haüy at the end of the 18th Century.

Today we know that these building blocks (which we would call a unit cell) are made up of a small number of atoms, or molecules. One consequence of this is that the geometrical shape of a crystal which may be of dimensions cm is a direct consequence of the arrangement of atoms in the unit cell which is of dimensions nm.

A crystal thus consists of something like 10^{27} atoms arranged in an almost perfect geometrical array. As ever with nature perfection is unlikely and there are exceptions; for some solid systems the regular array of atoms is not at all obvious.

Over 2/3 the periodic table consists of metals which are malleable and which can be shaped into almost any physical form. Does this mean that the arrangement of atoms in a metal is random? No. Under a microscope it is observed that metals consist of a large number of small crystals or grains. This state is often described as polycrystalline. Within individual grains the atoms are arranged in a regular periodic array but the orientation of the atoms in individual grains is different from the arrangement in adjacent atoms. At the boundaries between grains the crystalline order is disrupted.

In 1912 the diffraction of X-rays by crystals was discovered. X-rays have a higher energy than visible light and a corresponding wavelength which is comparable to the separation of atoms in crystals. X-ray diffraction proved conclusively what had been known for over 100 years.

We know a perfect crystal consists of a periodic array of atoms. How do we describe this mathematically? How can we describe a crystal mathematically in such a way as to allow the development of theoretical predictions of the properties of crystals?

Crystals (or solids more generally) can be classified according to their physical properties or their structure. We will look at both in this course. Obviously, there will be well defined relationships between the structure of the crystal, determined from the bonds, and a range of physical properties.

TABLE
Classes of Solids

CLASS	SECTION OF PERIODIC TABLE	PROPERTIES
Metal	Groups I and II elements	Good electrical and thermal conductivity
	Heavy elements	Opaque to electromagnetic radiation,
	Rare earths	Good reflectors Softness, ductility, malleability Weak binding, low melting points
Ionic Crystal	Group I-VII elements	Low electrical and thermal conductivity
	Group I-VI compounds	Transparent over wide range of electromagnetic spectrum
	Group II-VII compounds	High melting point, brittle, colorless Tight binding Ionic semiconductors
Covalent Crystal	Group IV elements	Electronic semiconductors
	Group III-V compounds	Transparent in infrared, opaque at higher frequencies
	Group II-VI compounds	Hardness, poor cleavability Tight binding
Molecular Crystal	Group VIII elements	Low electrical and thermal conductivity
	Group VII elements	Transparent
	Oxygen	Soft, flaky
	Nitrogen Hydrogen	Lowest melting points, weakest binding

Levy Table 2.1

A *perfect* crystal is assumed to be an infinite repetition of a regular group of atoms.

This repeating array of atoms will have a well-defined spatial relationship between the constituent components.

The set of mathematical points from which the crystal is constructed is called the **lattice**.

The group of atoms (this can be one or more atoms) placed at each *lattice point* is called the **basis**.

The resulting **crystal structure** consists of both the **lattice** and the **basis**.

In three dimensions the lattice is defined using three translational unit vectors:

$$\mathbf{a}_1 \ \mathbf{a}_2 \ \text{and} \ \mathbf{a}_3$$

The repeating nature of the lattice means that the arrangement of atoms in the crystal is the same when viewed from the points \underline{r}' and \underline{r} where they are related by:

$$\underline{r}' = \underline{r} + n_1 \underline{a}_1 + n_2 \underline{a}_2 + n_3 \underline{a}_3$$

where n_1 n_2 and n_3 are arbitrary integers.

We can also *postulate* that, in addition to the crystal structure being identical at \underline{r} and \underline{r}' the physical environment will be identical. This means that any physical properties of crystals which depend on the position of electrons (or any other particle) will be subject to the same behaviour and constraints.

The set of points defined by \underline{r}' above for all values of n_1 n_2 and n_3 defines the lattice.

The lattice is called a primitive lattice if any two points (for example \underline{r}' and \underline{r} as above) always satisfy the equation for all possible values of integer n_1 n_2 and n_3 . In other words the equation cannot be reduced any further. If the equation is not satisfied with some combination of integer values then the vectors are not primitive. (Note that for more complex crystal structures not all vectors are primitive.)

Using the definition of primitive lattice as above gives rise to the primitive lattice vectors represented by \underline{a}_i . The volume defined by \underline{a}_1 \underline{a}_2 and \underline{a}_3 describes the volume of the smallest unit used to build up the crystal.

