3

Diffraction I: Directions of Diffracted Beams

3-1 INTRODUCTION

After our preliminary survey of the physics of x-rays and the geometry of crystals, we can now proceed to fit the two together and discuss the phenomenon of x-ray diffraction, which is an interaction of the two. Historically, this is exactly the way this field of science developed. For many years, mineralogists and crystallographers had accumulated knowledge about crystals, chiefly by measurement of interfacial angles, chemical analysis, and determination of physical properties. There was little knowledge of interior structure, however, although some very shrewd guesses had been made, namely, that crystals were built up by periodic repetition of some unit, probably an atom or molecule, and that these units were situated some 1 or 2 Å apart. On the other hand, there were indications, but only indications, that x-rays might be electromagnetic waves about 1 or 2 Å in wavelength. In addition, the phenomenon of diffraction was well understood, and it was known that diffraction, as of visible light by a ruled grating, occurred whenever wave motion encountered a set of regularly spaced scattering objects, provided that the wavelength of the wave motion was of the same order of magnitude as the repeat distance between the scattering centers.

Such was the state of knowledge in 1912 when the German physicist von Laue (1879–1960) took up the problem. He reasoned that, *if* crystals were composed of regularly spaced atoms which might act as scattering centers for x-rays, and *if* x-rays were electromagnetic waves of wavelength about equal to the interatomic distance in crystals, then it should be possible to diffract x-rays by means of crystals. Under his direction, experiments to test this hypothesis were carried out: a crystal of copper sulfate was set up in the path of a narrow beam of x-rays and a photographic plate was arranged to record the presence of diffracted beams, if any. The second attempt was successful and showed without doubt that x-rays *were* diffracted by the crystal out of the primary beam to form a pattern of spots on the photographic plate. These experiments proved, at one and the same time, the wave nature of x-rays and the periodicity of the arrangement of atoms within a crystal. Hindsight is always easy and these ideas appear quite simple to us now, when viewed from the vantage point of more than sixty years' development of the subject, but they were not at all obvious in 1912, and von Laue's hypothesis and its experimental verification must stand as a great intellectual achievement [3.1].

The account of these experiments was read with great interest by two English physicists, W. H. Bragg (1862–1942) and his son W. L. Bragg (1890–1971). The

latter, although only a young student at the time—it was still the year 1912—successfully analyzed the Laue experiment and was able to express the necessary conditions for diffraction in a considerably simpler mathematical form than that used by von Laue. He also attacked the problem of crystal structure with the new tool of x-ray diffraction and, in the following year, solved the structures of NaCl, KCl, KBr, and KI, all of which have the NaCl structure; these were the first complete crystal-structure determinations ever made [3.2]. The simpler structures of metals like iron and copper were not determined until later.

3-2 DIFFRACTION

Diffraction is due essentially to the existence of certain phase relations between two or more waves, and it is advisable, at the start, to get a clear notion of what is meant by phase relations. Consider a beam of x-rays, such as beam 1 in Fig. 3-1, proceeding from left to right. For convenience only, this beam is assumed to be plane-polarized in order that we may draw the electric field vector E always in one plane. We may imagine this beam to be composed of two equal parts, ray 2 and ray 3, each of half the amplitude of beam 1. These two rays, on the wave front AA', are said to be completely *in phase* or in step; i.e., their electric-field vectors have the same magnitude and direction at the same instant at any point x measured along the direction of propagation of the wave. A *wave front* is a surface perpendicular to this direction of propagation.

Now consider an imaginary experiment, in which ray 3 is allowed to continue in a straight line but ray 2 is diverted by some means into a curved path before
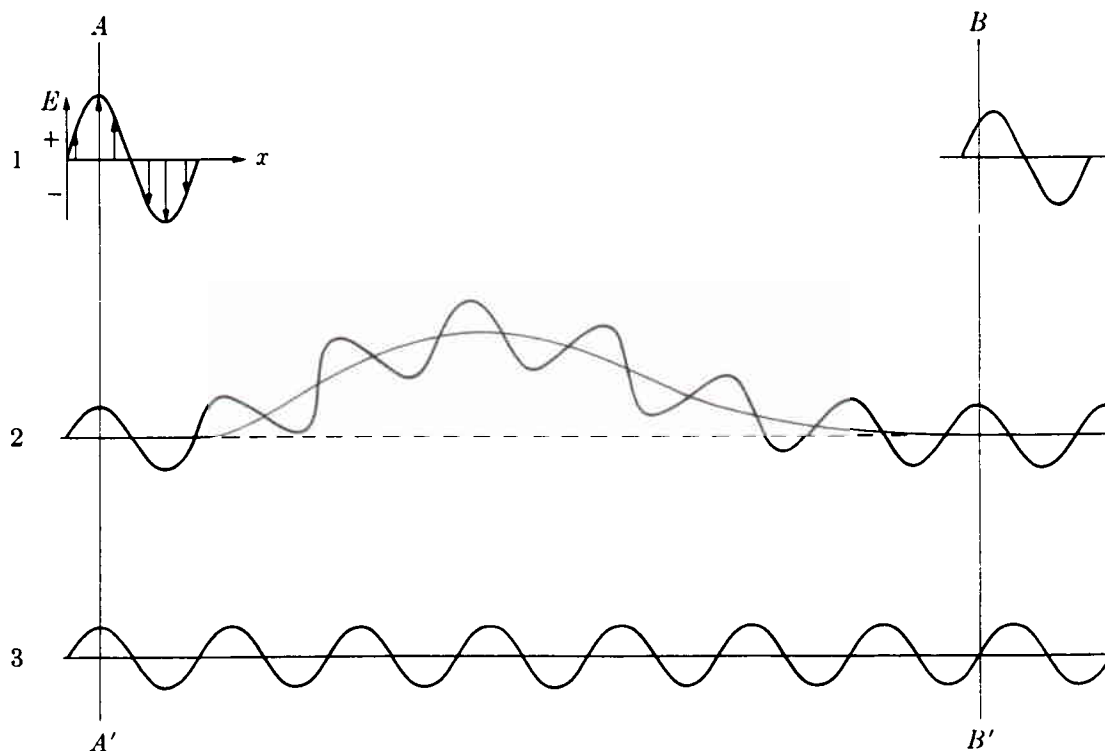

Fig. 3-1   Effect of path difference on relative phase.

rejoining ray **3**. What is the situation on the wave front *BB'* where both rays are proceeding in the original direction? On this front, the electric vector of ray **2** has its maximum value at the instant shown, but that of ray **3** is zero. The two rays are therefore *out of phase*. If we add these two imaginary components of the beam together, we find that beam **1** now has the form shown in the upper right of the drawing. If the amplitudes of rays **2** and **3** are each 1 unit, then the amplitude of beam **1** at the left is 2 units and that of beam **1** at the right is 1.4 units, if a sinusoidal variation of **E** with *x* is assumed.

