

43-4 X-RAY DIFFRACTION

X rays are electromagnetic radiation with wavelengths of the order of 0.1 nm (compared with 500 nm for a typical wavelength of visible light). Figure 43-12 shows how x rays are produced when electrons from a heated filament

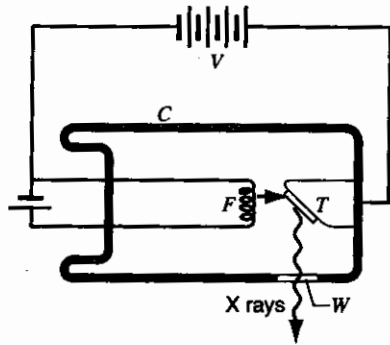


FIGURE 43-12. X rays are generated when electrons from heated filament F , accelerated through a potential difference V , strike a metal target T in the evacuated chamber C . Window W is transparent to x rays.

F are accelerated by a potential difference V and strike a metal target.

For such small wavelengths, a standard optical diffraction grating, as normally employed, cannot be used. For $\lambda = 0.10 \text{ nm}$ and $d = 3000 \text{ nm}$, for example, Eq. 43-1 shows that the first-order maximum occurs at

$$\theta = \sin^{-1} \left(\frac{m\lambda}{d} \right) = \sin^{-1} \left(\frac{(1)(0.10 \text{ nm})}{3 \times 10^3 \text{ nm}} \right) = 0.0019^\circ.$$

This is too close to the central maximum to be practical. A grating with $d \approx \lambda$ is desirable, but, because x-ray wavelengths are about equal to atomic diameters, such gratings cannot be constructed mechanically.

In 1912, it occurred to physicist Max von Laue that a crystalline solid, consisting as it does of a regular array of atoms, might form a natural three-dimensional "diffraction grating" for x rays. Figure 43-13 shows that if a collimated beam of x rays, continuously distributed in wavelength, is allowed to fall on a crystal, such as sodium chloride, intense beams (corresponding to constructive interference from the many diffracting centers of which the crystal is

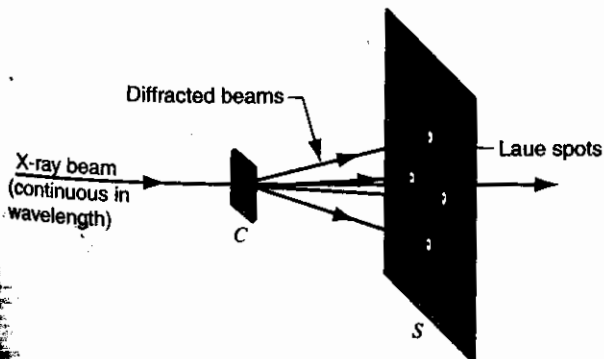


FIGURE 43-13. A beam of x rays strikes a crystal C . Strong diffracted beams appear in certain directions, forming a Laue pattern on the photographic film S .

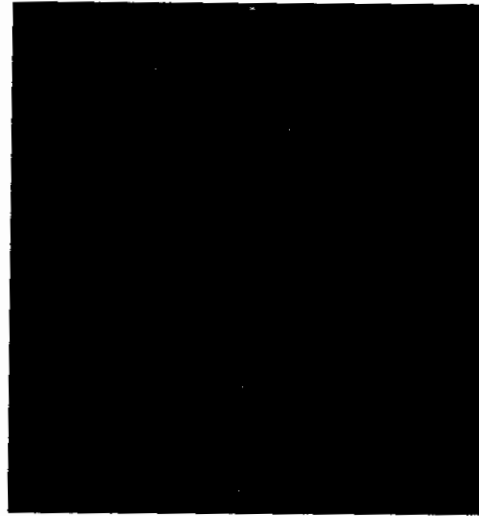


FIGURE 43-14. A Laue x-ray diffraction pattern from a crystal of sodium chloride.

made up) appear in certain sharply defined directions. If these beams fall on a photographic film, they form an assembly of "Laue spots." Figure 43-14, which shows an actual example of these spots, demonstrates that the hypothesis of Laue is indeed correct. The atomic arrangements in the crystal can be deduced from a careful study of the positions and intensities of the Laue spots in much the same way that we might deduce the structure of an optical grating (that is, the detailed profile of its slits) by a study of the positions and intensities of the lines in the interference pattern. Other experimental arrangements have supplanted the Laue technique to a considerable extent today, but the principle remains unchanged (see Question 23).

