

## 5.2 Structure of Solids

Various types of bonds between atoms and molecules described in the previous section can continue among very large number of atoms and molecules when they form liquids and solids. Solids are fascinating materials characterized by machinable shape, strength, and stability. If a solid has a regular arrangement of atoms and molecules, it forms crystals. For instance, the crystal of sodium chloride, has sodium and chlorine ions at the corners and faces of a cubic structure such that each sodium ion is surrounded symmetrically by six chlorine ions and vice versa as illustrated in Fig. 5.5.

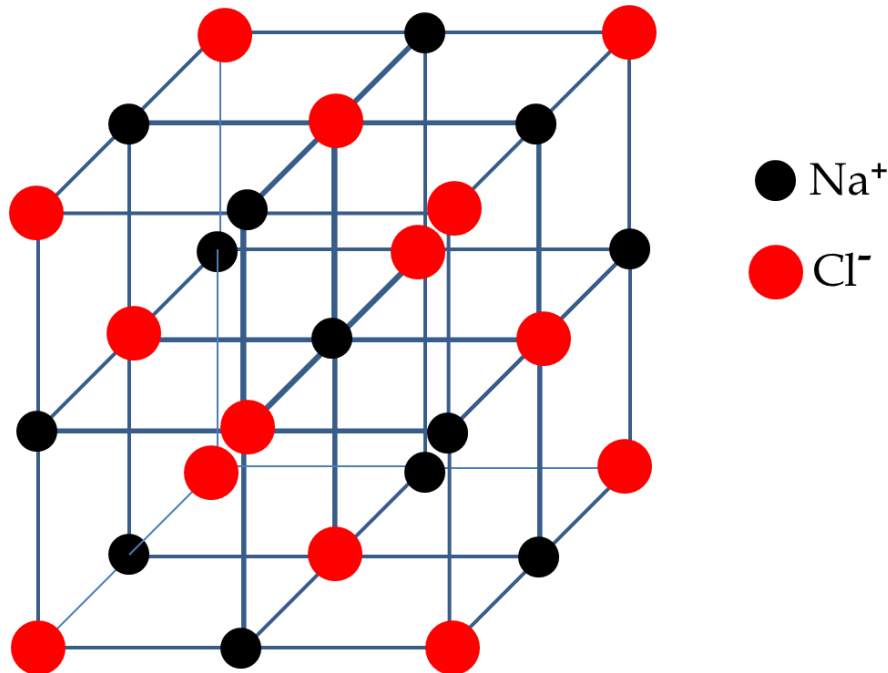


Figure 5.5: The arrangement of atoms in the sodium chloride crystal.

Many solids are found in crystalline form in nature. Fig. 5.6 shows three cubic crystals of pyrite ( $\text{FeS}_2$ ) in a rock sample. The flat surface of the crystal forms due to arrangement of atoms in a cubic lattice.

Most solids in nature are not crystalline. The atoms and molecules in them are randomly placed. They are called amorphous. Glass and sand are examples of amorphous materials.

### 5.2.1 X ray Diffraction from Single Crystals

X rays were discovered by William Röntgen in 1895 by the marks they left on photographic plates. They are produced when highly energetic electrons strike a target. X rays are very penetrating and can pass through human body and many other materials that are opaque to the visible light.



Figure 5.6: A rock containing three crystals of pyrite ( $\text{FeS}_2$ ). The arrangements of atoms in the crystal are in the form of a cubic lattice which over a macroscopic sample is reflected in the formation of cubic shaped crystal. Credits: Wikicommons.

Are X rays particles or waves? Wilhelm Wien calculated that if X rays were waves their wavelength will be very small, of the order of  $10^{-11}$  m. Based on the calculation of the inter-atomic distances in crystals to be of the order of  $10^{-10}$  m, Max von Laue wondered if crystals could act as a diffraction grating for X rays. Two of his assistants, Walter Friedrich and Paul Knipping, set up the experiment to test Laue's ideas. First they used copper sulfate crystal since it was readily available in the lab. The crystal was fixed to a holder with wax which was placed in a lead box with a 3 mm hole in one side for the X rays to enter while the back end and the sides were lined with photographic plates. They found that, in addition to the central spot, there were many smaller dots on the screen in a regular pattern where diffracted beams had formed constructive interferences. These patterns are often referred to as Laue pattern. Von Laue received Nobel prize for his discovery in 1914.