Two conclusions may be drawn from this illustration:

1. Differences in the length of the path traveled lead to differences in phase.

2. The introduction of phase differences produces a change in amplitude.

The greater the path difference, the greater the difference in phase, since the path difference, measured in wavelengths, exactly equals the phase difference, also measured in wavelengths. If the diverted path of ray **2** in Fig. 3–1 were a quarter wavelength longer than shown, the phase difference would be a half wavelength. The two rays would then be completely out of phase on the wave front *BB'* and beyond, and they would therefore annul each other, since at any point their electric vectors would be either both zero or of the same magnitude and opposite in direction. If the difference in path length were made three quarters of a wavelength greater than shown, the two rays would be one complete wavelength out of phase, a condition indistinguishable from being completely in phase since in both cases the two waves would combine to form a beam of amplitude 2 units, just like the original beam. We may conclude that two rays are completely in phase whenever their path lengths differ either by zero or by a whole number of wavelengths.

Differences in the path length of various rays arise quite naturally when we consider how a crystal diffracts x-rays. Figure 3–2 shows a section of a crystal, its atoms arranged on a set of parallel planes *A, B, C, D, . . .*, normal to the plane of the drawing and spaced a distance *d'* apart. Assume that a beam of perfectly parallel, perfectly monochromatic x-rays of wavelength λ is incident on this crystal at an angle θ, called the Bragg angle, where θ is measured between the incident beam and the particular crystal planes under consideration.

We wish to know whether this incident beam of x-rays will be diffracted by the crystal and, if so, under what conditions. *A diffracted beam may be defined as a beam composed of a large number of scattered rays mutually reinforcing one another.* Diffraction is, therefore, essentially a scattering phenomenon and not one involving any "new" kind of interaction between x-rays and atoms. We saw in Sec. 1–5 that atoms scatter incident x-rays in all directions, and we shall see presently that in some of these directions the scattered beams will be completely in phase and so reinforce each other to form diffracted beams.

For the particular conditions described by Fig. 3–2 the only diffracted beam formed is that shown, namely one making an angle θ of reflection* equal to the

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* Note that these angles are defined differently in x-ray diffraction and in general optics. In the latter, the angles of incidence and reflection are the angles which the incident and reflected beams make with the *normal* to the reflecting surface.
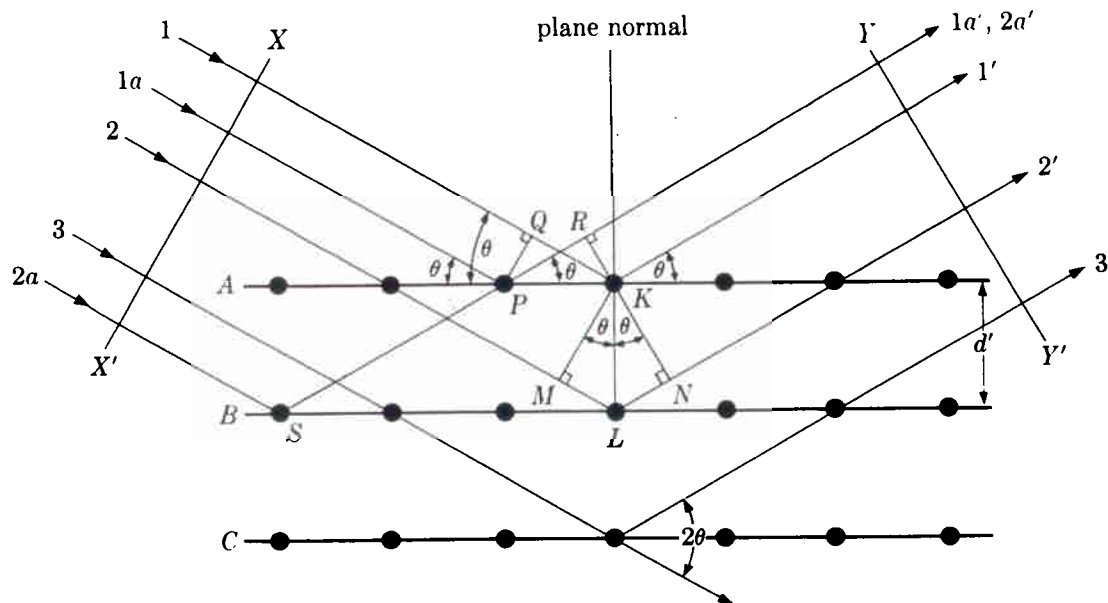
Fig. 3–2 Diffraction of x-rays by a crystal.

angle θ of incidence. We will show this, first, for one plane of atoms and, second, for all the atoms making up the crystal. Consider rays **1** and **1a** in the incident beam; they strike atoms K and P in the first plane of atoms and are scattered in all directions. Only in the directions **1'** and **1a'**, however, are these scattered beams completely in phase and so capable of reinforcing one another; they do so because the difference in their length of path between the wave fronts XX' and YY' is equal to

$$QK - PR = PK \cos \theta - PK \cos \theta = 0.$$

Similarly, the rays scattered by all the atoms in the first plane in a direction parallel to **1'** are in phase and add their contributions to the diffracted beam. This will be true of all the planes separately, and it remains to find the condition for reinforcement of rays scattered by atoms in different planes. Rays **1** and **2**, for example, are scattered by atoms K and L, and the path difference for rays $1K1'$ and $2L2'$ is

$$ML + LN = d' \sin \theta + d' \sin \theta.$$

This is also the path difference for the overlapping rays scattered by S and P in the direction shown, since in this direction there is no path difference between rays scattered by S and L or P and K. Scattered rays **1'** and **2'** will be completely in phase if this path difference is equal to a whole number n of wavelengths, or if

$$n\lambda = 2d' \sin \theta. \qquad (3\text{--}1)$$

This relation was first formulated by W. L. Bragg and is known as the Bragg law. It states the essential condition which must be met if diffraction is to occur. n is called the order of reflection; it may take on any integral value consistent with $\sin \theta$ not exceeding unity and is equal to the number of wavelengths in the path difference between rays scattered by *adjacent* planes. Therefore, for fixed values of λ and d', there may be several angles of incidence $\theta_1, \theta_2, \theta_3 \ldots$ at which diffraction may occur, corresponding to $n = 1, 2, 3, \ldots$. In a first-order reflection

($n = 1$), the scattered rays **1'** and **2'** of Fig. 3-2 would differ in length of path (and in phase) by one wavelength, rays **1'** and **3'** by two wavelengths, rays **1'** and **4'** by three wavelengths, and so on throughout the crystal. The rays scattered by all the atoms in all the planes are therefore completely in phase and reinforce one another (constructive interference) to form a diffracted beam in the direction shown. In all other directions of space the scattered beams are out of phase and annul one another (destructive interference). The diffracted beam is rather strong compared to the sum of all the rays scattered in the same direction, simply because of the reinforcement which occurs,* but extremely weak compared to the incident beam since the atoms of a crystal scatter only a small fraction of the energy incident on them.

It is helpful to distinguish three scattering modes:

1. By atoms arranged randomly in space, as in a monatomic gas. This scattering occurs in *all* directions and is weak. Intensities add.

2. By atoms arranged periodically in space, as in a perfect crystal:

a) In a very few directions, those satisfying the Bragg law, the scattering is strong and is called diffraction. Amplitudes add.

b) In most directions, those not satisfying the Bragg law, there is *no* scattering because the scattered rays cancel one another.