In vector notation: $V = \underline{a}_1 \times \underline{a}_2 \cdot \underline{a}_3$

The primitive lattice vectors generally define the crystal axes.

The primitive lattice cell is defined by the primitive axes by \underline{a}_1 \underline{a}_2 and \underline{a}_3 .

The basis is established from a comparison of the lattice and the crystal structure.

There is always a minimum of one atom per unit cell. (Example of shared adjacent cells)

The primitive unit cell is called the Wigner-Seitz cell.

The basis (whether 1, 2 or many atoms) is identical throughout the lattice.

We can think of crystal lattices as **mathematical constructs for filling space**. We can therefore envisage a variety of patterns and arrangement of atoms (at this stage conceptualised as spheres) which fill space. We also might expect that nature uses symmetry (e.g. snow flake) and therefore crystal lattices can have a very high degree of **symmetry**.

Crystal structures are built up of a repetitive lattice and the basis or repeating unit. Crystals are constructed using the formalism above which is known as a translation (described by a vector in 3 dimensions).

Translations are an operator and part of a broader class of **symmetry operations**. A symmetry operation is one that leaves the crystal environment invariant. We have already seen how translations can leave the crystal environment unchanged.

Translations are just one class of symmetry operator.

Other types of symmetry operators are:

- Translations
- Rotations
- Reflections
- Inversions
- Combinations

We have discussed translational symmetry, another class of symmetry operations frequently used in crystallography is called *point symmetry* operations. This does not involve a translation. Rotation, reflection and inversion are all types of point symmetry operators as they operate about a fixed point. The collection of point operations which leave an object invariant is called the *point group* for that object.

Note that point operations apply to objects but translation operations apply only to lattices.

Point operators can be illustrated in two dimensions by considering **rotations** (about an axis at a fixed point) and reflections (about a line in 2D, or a plane in 3D).

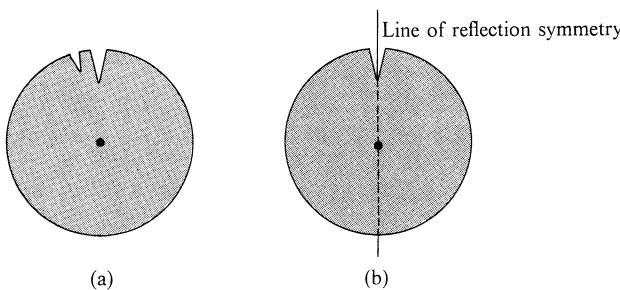
A body has rotational symmetry about an axis if the angle of rotation is θ which satisfies:

$$\theta = 2\pi / n$$

i.e. there must be an integral number of rotations in a 2π cycle.

The integer n is called the multiplicity of the rotation axis. In the notation of symmetry operators a rotation axis is denoted by n .

Reflections A body has reflection symmetry about a plane if it is left invariant after reflection.

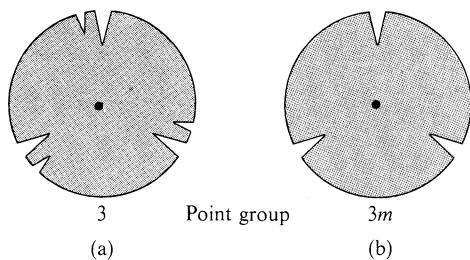


Levy Figure 2.12

Fig. Illustration of reflection symmetry using notched wheels.
In (a) there are no reflection lines but the wheel in (b) has a reflection line through the center of the notch.

Notched wheel (a) above does not have reflection symmetry. The wheel (b) does have a reflection through the notch.

It is very common for bodies to possess both *rotation* and *reflection* symmetry. In two dimensions the only point operations are rotation and reflection, these comprise the point group for an object (the collection of all point operations which leave the body invariant).