\*\*\*\*\*Note to publisher: It will be great to have a picture of a real Laue pattern such as DNA, Quasicrystal, NaCl, etc\*\*\*\*\*

Von Laue's patterns did not have all the diffraction spots expected from a source of continuous wavelengths. Von Laue took it to mean that the source he was using had only certain wavelengths. However, William Lawrence Bragg, the son of William Henry Bragg, the Cavendish Professor of Physics at the University of Leeds, thought differently. Lawrence Bragg was convinced that missing diffraction spots were due to some property of crystals themselves. He put forth a theory for diffraction of X rays based on their reflection from crystal planes.

Crystal planes are planes in space that are parallel to each other and spaced

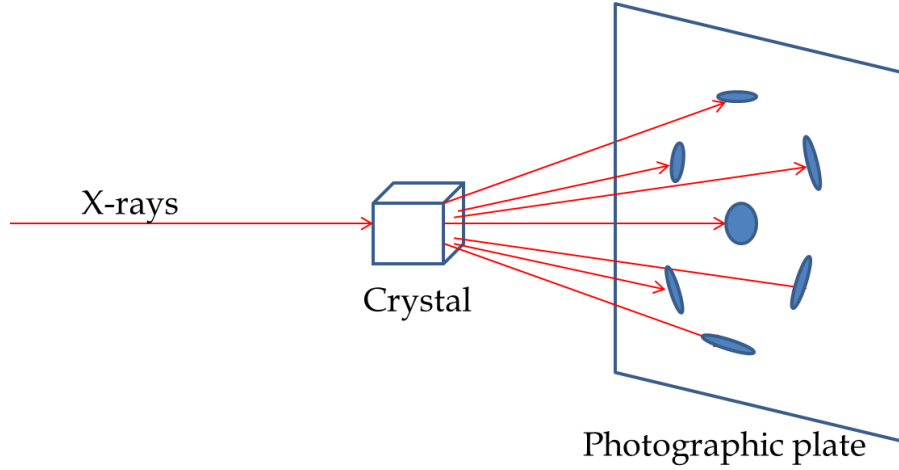


Figure 5.7: Von Laue experiment. A continuous wavelength X rays beam is incident on a crystal and diffracts from the atoms of the crystal forming Laue pattern on the photographic plate.

equally apart and every atom of the crystal belongs to one of these planes as illustrated for a square lattice in Fig. 5.9. According to [William] Lawrence Bragg each crystal plane acts as a reflecting surface. The X rays reflected from these planes would interfere constructively if they were all in phase. For instance, the ray reflected from the surface plane will have traveled smaller distance than the ray that reflected off the plane a distance  $d$  from the surface just below as shown in Fig. 5.8. The difference in the paths of the two rays will depend on the angle  $\theta$  and plane separation  $d$ .

$$\text{path difference} = 2d \sin \theta.$$

If this distance is an integral multiple of the wavelength  $\lambda$ , then then reflected rays will interfere constructively in that direction.

$$2d \sin \theta = n\lambda, \quad n = 1, 2, 3, \dots \quad (5.2)$$

The formula in Eq. 5.2 is called **Bragg's law**. This formula can be used to find  $\lambda$  of the X rays if we know  $d$  in a crystal and to find  $d$  between two crystal planes if we know  $\lambda$  of the X rays. By rotating the crystal, or changing the direction of the beam, or the direction of the detector, it is possible to figure out  $d$  corresponding to various crystal planes in the crystal as shown in Fig. 5.9. From the data for  $d$  for various crystal planes, the arrangements of atoms in the crystal can be determined. The father/son team of Braggs worked on the crystal structure determination using this formula and were awarded Nobel prizes in 1915.