Figure 43-15 shows how sodium and chlorine atoms (strictly, Na^+ and Cl^- ions) are stacked to form a crystal of sodium chloride. This pattern, which has *cubic* symmetry,

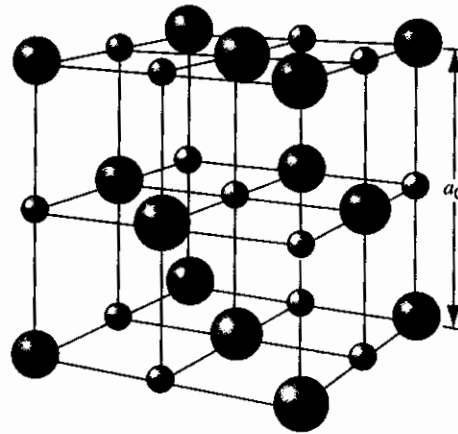


FIGURE 43-15. A model of a sodium chloride crystal, showing how the sodium ions Na^+ (small spheres) and chloride ions Cl^- (large spheres) are stacked in the unit cell, whose edge a_0 has the length 0.563 nm .

is one of the many possible atomic arrangements exhibited by solids. The model represents the *unit cell* for sodium chloride. This is the smallest unit from which the crystal may be built up by repetition in three dimensions. You should verify that no smaller assembly of atoms possesses this property. For sodium chloride, the length a_0 of the cube edge of the unit cell is 0.563 nm.

Each unit cell in sodium chloride has four sodium ions and four chlorine ions associated with it. In Fig. 43-15, the sodium ion in the center belongs entirely to the cell shown. Each of the other twelve sodium ions shown is shared with three adjacent unit cells so that each contributes one-fourth of an ion to the cell under consideration. The total number of sodium ions is then $1 + \frac{1}{4}(12) = 4$. By similar reasoning you can show that although there are fourteen chlorine ions in Fig. 43-15, only four are associated with the unit cell shown.

The unit cell is the fundamental repetitive diffracting unit in the crystal, corresponding to the slit (and its adjacent opaque strip) in the optical diffraction grating of Fig. 43-1. Figure 43-16a shows a particular plane in a sodium chloride crystal. If each unit cell intersected by this plane is represented by a small cube, Fig. 43-16b results. You may imagine each of these figures extended indefinitely in three dimensions.

Let us treat each small cube in Fig. 43-16b as an elementary diffracting center, corresponding to a slit in an optical grating. The *directions* (but not the intensities) of all the diffracted x-ray beams that can emerge from a sodium

chloride crystal (for a given x-ray wavelength and a given orientation of the incident beam) are determined by the geometry of this three-dimensional lattice of diffracting centers. In exactly the same way, the *directions* (but not the intensities) of all the diffracted beams that can emerge from a particular optical grating (for a given wavelength and orientation of the incident beam) are determined only by the geometry of the grating—that is, by the grating spacing d . Representing the unit cell by what is essentially a point, as in Fig. 43-16b, corresponds to representing the slits in a diffraction grating by lines, as we did in discussing the double-slit experiment in Section 41-2.

The *intensities* of the lines from an optical diffraction grating depend on the diffracting characteristics of a single slit, determined in particular by the slit width a ; see, for example, Fig. 43-1 for a set of slits. The characteristics of actual optical gratings are determined by the profile of the grating rulings.

In exactly the same way, the *intensities* of the diffracted beams emerging from a crystal depend on the diffracting characteristics of the unit cell. Fundamentally, the x rays are diffracted by electrons, diffraction by nuclei being negligible in most cases. Thus the diffracting characteristics of a unit cell depend on how the electrons are distributed throughout the volume of the cell. By studying the *directions* of diffracted x-ray beams, we can learn the basic symmetry of the crystal. By studying the *intensities* we can learn how the electrons are distributed in a unit cell. Figure 43-17 shows an example of this technique.

Bragg's Law

Bragg's law predicts the conditions under which diffracted x-ray beams from a crystal are possible. In deriving the law, we ignore the structure of the unit cell, which is related only to the intensities of these beams. The dashed sloping lines in Fig. 43-18a represent the intersection with the plane of the figure of an arbitrary set of planes passing through the elementary diffracting centers. The perpendicular distance between adjacent planes is d . Many other such families of planes, with different *interplanar spacings*, can be defined.