At first glance, the diffraction of x-rays by crystals and the reflection of visible light by mirrors appear very similar, since in both phenomena the angle of incidence is equal to the angle of reflection. It seems that we might regard the planes of atoms as little mirrors which "reflect" the x-rays. Diffraction and reflection, however, differ fundamentally in at least three aspects:

1. The diffracted beam from a crystal is built up of rays scattered by all the atoms of the crystal which lie in the path of the incident beam. The reflection of visible light takes place in a thin surface layer only.

2. The diffraction of monochromatic x-rays takes place only at those particular angles of incidence which satisfy the Bragg law. The reflection of visible light takes place at any angle of incidence.

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* If the scattering atoms were not arranged in a regular, periodic fashion but in some independent manner, then the rays scattered by them would have a random phase relationship to one another. In other words, there would be an equal probability of the phase difference between any two scattered rays having any value between zero and one wavelength. Neither constructive nor destructive interference takes place under these conditions, and the intensity of the beam scattered in a particular direction is simply *the sum of the intensities* of all the rays scattered in that direction. If there are N scattered rays each of amplitude A and therefore of intensity A^2 in arbitrary units, then the intensity of the scattered beam is NA^2. On the other hand, if the rays are scattered by the atoms of a crystal in a direction satisfying the Bragg law, then they are all in phase and the amplitude of the scattered beam is *the sum of the amplitudes* of the scattered rays. The total amplitude is then N times the amplitude A of each scattered ray, or NA. The intensity of the scattered beam is therefore N^2A^2, or N times as large as if reinforcement had not occurred. Since N is very large for the scattering of x-rays from even a small bit of crystal, ($N = 1.1 \times 10^{19}$ atoms for 1 mg of iron), the role of reinforcement in producing a strong diffracted beam is considerable.

3. The reflection of visible light by a good mirror is almost 100 percent efficient. The intensity of a diffracted x-ray beam is extremely small compared to that of the incident beam.

Despite these differences, we often speak of "reflecting planes" and "reflected beams" when we really mean diffracting planes and diffracted beams. This is common usage and, from now on, we will frequently use these terms without quotation marks but with the tacit understanding that we really mean diffraction and not reflection.*

To sum up, diffraction is essentially a scattering phenomenon in which a large number of atoms cooperate. Since the atoms are arranged periodically on a lattice, the rays scattered by them have definite phase relations between them; these phase relations are such that destructive interference occurs in most directions of scattering, but in a few directions constructive interference takes place and diffracted beams are formed. The two essentials are a wave motion capable of interference (x-rays) and a set of periodically arranged scattering centers (the atoms of a crystal).

3-3 THE BRAGG LAW

Two geometrical facts are worth remembering: (1) The incident beam, the normal to the reflecting plane, and the diffracted beam are always coplanar. (2) The angle between the diffracted beam and the transmitted beam is always 2θ. This is known as the diffraction angle, and it is this angle, rather than θ, which is usually measured experimentally.

As previously stated, diffraction in general occurs only when the wavelength of the wave motion is of the same order of magnitude as the repeat distance between scattering centers. This requirement follows from the Bragg law. Since $\sin \theta$ cannot exceed unity, we may write

$$\frac{n\lambda}{2d'} = \sin \theta < 1. \tag{3-2}$$

Therefore, $n\lambda$ must be less than $2d'$. For diffraction, the smallest value of n is 1. ($n = 0$ corresponds to the beam diffracted in the same direction as the transmitted beam. It cannot be observed.) Therefore the condition for diffraction at any observable angle 2θ is

$$\lambda < 2d'. \tag{3-3}$$

For most sets of crystal planes d' is of the order of 3 Å or less, which means that λ cannot exceed about 6 Å. A crystal could not possibly diffract ultraviolet radiation, for example, of wavelength about 500 Å. On the other hand, if λ is very small, the diffraction angles are too small to be conveniently measured.

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* For the sake of completeness, it should be mentioned that x-rays *can* be totally reflected by a solid surface, just as visible light is by a mirror, but only at very small angles of incidence (below about one degree).

The Bragg law may be written in the form

$$\lambda = 2\frac{d'}{n}\sin\theta. \qquad (3\text{–}4)$$

Since the coefficient of λ is now unity, we can consider a reflection of any order as a first-order reflection from planes, real or fictitious, spaced at a distance $1/n$ of the previous spacing. This turns out to be a real convenience, so we set $d = d'/n$ and write the Bragg law in the form

$$\boxed{\lambda = 2d\sin\theta}. \qquad (3\text{–}5)$$

This form will be used throughout this book.

This usage is illustrated by Fig. 3–3. Consider the second-order 100 reflection* shown in (a). Since it is second-order, the path difference ABC between rays scattered by adjacent (100) planes must be two whole wavelengths. If there is no real plane of atoms between the (100) planes, we can always imagine one as in Fig. 3–3(b), where the dotted plane midway between the (100) planes forms part of the (200) set of planes. For the same reflection as in (a), the path difference DEF between rays scattered by adjacent (200) planes is now only one whole wavelength, so that this reflection can properly be called a first-order 200 reflection. Similarly, 300, 400, etc., reflections are equivalent to reflections of the third, fourth, etc., orders from the (100) planes. In general, an nth-order reflection from (hkl) planes of spacing d' may be considered as a first-order reflection from the $(nh\ nk\ nl)$ planes of spacing $d = d'/n$. Note that this convention is in accord with the definition of Miller indices since $(nh\ nk\ nl)$ are the Miller indices of planes parallel to the (hkl) planes but with $1/n$th the spacing of the latter.
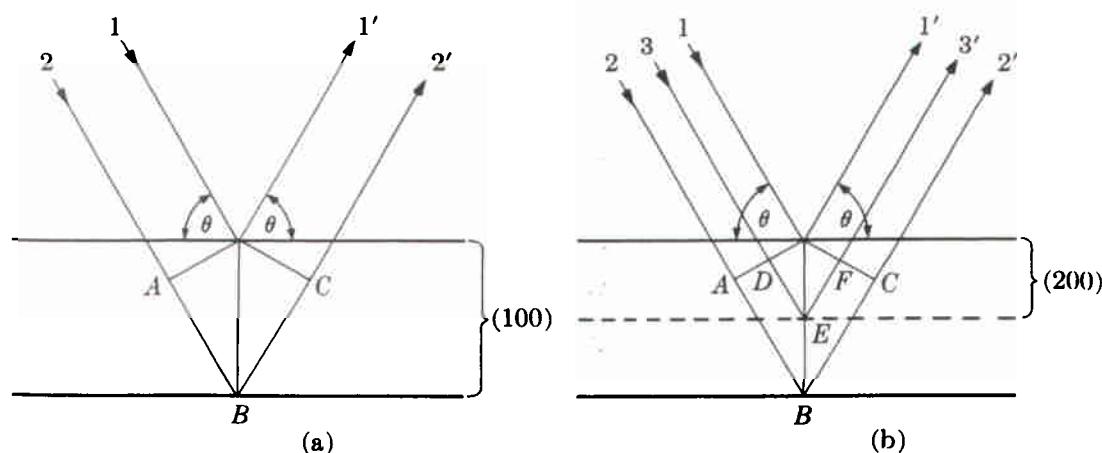

Fig. 3–3 Equivalence of (a) a second-order 100 reflection and (b) a first-order 200 reflection.

