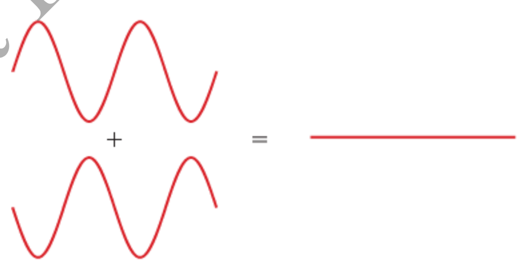
Pearson

12.2: Crystalline Solids: Determining Their Structures by X-Ray Crystallography

Recall that crystalline solids are composed of atoms or molecules arranged in structures with long-range order (see Section 11.2). If you have ever visited the mineral section of a natural history museum and seen crystals with smooth faces and well-defined angles between them, or if you have carefully observed the hexagonal shapes of snowflakes, you have witnessed some of the effects of the underlying order in crystalline solids. The often beautiful geometric shapes that we see on the macroscopic scale are the result of specific structural patterns on the molecular and atomic scales. But how do we study these patterns? How do we look into the atomic and molecular world to determine the arrangement of the atoms and measure the distances between them? In this section, we examine **X-ray diffraction**, a powerful laboratory technique that enables us to do exactly that.

In Section 2.2 we saw that electromagnetic (or light) waves interact with each other in a characteristic way called *interference:* waves can cancel each other out or reinforce each other, depending on the alignment of their crests and troughs. *Constructive interference* occurs when two waves interact with their crests and troughs in alignment. *Destructive interference* occurs when two waves interact with the crests of one aligning with the troughs of the other. Recall also that when light encounters two slits separated by a distance comparable to the wavelength of the light, constructive and destructive interference between the resulting beams produces a characteristic *interference pattern,* consisting of alternating bright and dark lines.



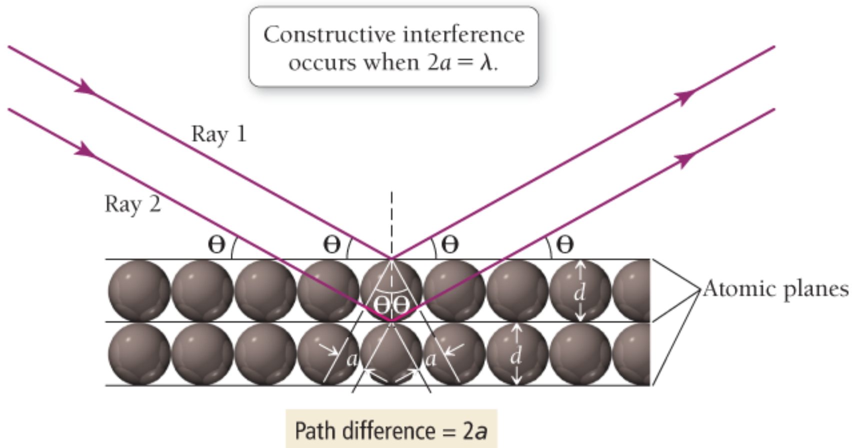
Atoms within crystal structures have spaces between them on the order of 10^2 pm, so light of similar wavelength (which happens to fall in the X-ray region of the electromagnetic spectrum) forms interference patterns or *diffraction patterns* when it interacts with those atoms in the crystals. The exact pattern of diffraction reveals the spacing between planes of atoms. Consider two planes of atoms within a crystalline lattice separated by a distance d, as shown in Figure 12.1. If two rays of light with wavelength λ that are initially in phase (that is, the crests of one wave are aligned with the crests of the other) diffract from the two planes, the diffracted rays may interfere with each other constructively or destructively, depending on the difference between the path lengths traveled by each ray. If the difference between the two path lengths ($2a$) is an integral number (n) of wavelengths, then the interference will be constructive:

[12.1]

$$n\lambda = 2a \qquad \text{(criterion for constructive interference)}$$

Figure 12.1 Diffraction from a Crystal

When X-rays strike parallel planes of atoms in a crystal, constructive interference occurs if the difference in path length between beams reflected from adjacent planes is an integral number of wavelengths.