Figure 43-18b shows an incident wave striking the *family* of planes, with the incident rays making an angle θ with the plane.* For a single plane, mirror-like "reflection" occurs for *any* value of θ . To have a constructive interference in the beam diffracted from the entire family of planes in the direction θ , the rays from the separate planes must reinforce each other. This means that the path difference for rays from adjacent planes (abc in Fig. 43-18b) must be an integral number of wavelengths or

$$2d \sin \theta = m\lambda \quad m = 1, 2, 3, \dots \quad (43-12)$$

* In x-ray diffraction it is customary to specify the direction of a wave by giving the angle between the ray and the plane (the *glancing angle*) rather than the angle between the ray and the normal.

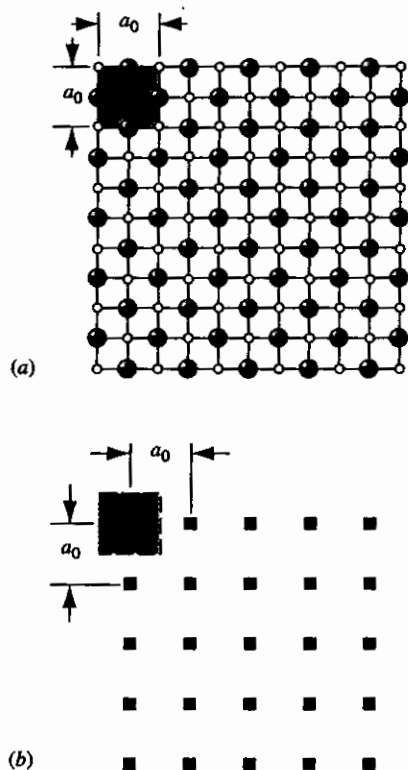


FIGURE 43-16. (a) A plane through a crystal of NaCl, showing the Na and Cl ions. (b) The corresponding unit cells in this section. Each cell is represented by a small black square.

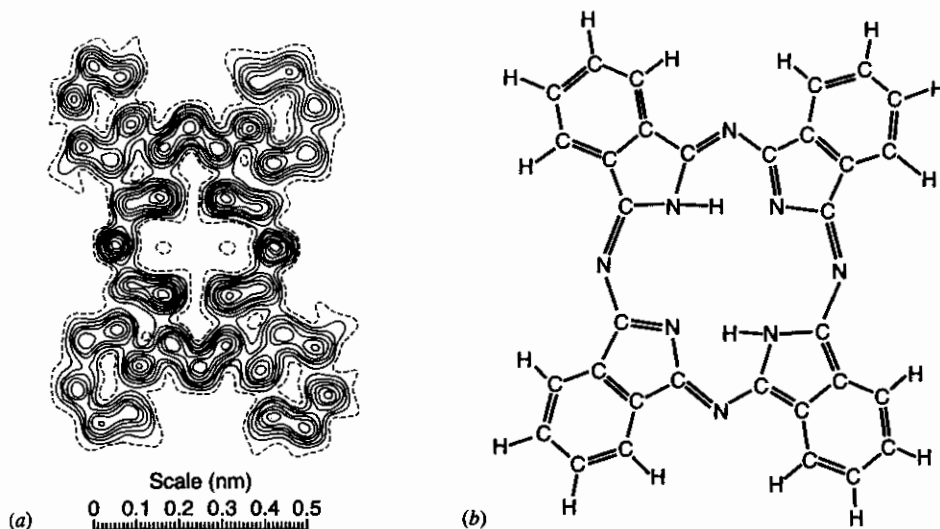


FIGURE 43-17. (a) Electron density contours for phthalocyanine ($C_{32}H_{18}N_8$) determined from the intensity distribution of scattered x rays. The dashed curves represent a density of one electron per 0.01 nm^2 , and each adjacent curve represents an increase of one electron per 0.01 nm^2 . (b) A structural representation of the molecule. Note that the greatest electron density occurs in (a) near the N atoms, which have the largest number of electrons (7). Note also that the H atoms, which contain only a single electron, are not prominent in (a).