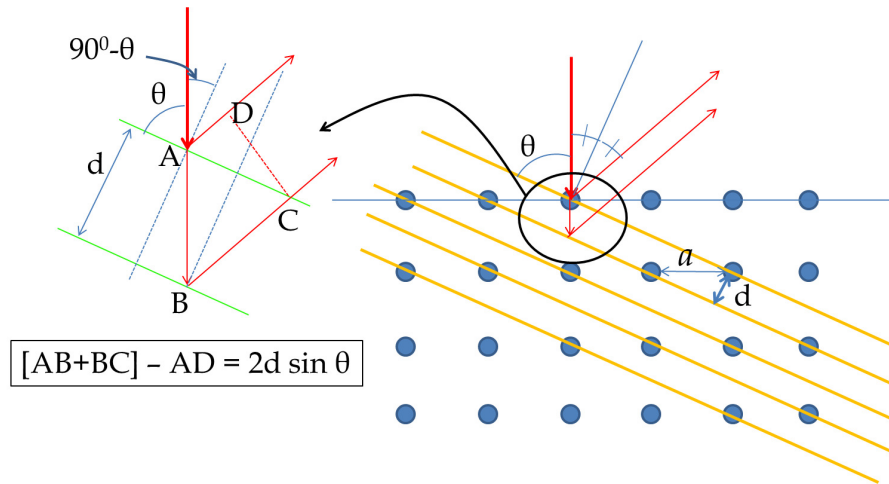


Figure 5.8: The path length difference for the reflections from successive crystal planes is equal to  $2d \sin \theta$ . If the path length difference is equal to an integral multiple of the wavelength, then there will be constructive interference of the two reflected waves in that direction.

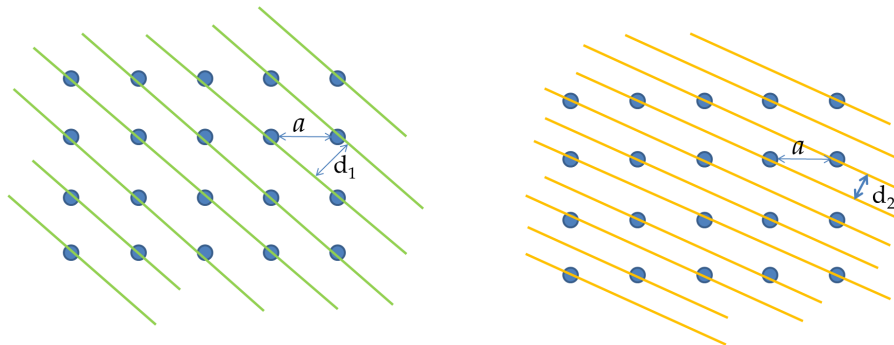


Figure 5.9: Two sets of crystal planes. The Bragg condition will occur at different angles  $\theta$  for the two sets of planes for the same  $n$  and same  $\lambda$ . Experimentally, one keeps the direction of the beam same and rotates the crystal to change  $\theta$ .

### 5.2.2 The Powder X ray Diffraction

If the single crystal is not large enough, you can still gain the information about the crystalline structure from a powder of the material. If each particle of the powder itself is a tiny crystal, then each crystallite will diffract X rays independently of the way some other particle of the powder would. Since particle of the powder would be randomly oriented with respect to each other, we get circles at the photographic plate instead of sharp dots as illustrated in Fig. 5.10. The rings are called the **Debye-Scherrer rings**.

When the crystallites become smaller each peak spreads out over larger angles. Eventually, when there is no long range order, the material is called **amorphous**. The X ray diffraction of amorphous materials are broad and lack the sharp peaks.