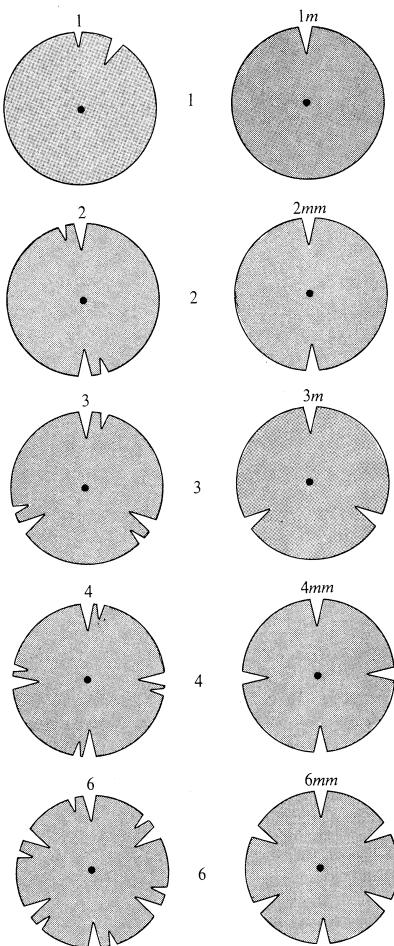
Levy Fig 2.13

Fig. Two-dimensional point groups illustrated by notched wheel. The point group of (a) is 3, of (b) is 3m.

In the diagram above the two notch wheel (a) has 3-fold axis of rotation symmetry but no reflection planes – its point group is denoted by 3. The wheel (b) has the same 3-fold axis and a reflection line so its point group is 3m. (Note there are three reflection lines denoted by m (mirror) – a consequence of the 3-fold axis).

If the axis is even the point group will always contain either zero or two independent sets of reflection lines. Point groups for odd-fold axes contain either zero or one set of reflection lines.

In considering whether lattices and crystal structures possess point symmetry it is a requirement that the crystal structure is invariant under a point operation. If there is a point r which is an axis of rotation then it must also be the case that $r' = r + \mathbf{T}$ is an axis of rotation, where \mathbf{T} is a lattice translation vector given by $n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$.



From this it can be shown that only 1-, 2-, 3-, 4- and 6-fold axes can exist in a 2D lattice. It can be shown that 5-fold rotation is incompatible with translational symmetry. (Try and construct a 2D sheet covered only with pentagons – not possible).

In 2 dimensions there are only five types of lattice which fill the plane (2 d space). Refer to Kittel Figure 7 page 8). These are:

1. Square lattice
2. Hexagonal lattice
3. Rectangular lattice
4. Centred rectangular
5. Oblique parallelogram

No other types of lattice will fill a 2D space

Levy Figure 2.14

al crystallographic point
of notched wheels.

TABLE
The Five Bravais Lattices in Two Dimensions

LATTICE	CRYSTAL AXES	POINT GROUP
Oblique	$a \neq b$ $\phi \neq 90^\circ$	2
Rectangular primitive	$a \neq b$ $\phi = 90^\circ$	2mm
Rectangular centered	$a \neq b$ $\phi \neq 90^\circ$	2mm
Square	$a = b$ $\phi = 90^\circ$	4mm
Hexagonal	$a = b$ $\phi = 120^\circ$	6mm

Levy Table 2.2

Three Dimensional Crystals

Three dimensional crystals are also **highly symmetric** structures.

We will see later that the crystal structure is intimately related to the arrangement of electrons in atomic orbitals and that quantum mechanics can be used to predict the shape of the bonds arranged around any given atom with a specific number of electrons.

In three dimensions there 7 crystal systems which fill space:

1. Cubic
2. Tetragonal
3. Hexagonal
4. Rhombohedral
5. Orthorhombic
6. Triclinic
7. Monoclinic

TABLE
The Fourteen Bravais Lattices and Conventional Unit Cells in Three Dimensions*

SYSTEM	NUMBER OF LATTICES IN SYSTEM	LATTICE SYMBOLS	NATURE OF UNIT-CELL AXES AND ANGLES	LENGTHS AND ANGLES TO BE SPECIFIED
Triclinic	1	P	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	a, b, c α, β, γ
Monoclinic	2	P C	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	a, b, c β
Orthorhombic	4	P C I F	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	a, b, c
Tetragonal	2	P I	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	a, c
Rhombohedral (Trigonal)	1	R	$a = b = c$ $\alpha = \beta = \gamma$ $<120^\circ, \neq 90^\circ$	a α
Hexagonal	1	P	$a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	a, c
Cubic	3	P I F	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	a

Levy Table 2.3

For each crystal system there are four possible variants:

1. Primitive (or simple lattice)
2. Innenzentriert (or body centred)
3. Face centred
4. Base centred

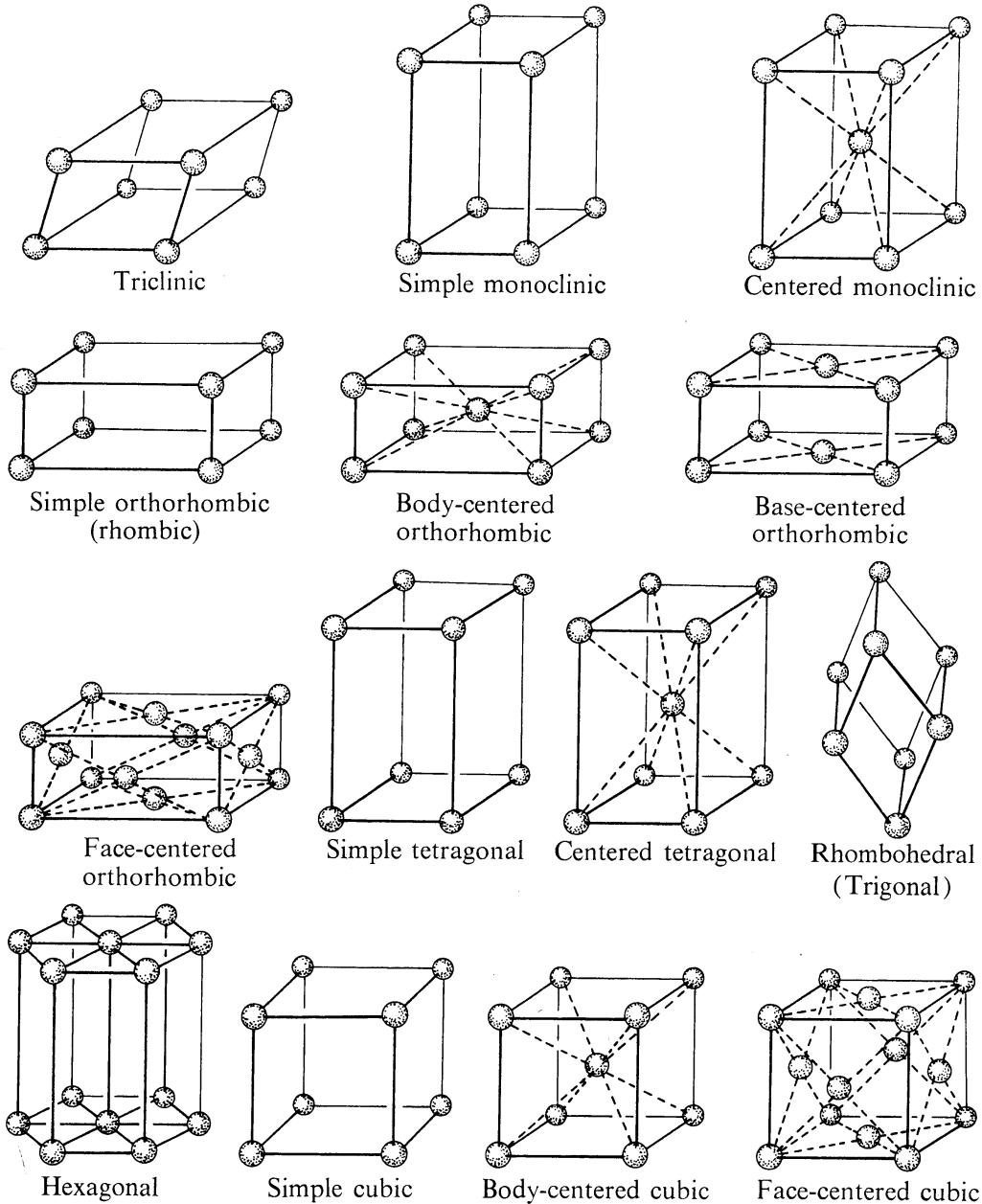


Fig. The fourteen three-dimensional Bravais lattices.

Levy Fig 2.22

Of the 28 different possible combinations there are only 14 distinct **Bravais Lattices** belonging to 7 distinct crystal systems.