This relation is called *Bragg's law* after W. L. Bragg, who first derived it. The quantity d in this equation (the interplanar spacing) is the perpendicular distance between the planes. For the planes of Fig. 43-18a we see that d is related

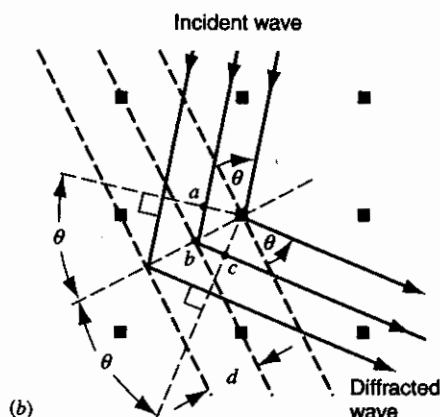
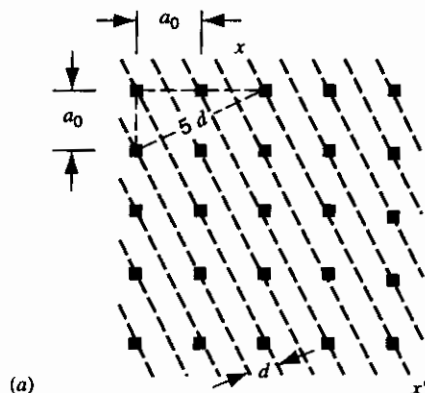


FIGURE 43-18. (a) A section through the NaCl lattice of Fig. 43-16. The dashed lines represent an arbitrary set of parallel planes connecting unit cells. The interplanar spacing is d . (b) An incident beam falls on a set of planes. A strong diffracted beam will be observed if Bragg's law is satisfied.

to the unit cell dimension a_0 by

$$d = \frac{a_0}{\sqrt{5}}. \quad (43-13)$$

If an incident monochromatic x-ray beam falls at an arbitrary angle θ on a particular set of atomic planes, a diffracted beam will *not* result because Eq. 43-12 will not, in general, be satisfied. If the incident x rays are *continuous* in wavelength, diffracted beams will result when wavelengths given by

$$\lambda = \frac{2d \sin \theta}{m} \quad m = 1, 2, 3, \dots$$

are present in the incident beam (see Eq. 43-12).

X-ray diffraction is a powerful tool for studying both x-ray spectra and the arrangement of atoms in crystals. To study the spectrum of an x-ray source, a particular set of crystal planes, having a known spacing d , is chosen. Diffraction from these planes locates different wavelengths at different angles. A detector that can discriminate one angle from another can be used to determine the wavelength of radiation reaching it. On the other hand, we can study the crystal itself, using a monochromatic x-ray beam to determine not only the spacings of various crystal planes but also the structure of the unit cell. The DNA molecule and many other equally complex structures have been mapped by x-ray diffraction methods.

SAMPLE PROBLEM 43-5. At what angles must an x-ray beam with $\lambda = 0.110 \text{ nm}$ fall on the family of planes represented in Fig. 43-18b if a diffracted beam is to exist? Assume the material to be sodium chloride ($a_0 = 0.563 \text{ nm}$).

Solution The interplanar spacing d for these planes is given by Eq. 43-13, or

$$d = \frac{a_0}{\sqrt{5}} = \frac{0.563 \text{ nm}}{\sqrt{5}} = 0.252 \text{ nm}.$$

Equation 43-12 gives

$$\theta = \sin^{-1} \left(\frac{m\lambda}{2d} \right) = \sin^{-1} \left(\frac{(m)(0.110 \text{ nm})}{(2)(0.252 \text{ nm})} \right).$$

Diffracted beams are possible for $\theta = 12.6^\circ$ ($m = 1$), $\theta = 25.9^\circ$ ($m = 2$), $\theta = 40.9^\circ$ ($m = 3$), and $\theta = 60.8^\circ$ ($m = 4$). Higher-order beams cannot exist because they require that $\sin \theta > 1$.

Actually, the unit cell in cubic crystals such as NaCl has symmetry properties that require the intensity of diffracted x-ray beams corresponding to odd values of m to be zero. (See Problem 35.) Thus the only beams that are expected are $\theta = 25.9^\circ$ ($m = 2$) and $\theta = 60.9^\circ$ ($m = 4$).