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* This means the reflection from the (100) planes. Conventionally, the Miller indices of a reflecting plane hkl, written without parentheses, stand for the reflected beam from the plane (hkl).

3-4 X-RAY SPECTROSCOPY

Experimentally, the Bragg law can be applied in two ways. By using x-rays of known wavelength λ and measuring θ, we can determine the spacing d of various planes in a crystal: this is *structure analysis* and is the subject, in one way or another, of the greater part of this book. Alternatively, we can use a crystal with planes of known spacing d, measure θ, and thus determine the wavelength λ of the radiation used: this is *x-ray spectroscopy*.

The essential features of an x-ray spectrometer are shown in Fig. 3-4. X-rays from the tube T are incident on a crystal C which may be set at any desired angle to the incident beam by rotation about an axis through O, the center of the spectrometer circle. D is a counter which measures the intensity of the diffracted x-rays; it can also be rotated about O and set at any desired angular position. The crystal is usually cut or cleaved so that a particular set of reflecting planes of known spacing is parallel to its surface, as suggested by the drawing. In use, the crystal is positioned so that its reflecting planes make some particular angle θ with the incident beam, and D is set at the corresponding angle 2θ. The intensity of the diffracted beam is then measured and its wavelength calculated from the Bragg law, this procedure being repeated for various angles θ. It is in this way that curves such as Fig. 1-5 and the characteristic wavelengths tabulated in Appendix 7 were obtained. W. H. Bragg designed and used the first x-ray spectrometer, and the Swedish physicist Siegbahn developed it into an instrument of very high precision.

Except for one application, the subject of chemical analysis described in Chap. 15, we are here concerned with x-ray spectroscopy only insofar as it concerns certain units of wavelength. Wavelength measurements made in the way just described are obviously relative, and their accuracy is no greater than the accuracy with which the plane spacing of the crystal is known.

Before considering how the first plane spacing was determined, we must digress to consider the subject of *x-ray density*. Normally the density of a solid is found by measuring the volume, usually of the order of a few cubic centimeters, and the weight of a particular specimen. But x-ray diffraction allows us to determine the lattice parameters of a crystal's unit cell, and therefore its volume, together with the number of atoms in the cell. We can therefore base a density
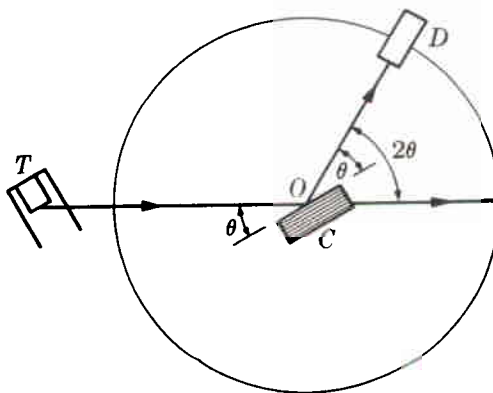

Fig. 3-4 The x-ray spectrometer.

determination, not on a few cubic centimeters but on the volume of a single unit cell, by defining the

$$\text{x-ray density} = \frac{\text{weight of atoms in unit cell}}{\text{volume of unit cell}}.$$

$$\rho = \frac{\sum A/N}{V} \qquad (3\text{-}6)$$

where ρ = density (gm/cm^3), $\sum A$ = sum of the atomic weights of all the atoms in the unit cell, N = Avogadro's number, and V = volume of unit cell (cm^3). Inserting the current value of N, we have

$$\rho = \frac{\sum A}{NV} = \frac{\sum A}{(6.02257 \times 10^{23})(V' \times 10^{-24})} = \frac{1.66042 \sum A}{V'} \qquad (3\text{-}7)$$

where ρ is in gm/cm^3 and V' is the unit-cell volume in Å^3.

The macroscopic density of a particular specimen, determined from the weight and volume of that specimen, is usually less than, and cannot exceed, the x-ray density, because the macroscopic specimen will usually contain minute cracks and pores. The x-ray density is therefore a useful quantity to know. By comparing it to the macroscopic density of, for example, a pressed and sintered metal or ceramic compact, one can calculate the percent porosity in the compact. X-ray densities are sometimes loosely called "theoretical densities"; they are not theoretical because they are determined experimentally.

To return to the problem of wavelength determination, it is an interesting and crucial fact that Bragg was able to solve the cyrstal structure of NaCl without knowing the wavelength of the x-rays being diffracted. All he knew—all he needed to know—was that there was one *single*, strong wavelength in the radiation from the x-ray tube, namely, the strong $K\alpha$ line of the tube target. Once the NaCl structure is known [Fig. 2-18(b)], it follows that there are four sodium and four chlorine atoms per unit cell, and that

$$\sum A = 4(\text{at. wt. Na}) + 4(\text{at. wt. Cl}).$$

If this value is inserted into Eq. (3-7) together with the macroscopic density ρ, the volume V' of the unit cell can be found. Because NaCl is cubic, the lattice parameter a is given simply by the cube root of V'. From this value of a and the cubic plane-spacing equation (Eq. 2-5), the spacing of any set of planes can be found.

In this way, Siegbahn obtained a value of 2.814 Å for the spacing of the (200) planes of rock salt (NaCl), which he could use as a basis for wavelength measurements. This spacing was known to only four significant figures, because it was derived from a macroscopic density of that precision. However, Siegbahn was able to measure wavelengths in terms of this spacing much more accurately, namely, to six significant figures. Not wishing to throw away the high relative precision he could attain, he wisely decided to arbitrarily define a new unit in which relative wavelengths could be expressed. This was the X unit (XU), so called because its true value in absolute units (angstroms) was unknown. By defining the

(200) spacing of rock salt to six significant figures as 2814.00 XU, the new unit was made as nearly as possible equal to 0.001 Å.

Once a particular wavelength was determined in terms of this spacing, the spacing of a given set of planes in any other crystal could be measured. Siegbahn thus measured the (211) spacing of calcite (CaCO$_3$), which he found more suitable as a standard crystal, and thereafter based all his wavelength measurements on this spacing. Its value is 3029.45 XU. Later on, the kilo X unit (kX) was introduced, a thousand times as large as the X unit and nearly equal to an angstrom. The kX unit is therefore *defined* by the relation

$$1 \text{ kX} = \frac{(211) \text{ plane spacing of calcite}}{3.02945}. \tag{3-8}$$

On this basis, Siegbahn and his associates made very accurate measurements of wavelength in relative (kX) units and these measurements form the basis of most published wavelength tables.