Table 1 The 14 lattice types in three dimensions

System	Number of lattices	Restrictions on conventional cell axes and angles
Triclinic	1	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3$ $\alpha = \gamma = 90^\circ \neq \beta$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	2	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$
Cubic	3	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90^\circ$
Trigonal	1	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$
Hexagonal	1	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$

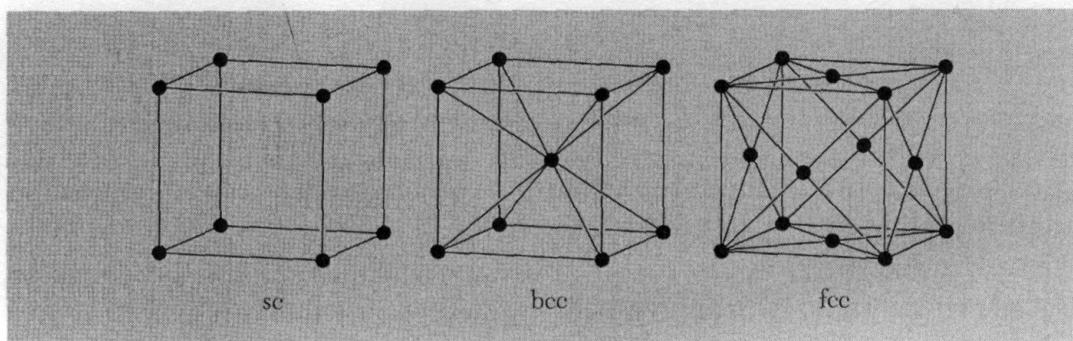


Figure 8 The cubic space lattices. The cells shown are the conventional cells.

The diagram also shows the three lattices in the cubic system:

- Simple, or primitive, cubic
- Body centred cubic
- Face centred cubic

Kittel Table 2 presents the characteristics of the different cubic lattices.

Miller Indices

The notation we use to describe crystals is called Miller Indices.

Miller indices describe a particular crystallographic plane or direction within the crystal.

The orientation of any crystal plane can be determined from any three points which lie on the plane (provided they are not in a straight line).

When using crystal planes for structural analysis the most useful approach is to follow rules for determining the crystal plane:

1. Find the intercepts on the axes in terms of the three lattice constants a_1 , a_2 and a_3
2. Take the reciprocal of these numbers
3. Reduce to three integers having the same ratio, normally the smallest three integers
4. This result will give the index of the plane normally denoted by (hkl) .
5. If one of the indices is negative this is denoted by a bar above the index.

This plane will intersect the unit cell at \underline{a}_1/h , \underline{a}_2/k and \underline{a}_3/l

(Note: Kittel for some weird reason uses the notation $\nu_1 \nu_2 \nu_3$ instead of hkl !!!

The separation between planes is given by the distance from the origin of the unit cell to the closest plane which intercepts the unit cell:

$$d = \frac{1}{\sqrt{\frac{h^2}{a_1^2} + \frac{k^2}{a_2^2} + \frac{l^2}{a_3^2}}}$$

For a cube this reduces to:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{a}{\sqrt{N}}$$

As an example the six faces of the simple cubic lattice are denoted by the six planes: (100) , (010) , (001) , $(\bar{1}00)$, $(0\bar{1}0)$ and $(00\bar{1})$. In the notation the bar above the number denotes a negative.

Some examples of common crystal planes are shown in the diagram.

Reciprocals are important for a number of reasons:

1. By taking reciprocals we bring all the planes inside a single unit cell. (Even very high order planes can be made to intersect the unit cell).
2. The unit cell is used to generate the crystal and therefore the unit cell is representative of the whole crystal. The properties of the unit cell will be the properties of the crystal.
3. The unit cell is analogous to the molecule in chemistry – it is the fundamental building block. Every equation which applies to the unit cell applies to the whole crystal.

The use of reciprocals is key to crystal structure and the properties of crystals. We will return to reciprocals again when we look at mechanisms for probing and describing the properties of crystals. The concept of **reciprocal space** is fundamental to condensed matter physics.