**Example 5.2. Lattice plane spacing and smallest angle of diffraction (a)**

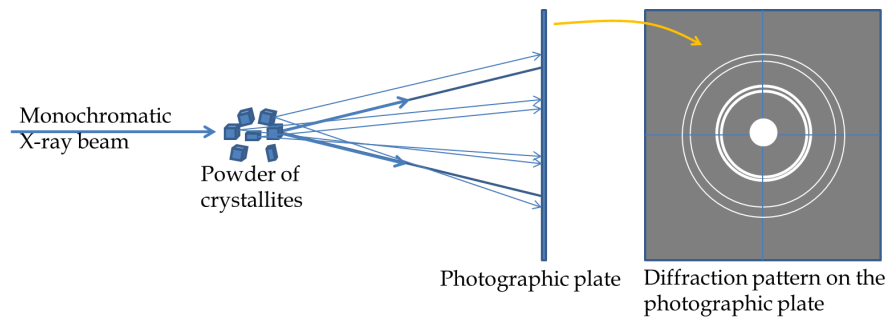
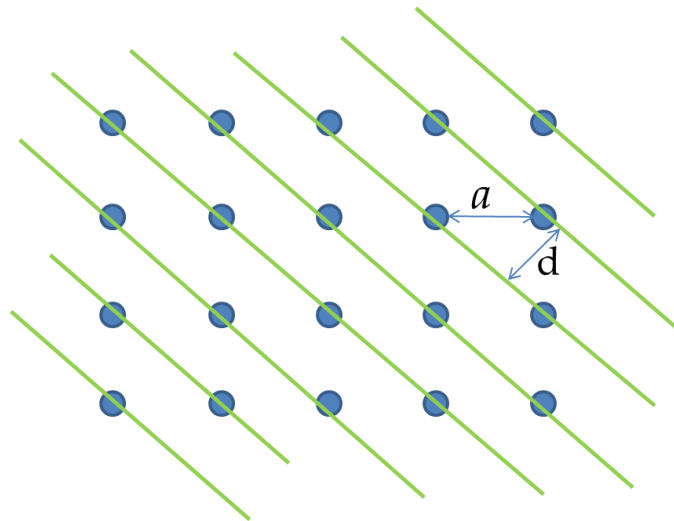


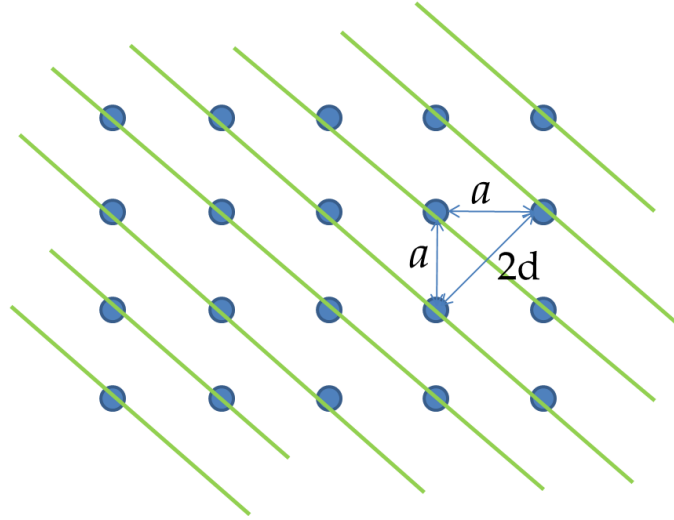
Figure 5.10: X ray diffraction of powder of a crystalline material. Powder particles, though small, have many thousands of atoms in a crystal lattice. Each crystallite produces diffraction peaks at particular angles. Since the crystallites are randomly oriented, the dots from different crystallite fall on circles as shown here.

If the distance between atoms in the following figure is  $6.00 \text{ \AA}$ , what is the distance between the lattice planes? (b) If X rays of wavelength  $1.54 \text{ \AA}$  are incident on the crystal, what will be the smallest angle to the plane should the beam direction be such that there will be a constructive diffraction in that direction?



**Solution.**

(a) We begin by noting that there is a right-angled triangle possible whose sides are  $a$ ,  $a$ , and  $2d$  as shown in the following figure.



Therefore, we will have

$$(2d)^2 = a^2 + a^2,$$

which gives

$$d = \frac{a}{\sqrt{2}}.$$

Plugging in the numerical value of  $a$  we find the spacing between the given lattice planes to be

$$d = \frac{6.00 \text{ \AA}}{\sqrt{2}} = 4.24 \text{ \AA}.$$

(b) Now, we have the  $d = 4.24 \text{ \AA}$ . We are given  $n = 1$  ( which corresponds to the smallest angle) and  $\lambda = 1.54 \text{ \AA}$ . We plug these values in the Bragg law to obtain

$$\sin \theta = \frac{1 \times 1.54 \text{ pm}}{4.24 \text{ pm}} = 0.363.$$

Therefore,

$$\theta = 21.3^\circ.$$