It was found later that x-rays could be diffracted by a ruled grating such as is used in the spectroscopy of visible light, provided that the angle of incidence (the angle between the incident beam and the plane of the grating) is kept below the critical angle for total reflection. Gratings thus offer a means of making absolute wavelength measurements, independent of any knowledge of crystal structure. By a comparison of values so obtained with those found by Siegbahn from crystal diffraction, it was possible to calculate the following relation between the relative and absolute units:

$$1 \text{ kX} = 1.00202 \text{ Å}.$$

This conversion factor was decided on in 1946 by international agreement. Later work improved the accuracy of this factor, and the relation is now believed to be

$$\boxed{1 \text{ kX} = 1.002056 \text{ Å*}}. \tag{3-9}$$

Note that this relation is stated in terms of still another unit, the Å* unit, which was introduced because of the still remaining uncertainty in the conversion factor. The difference between Å and Å* is only some five parts per million, and the distinction between the two units is negligible except in work of the very highest accuracy.

The present situation is not entirely clear, but the wavelength tables published in 1974 by the International Union of Crystallography [Vol. 4, G.11], which are reproduced in Appendix 7, are based on Eq. (3-9).

The distinction between kX and Å is unimportant if no more than about three significant figures are involved, because the kX unit is only about 0.2 percent larger than the angstrom. In precise work, on the other hand, units must be correctly stated, and on this point there has been considerable confusion in the past. Some wavelength values published prior to about 1946 are stated to be in angstrom units but are actually in kX units. Some crystallographers have used such a value as the basis for a precise measurement of the lattice parameter of a crystal and the result has been stated, again incorrectly, in angstrom units. Many

published parameters are therefore in error, and it is unfortunately not always easy to determine which ones are and which ones are not. The only safe rule to follow, in stating a precise parameter, is to give the wavelength of the radiation used in its determination. Similarly, any published table of wavelengths can be tested for the correctness of its units by noting the wavelength given for a particular characteristic line, Cu $K\alpha_1$ for example. The wavelength of this line is 1.540562 Å* (1974 value, 1.002056 as conversion factor), 1.54051 Å (1946 value, 1.00202 factor), or 1.53740 kX. See Appendix 7 for the estimated accuracy of the wavelengths listed there.

3-5 DIFFRACTION DIRECTIONS

What determines the possible directions, i.e., the possible angles 2θ, in which a given crystal can diffract a beam of monochromatic x-rays? Referring to Fig. 3-3, we see that various diffraction angles $2\theta_1$, $2\theta_2$, $2\theta_3$, ... can be obtained from the (100) planes by using a beam incident at the correct angle θ_1, θ_2, θ_3, ... and producing first-, second-, third-, ... order reflections. But diffraction can also be produced by the (110) planes, the (111) planes, the (213) planes, and so on. We obviously need a general relation which will predict the diffraction angle for *any* set of planes. This relation is obtained by combining the Bragg law and the plane-spacing equation (Appendix 3) applicable to the particular crystal involved.

For example, if the crystal is cubic, then

$$\lambda = 2d \sin \theta$$

and

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2}.$$

Combining these equations, we have

$$\sin^2 \theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2). \tag{3-10}$$

This equation predicts, for a particular incident wavelength λ and a particular cubic crystal of unit cell size a, all the possible Bragg angles at which diffraction can occur from the planes (hkl). For (110) planes, for example, Eq. (3-10) becomes

$$\sin^2 \theta_{110} = \frac{\lambda^2}{2a^2}.$$

If the crystal is tetragonal, with axes a and c, then the corresponding general equation is

$$\sin^2 \theta = \frac{\lambda^2}{4}\left(\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}\right), \tag{3-11}$$

and similar equations can readily be obtained for the other crystal systems.

These examples show that the directions in which a beam of given wavelength is diffracted by a given set of lattice planes are determined by the crystal system to which the crystal belongs and its lattice parameters. In short, *diffraction directions are determined solely by the shape and size of the unit cell*. This is an important

point and so is its converse: all we can possibly determine about an unknown crystal by measurements of the *directions* of diffracted beams are the shape and size of its unit cell. We will find, in the next chapter, that the *intensities* of diffracted beams are determined by the positions of the atoms within the unit cell, and it follows that we must measure intensities if we are to obtain any information at all about atom positions. We will find, for many crystals, that there are particular atomic arrangements which reduce the intensities of some diffracted beams to zero. In such a case, there is simply no diffracted beam at the angle predicted by an equation of the type of Eqs. (3-10) and (3-11). It is in this sense that equations of this kind predict all *possible* diffracted beams.

3-6 DIFFRACTION METHODS

Diffraction can occur whenever the Bragg law, $\lambda = 2d \sin \theta$, is satisfied. This equation puts very stringent conditions on λ and θ for any given crystal. With monochromatic radiation, an arbitrary setting of a single crystal in a beam of x-rays will not in general produce *any* diffracted beams. Some way of satisfying the Bragg law must be devised, and this can be done by continuously varying either λ or θ during the experiment. The ways in which these quantities are varied distinguish the three main diffraction methods:

	λ	θ
Laue method	Variable	Fixed
Rotating-crystal method	Fixed	Variable (in part)
Powder method	Fixed	Variable

Laue Method

The Laue method was the first diffraction method ever used, and it reproduces von Laue's original experiment. A beam of white radiation, the continuous spectrum from an x-ray tube, is allowed to fall on a fixed single crystal. The Bragg angle θ is therefore fixed for every set of planes in the crystal, and each set picks out and diffracts that particular wavelength which satisfies the Bragg law for the particular values of d and θ involved. Each diffracted beam thus has a different wavelength.

There are two variations of the Laue method, depending on the relative positions of source, crystal, and film (Fig. 3-5). In each, the film is flat and placed perpendicular to the incident beam. The film in the *transmission Laue method* (the original Laue method) is placed behind the crystal so as to record the beams diffracted in the forward direction. This method is so called because the diffracted beams are partially transmitted through the crystal. In the *back-reflection Laue method* the film is placed between the crystal and the x-ray source, the incident beam passing through a hole in the film, and the beams diffracted in a backward direction are recorded.

In either method, the diffracted beams form an array of spots on the film as shown in Fig. 3-6. This array of spots is commonly called a *pattern*, but the term is not used in any strict sense and does not imply any periodic arrangement of the
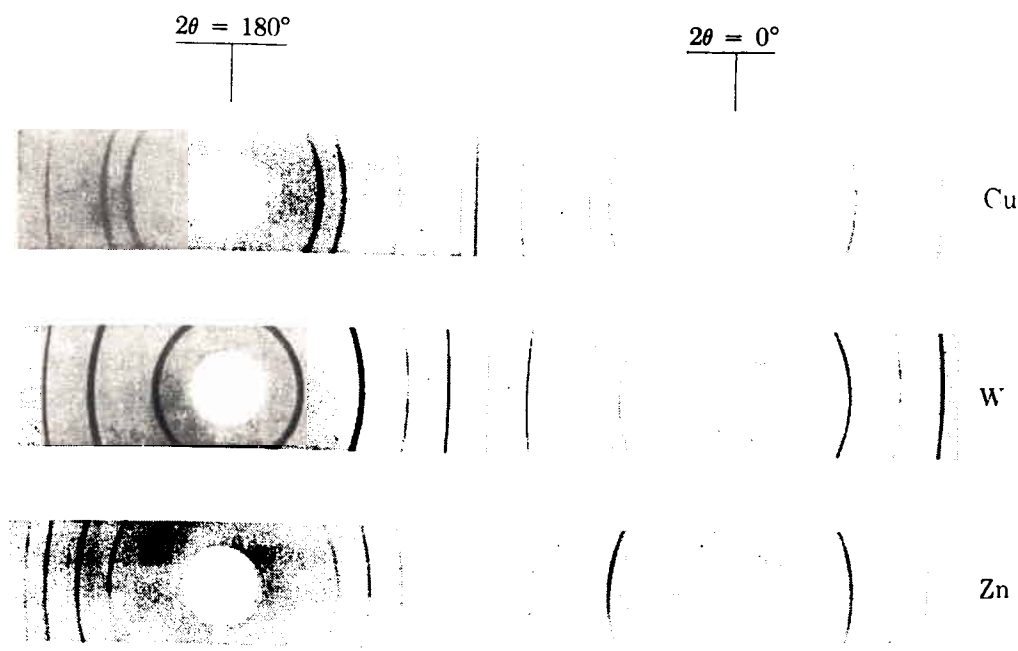
$2\theta = 180°$ $2\theta = 0°$