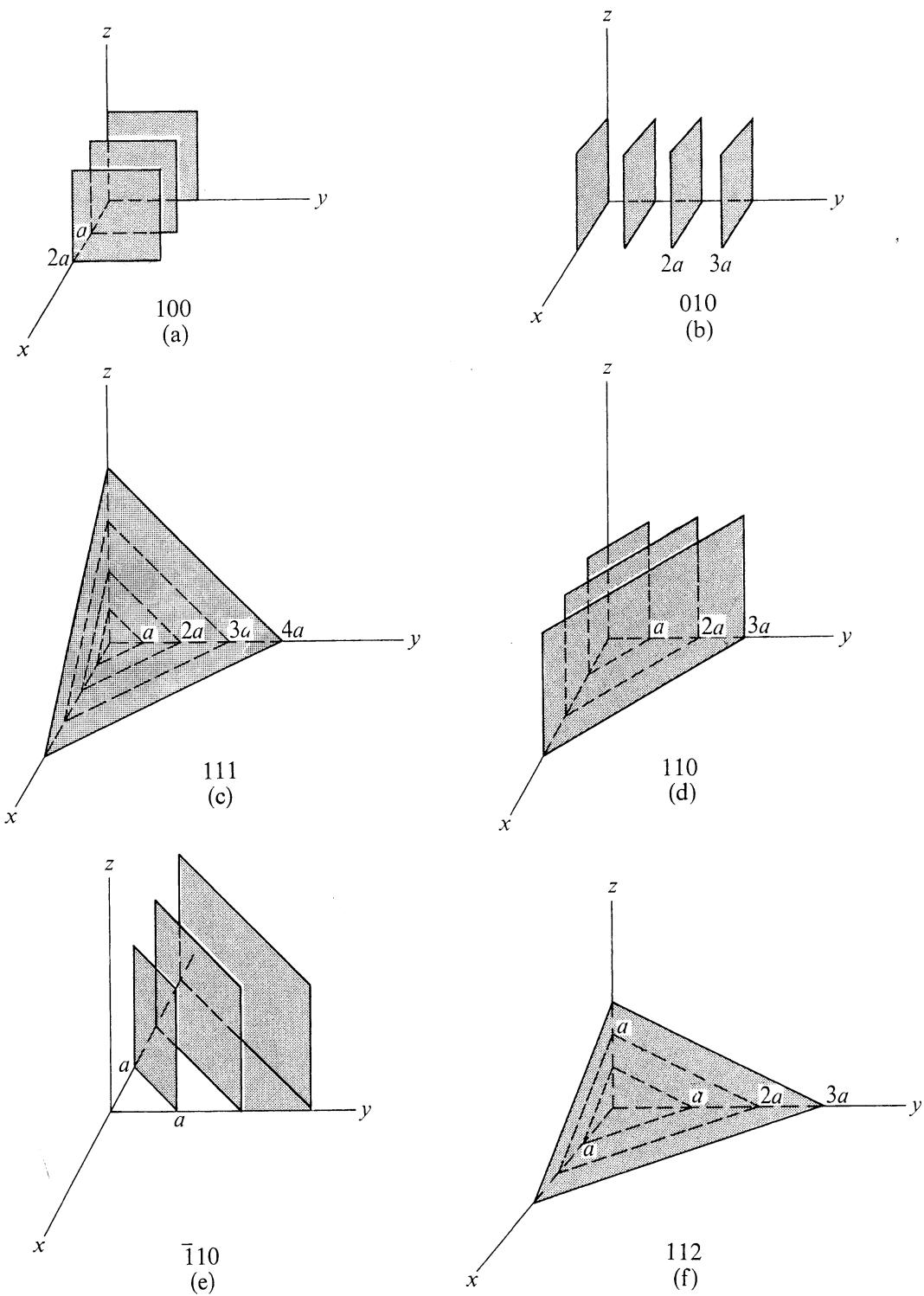


Fig. Examples of important cubic crystal planes. (a) 100 planes; (b) 010 planes; (c) 111 planes; (d) 110 planes; (e) $\bar{1}10$ planes; (f) 112 planes. (After C. A. Wert and R. M. Thomson, *Physics of Solids*. New York: McGraw-Hill, 1964.)

Levy Fig 2.25

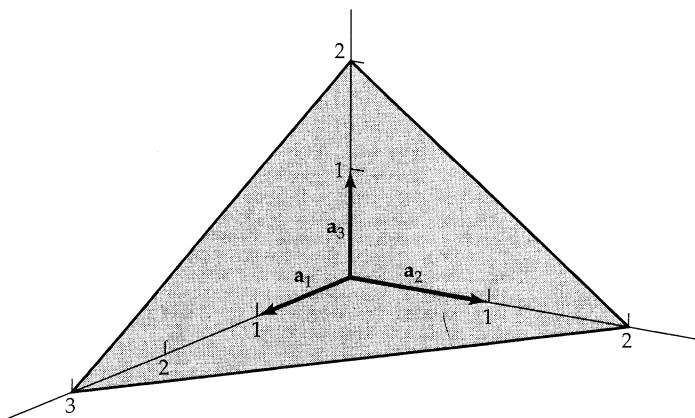


Figure 13 This plane intercepts the \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 axes at $3\mathbf{a}_1$, $2\mathbf{a}_2$, $2\mathbf{a}_3$. The reciprocals of these numbers are $\frac{1}{3}, \frac{1}{2}, \frac{1}{2}$. The smallest three integers having the same ratio are 2, 3, 3, and thus the indices of the plane are (233).