Using trigonometry, we can see that the angle of reflection (θ) is related to the distance *a* and the separation between layers (*d*) by the following relation:

[12.2]

$$\sin\theta = \frac{a}{d}$$

Rearranging, we get:

[12.3]

$$a = d\sin\theta$$

By substituting Equation 12.1 into Equation 12.3, we arrive at the following important relationship:

$$n\lambda = 2d\sin\theta \qquad \text{Bragg's law}$$

This equation is known as *Bragg's law*. For a given wavelength of light incident on atoms arranged in layers, we can measure the angle that produces constructive interference (which appears as a bright spot on the X-ray diffraction pattern) and then calculate *d*, the distance between the atomic layers:

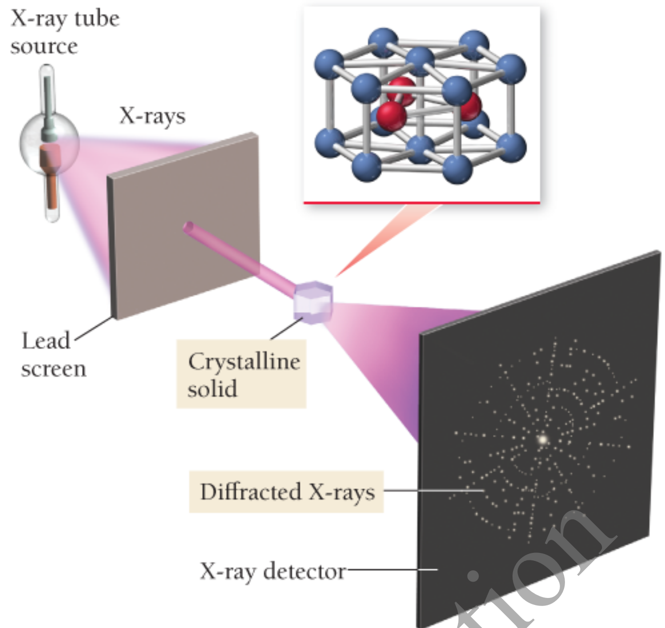
[12.4]

$$d = \frac{n\lambda}{2\sin\theta}$$

In a modern X-ray diffractometer (Figure 12.2), the diffraction pattern from a crystal is collected and analyzed by a computer. By rotating the crystal and collecting the resulting diffraction patterns at different angles, the distances between various crystalline planes can be measured, eventually yielding the entire crystalline structure. This process is *X-ray crystallography*. Researchers use X-ray crystallography to determine not only the structures of simple atomic lattices, but also the structures of proteins, DNA, and other biologically important molecules. For example, the famous X-ray diffraction photograph, obtained by Rosalind Franklin and Maurice Wilkins, helped Watson and Crick determine the double-helical structure of DNA. Researchers also used X-ray diffraction to determine the structure of HIV protease, a protein critical to the reproduction of HIV and the development of AIDS. That structure was used to design drug molecules that inhibit the action of HIV protease, thus halting the advance of the disease.

Figure 12.2 **X-Ray Diffraction Analysis**

In X-ray crystallography, an X-ray beam is passed through a crystalline solid sample, which is rotated to allow diffraction from different crystalline planes. The resulting patterns, representing constructive interference from various planes, are analyzed to determine crystalline structure.



X-Ray diffraction of DNA

Example 12.1 Using Bragg's Law

When an X-ray beam of $\lambda = 154$ is incident on the surface of an iron crystal, it produces a maximum reflection at an angle of $\theta = 32.6^\circ$. Assuming $n = 1$, calculate the separation between layers of iron atoms in the crystal.

SOLUTION To solve this problem, use Bragg's law in the form of Equation 12.4. The distance, d, is the separation between layers in the crystal.

$$
\begin{aligned}
d &= \frac{n\lambda}{2 \sin \theta} \\
&= \frac{154 \text{ pm}}{2 \sin (32.6^\circ)}
\end{aligned}
$$

$$2 \sin (32.6^{\circ})$$

$$= 143 \text{ pm}$$

FOR PRACTICE 12.1 The spacing between layers of molybdenum atoms is 157 pm. Calculate the angle at which 154 pm X-rays produce a maximum reflection for $n = 1$.