Fig. 3–13 Debye–Scherrer powder patterns of copper (FCC), tungsten (BCC), and zinc (HCP). Filtered copper radiation, camera diameter = 5.73 cm.

in that the counter intercepts and measures only a short arc of any one cone of diffracted rays.

3-7 DIFFRACTION UNDER NONIDEAL CONDITIONS

Before going any further, it is important to stop and consider with some care the derivation of the Bragg law given in Sec. 3-2 in order to understand precisely under what conditions it is strictly valid. In our derivation we assumed certain ideal conditions, namely a perfect crystal and an incident beam composed of perfectly parallel and strictly monochromatic radiation. These conditions never actually exist, so we must determine the effect on diffraction of various kinds of departure from the ideal.

In particular, the way in which destructive interference is produced in all directions except those of the diffracted beams is worth examining in some detail, both because it is fundamental to the theory of diffraction and because it will lead us to a method for estimating the size of very small crystals. We will find that only the infinite crystal is really perfect and that small size alone, of an otherwise perfect crystal, can be considered a crystal imperfection.

The condition for reinforcement used in Sec. 3-2 is that the waves involved must differ in path length, that is, in phase, by exactly an integral number of wavelengths. But suppose that the angle θ in Fig. 3-2 is such that the path difference for rays scattered by the first and second planes is only a quarter wavelength. These rays do not annul one another but, as we saw in Fig. 3-1, simply unite to form a beam of smaller amplitude than that formed by two rays which are completely in phase. How then does destructive interference take place? The answer lies in the contributions from planes deeper in the crystal. Under the assumed

conditions, the rays scattered by the second and third planes would also be a quarter wavelength out of phase. But this means that the rays scattered by the first and third planes are exactly half a wavelength out of phase and would completely cancel one another. Similarly, the rays from the second and fourth planes, third and fifth planes, etc., throughout the crystal, are completely out of phase; the result is destructive interference and no diffracted beam. *Destructive interference is therefore just as much a consequence of the periodicity of atom arrangement as is constructive interference.*

This is an extreme example. If the path difference between rays scattered by the first two planes differs only slightly from an integral number of wavelengths, then the plane scattering a ray exactly out of phase with the ray from the first plane will lie deep within the crystal. If the crystal is so small that this plane does not exist, then complete cancellation of all the scattered rays will not result. It follows that there is a connection between the amount of "out-of-phaseness" that can be tolerated and the size of the crystal. We will find that very small crystals cause broadening (a small angular divergence) of the diffracted beam, i.e., diffraction (scattering) at angles near to, but not equal to, the exact Bragg angle. We must therefore consider the scattering of rays incident on the crystal planes at angles deviating slightly from the exact Bragg angle.

Suppose, for example, that the crystal has a thickness t measured in a direction perpendicular to a particular set of reflecting planes (Fig. 3-14). Let there be $(m + 1)$ planes in this set. We will regard the Bragg angle θ as a variable and call θ_B the angle which exactly satisfies the Bragg law for the particular values of λ and d involved, or

$$\lambda = 2d \sin \theta_B.$$

In Fig. 3-14, rays $A, D, \ldots, M$ make exactly this angle θ_B with the reflecting planes. Ray D', scattered by the first plane below the surface, is therefore one
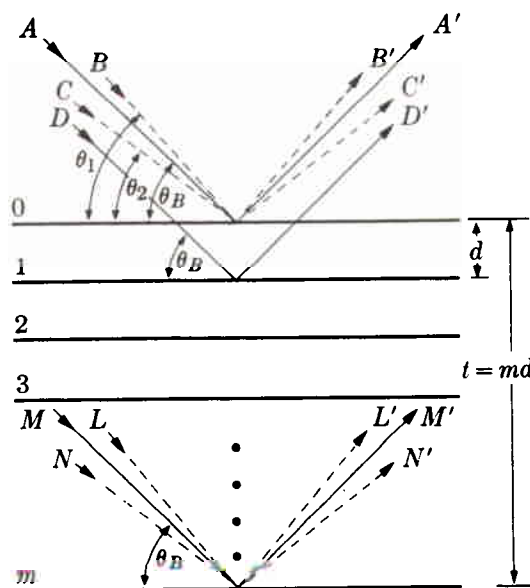

Fig. 3-14 Effect of crystal size on diffraction.

wavelength out of phase with **A′**; and ray **M′**, scattered by the mth plane below the surface, is m wavelengths out of phase with **A′**. Therefore, at a diffraction angle $2\theta_B$, rays **A′**, **D′**, ..., **M′** are completely in phase and unite to form a diffracted beam of maximum amplitude, i.e., a beam of maximum intensity, since the intensity is proportional to the square of the amplitude.

When we consider incident rays that make Bragg angles only slightly different from θ_B, we find that destructive interference is not complete. Ray **B**, for example, makes a slightly larger angle θ_1, such that ray **L′** from the mth plane below the surface is $(m + 1)$ wavelengths out of phase with **B′**, the ray from the surface plane. This means that midway in the crystal there is a plane scattering a ray which is one-half (actually, an integer plus one-half) wavelength out of phase with ray **B′** from the surface plane. These rays cancel one another, and so do the other rays from similar pairs of planes throughout the crystal, the net effect being that rays scattered by the top half of the crystal annul those scattered by the bottom half. The intensity of the beam diffracted at an angle $2\theta_1$ is therefore zero. It is also zero at an angle $2\theta_2$ where θ_2 is such that ray **N′** from the mth plane below the surface is $(m - 1)$ wavelengths out of phase with ray **C′** from the surface plane. We have therefore found two limiting angles, $2\theta_1$ and $2\theta_2$, at which the diffracted intensity must drop to zero. It follows that the diffracted intensity at angles near $2\theta_B$, but not greater than $2\theta_1$ or less than $2\theta_2$, is *not zero* but has a value intermediate between zero and the maximum intensity of the beam diffracted at an angle $2\theta_B$. The curve of diffracted intensity vs. 2θ will thus have the form of Fig. 3-15(a) in contrast to Fig. 3-15(b), which illustrates the hypothetical case of diffraction occurring only at the exact Bragg angle.