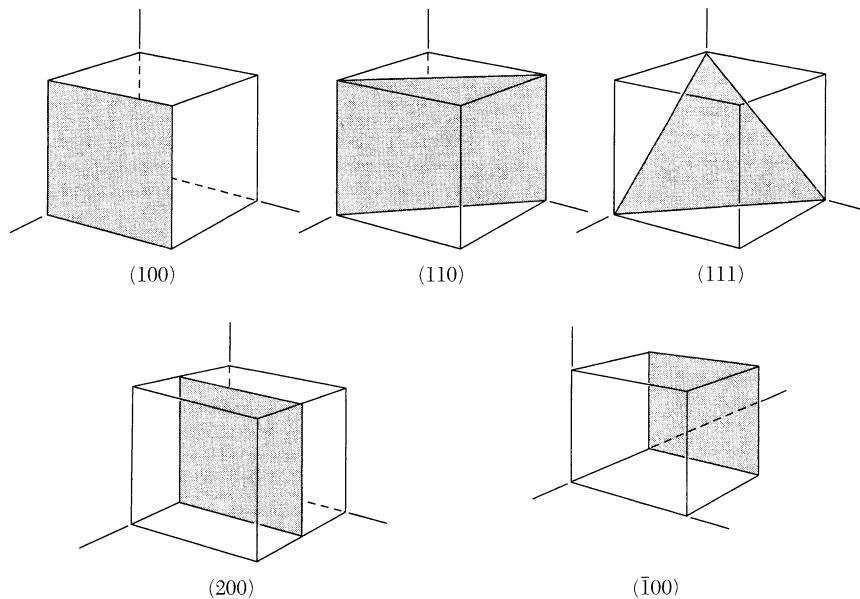


Figure 14 Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) and to (100).

Notation

A brief word about notation of crystal structures. The type of bracket is important.

$(h k l)$ represents a single plane e.g. (100) (110) etc.

$\{h k l\}$ represents a family of planes e.g. {100} is equivalent to all (100), (010), (001)

$[u v w]$ represents a single direction e.g. [100] [001] etc.

$\langle u v w \rangle$ represents a family of directions e.g. <100> is equivalent to all of [100], [010] [001]

Some definitions for you to be familiar with:

TABLE
Definitions

Lattice, space lattice	A parallel netlike arrangement of points with the property that the environment about any point is identical to the environment about any other point in the lattice.
Basis	The unit assembly of atoms, ions, or molecules located at each lattice point. To be consistent with the definition of a lattice, the basis at any lattice point must be identical in all respects with all others.
Crystal structure	The lattice plus the basis.
Unit cell	Any cell that will cover all space under action of the translation operations of the crystal: defined by fundamental translation vectors.
Primitive cell	The smallest unit cell, containing lattice points only at corners.
Crystal axes, translation vectors	Vectors that generate the lattice under translation operations.
Lattice constant	The length of the crystal axes.
Translation operation	The act of displacing a crystal parallel to itself by an integral multiple of each of its fundamental translation vectors, that is, by $\mathbf{T} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$.
Translation group	The totality of all possible translation operations, that is, all possible values of the n 's.
Point group	The collection of symmetry operations excluding translations which leave a body invariant. In two dimensions these include rotations and rotation-reflections, making a total of 10. In three dimensions these include rotations, rotation-reflections, and rotation-inversions, making a total of 32.
Bravais lattice	The types of lattice required by the point group operations applied to lattice points: 5 in 2 dimensions, 14 in 3 dimensions.
Crystal system, crystal class	Classification of lattices according to axial relationships: 4 in 2 dimensional, 7 in 3 dimensional.
Space group	The repetitive pattern of symmetry elements of a given crystal structure. It is the collection of symmetry elements that leaves space invariant since it includes translations. There are 17 two-dimensional and 230 three-dimensional space groups.

Levy Table 2.4