The width of the diffraction curve of Fig. 3-15(a) increases as the thickness of the crystal decreases, because the angular range $(2\theta_1 - 2\theta_2)$ increases as m
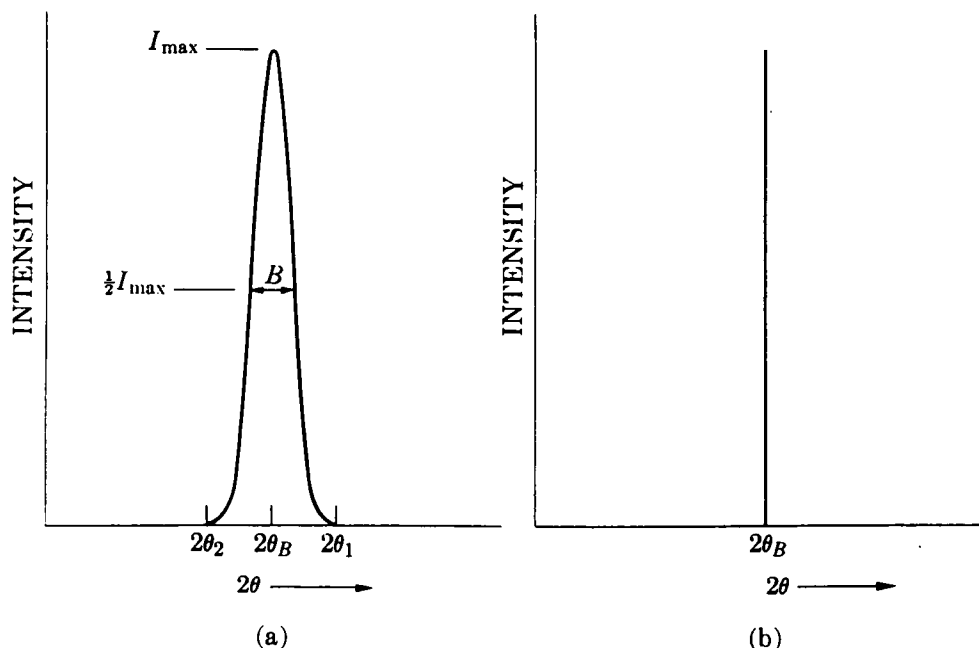

Fig. 3-15   Effect of fine particle size on diffraction curves (schematic).

decreases. The width B is usually measured, in radians, at an intensity equal to half the maximum intensity. [Note that B is an angular width, in terms of 2θ (not θ), and not a linear width.] As a rough measure of B, we can take half the difference between the two extreme angles at which the intensity is zero, which amounts to assuming that the diffraction line is triangular in shape. Therefore,

$$B = \tfrac{1}{2}(2\theta_1 - 2\theta_2) = \theta_1 - \theta_2.$$

We now write path-difference equations for these two angles, similar to Eq. (3–1) but related to the entire thickness of the crystal rather than to the distance between adjacent planes:

$$2t \sin \theta_1 = (m + 1)\lambda,$$
$$2t \sin \theta_2 = (m - 1)\lambda.$$

By subtraction we find

$$t(\sin \theta_1 - \sin \theta_2) = \lambda,$$
$$2t \cos \left(\frac{\theta_1 + \theta_2}{2}\right) \sin \left(\frac{\theta_1 - \theta_2}{2}\right) = \lambda.$$

But θ_1 and θ_2 are both very nearly equal to θ_B, so that

$$\theta_1 + \theta_2 = 2\theta_B \quad \text{(approx.)}$$

and

$$\sin \left(\frac{\theta_1 - \theta_2}{2}\right) = \left(\frac{\theta_1 - \theta_2}{2}\right) \quad \text{(approx.).}$$

Therefore

$$2t \left(\frac{\theta_1 - \theta_2}{2}\right) \cos \theta_B = \lambda,$$
$$t = \frac{\lambda}{B \cos \theta_B}. \tag{3–12}$$

A more exact treatment of the problem gives

$$t = \frac{0.9\lambda}{B \cos \theta_B}, \tag{3–13}$$

which is known as the Scherrer formula. It is used to estimate the *particle size* of very small crystals from the measured width of their diffraction curves. What is the order of magnitude of this effect? Suppose $\lambda = 1.5$ Å, $d = 1.0$ Å, and $\theta = 49°$. Then for a crystal 1 mm in diameter the breadth B, due to the small crystal effect alone, would be about 2×10^{-7} radian (10^{-5} degree), or too small to be observable. Such a crystal would contain some 10^7 parallel lattice planes of the spacing assumed above. However, if the crystal were only 500 Å thick, it would contain only 500 planes, and the diffraction curve would be relatively broad, namely about 4×10^{-3} radian (0.2°), which is easily measurable.

Nonparallel incident rays, such as B and C in Fig. 3–14, actually exist in any real diffraction experiment, since the "perfectly parallel beam" assumed in Fig. 3–2 has never been produced in the laboratory. As will be shown in Sec. 5–4, any actual beam of x-rays contains divergent and convergent rays as well as parallel

rays, so that the phenomenon of diffraction at angles not exactly satisfying the Bragg law actually takes place.

Neither is any real beam ever strictly monochromatic. The usual "monochromatic" beam is simply one containing the strong $K\alpha$ component superimposed on the continuous spectrum. But the $K\alpha$ line itself has a width of about 0.001 Å and this narrow range of wavelengths in the nominally monochromatic beam is a further cause of line broadening, i.e., of measurable diffraction at angles close, but not equal, to $2\theta_B$, since for each value of λ there is a corresponding value of θ. (Translated into terms of diffraction line width, a range of wavelengths extending over 0.001 Å leads to an increase in line width, for $\lambda = 1.5$ Å and $\theta = 45°$, of about 0.08° over the width one would expect if the incident beam were strictly monochromatic.) Line broadening due to this natural "spectral width" is proportional to $\tan \theta$ and becomes quite noticeable as θ approaches 90°.

Finally, there is a kind of crystal imperfection known as *mosaic structure* which is possessed by all real crystals to a greater or lesser degree and which has a decided effect on diffraction phenomena. It is a kind of substructure into which a "single" crystal is broken up and is illustrated in Fig. 3–16 in an enormously exaggerated fashion. A crystal with mosaic structure does not have its atoms arranged on a perfectly regular lattice extending from one side of the crystal to the other; instead, the lattice is broken up into a number of tiny blocks, each slightly disoriented one from another. The size of these blocks is of the order of 1000 Å, while the maximum angle of disorientation between them may vary from a very small value to as much as one degree, depending on the crystal. If this angle is ε, then diffraction of a parallel monochromatic beam from a "single" crystal will occur not only at an angle of incidence θ_B but at all angles between θ_B and $\theta_B + \varepsilon$. Another effect of mosaic structure is to increase the integrated intensity of the reflected beam relative to that theoretically calculated for an ideally perfect crystal (Sec. 4–12).

The notion of the mosaic crystal dates from the early years of x-ray diffraction and depends on much indirect evidence, both theoretical and experimental. In the 1960s the electron microscope provided direct evidence. It showed that real crystals, whether single crystals or individual grains in a polycrystalline aggregate,
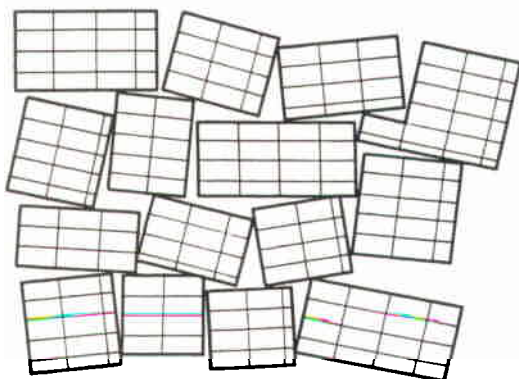

Fig. 3–16 The mosaic structure of a real crystal.

had a substructure defined by the dislocations present. The density of these dis-
locations is not uniform; they tend to group themselves into walls (sub-grain
boundaries) surrounding small volumes having a low dislocation density (sub-
grains or cells). Today the term "mosaic structure" is seldom used, but the little
blocks of Fig. 3-16 are identical with sub-grains and the regions between the blocks
are the dislocation walls.

These, then, are some examples of diffraction under nonideal conditions, that
is, of diffraction as it actually occurs. We should not regard these as "deviations"
from the Bragg law, and we will not as long as we remember that this law is derived
for certain ideal conditions and that diffraction is only a special kind of scattering.
This latter point cannot be too strongly emphasized. A single atom scatters an
incident beam of x-rays in all directions in space, but a large number of atoms
arranged in a perfectly periodic array in three dimensions to form a crystal scatters
(diffracts) x-rays in relatively few directions, as illustrated schematically in Fig.
3-17. It does so precisely because the periodic arrangement of atoms causes
destructive interference of the scattered rays in all directions *except* those predicted
by the Bragg law, and in these directions constructive interference (reinforcement)
occurs. It is not surprising, therefore, that measurable diffraction (scattering)
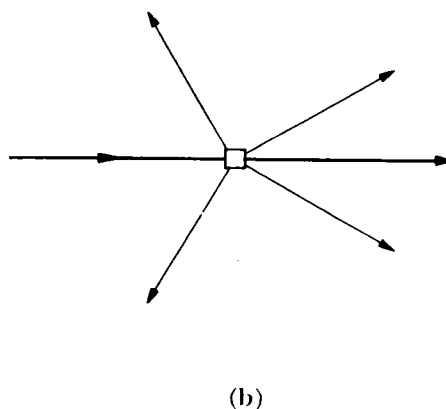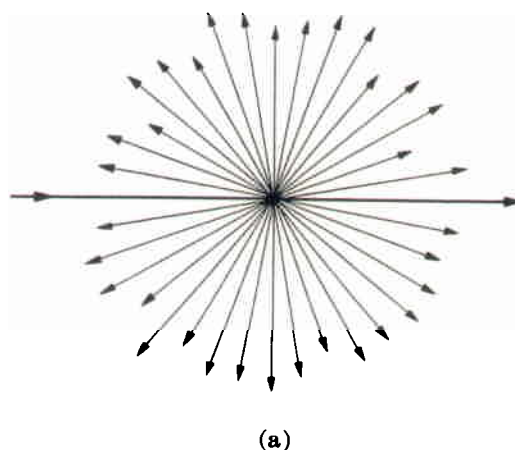occurs at non-Bragg angles whenever any crystal imperfection results in the partial

(a)

(b)

Fig. 3-17 (a) Scattering by an atom. (b) Diffraction by a crystal.

absence of one or more of the necessary conditions for perfect destructive inter-ference at these angles. These imperfections are generally slight compared to the over-all regularity of the lattice, with the result that diffracted beams are confined to very narrow angular ranges centered on the angles predicted by the Bragg law for ideal conditions.

This relation between destructive interference and structural periodicity can be further illustrated by a comparison of x-ray scattering by solids, liquids, and gases (Fig. 3-18). The curve of scattered intensity vs. 2θ for a crystalline solid is almost zero everywhere except at certain angles where high sharp maxima occur: these are the diffracted beams. Both amorphous solids and liquids have structures characterized by an almost complete lack of periodicity and a tendency to "order" only in the sense that the atoms are fairly tightly packed together and show a statistical preference for a particular interatomic distance; the result is an x-ray scattering curve showing nothing more than one or two broad maxima. Finally, there are the monatomic gases, which have no structural periodicity whatever; in such gases, the atoms are arranged perfectly at random and their relative positions
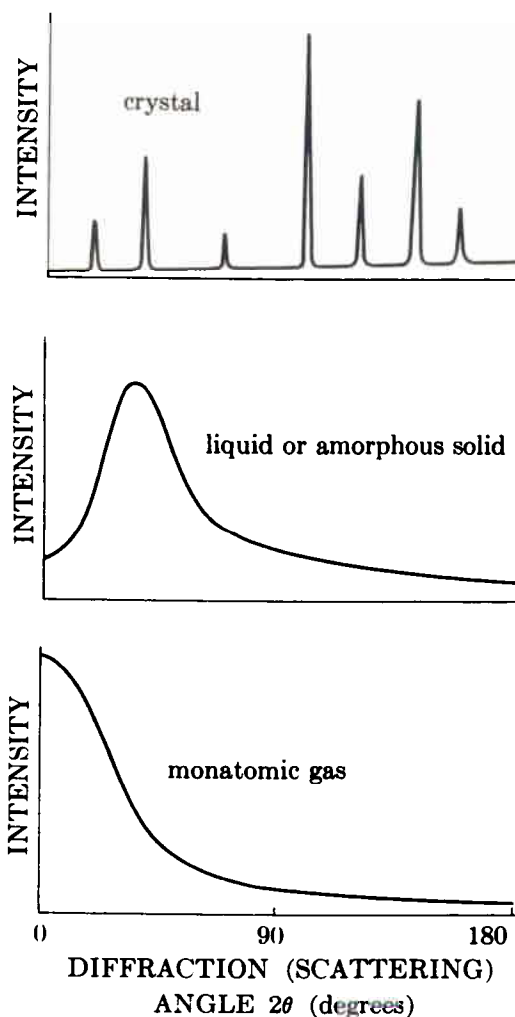

Fig. 3-18 Comparative x-ray scattering by crystalline solids, amorphous solids, liquids, and monatomic gases (schematic). The three vertical scales are not equal.

change constantly with time. The corresponding scattering curve shows no maxima, merely a regular decrease of intensity with increase in scattering angle. This curve would be entirely featureless, i.e., horizontal, if it were not for the fact that isolated atoms scatter x-rays more intensely at low 2θ angles than at high (Sec. 4-3).

PROBLEMS

3-1 A transmission Laue pattern is made of a cubic crystal having a lattice parameter of 4.00 Å. The x-ray beam is horizontal. The [0$\bar{1}$0] axis of the crystal points along the beam towards the x-ray tube, the [$\bar{1}$00] axis points vertically upward, and the [001] axis is horizontal and parallel to the photographic film. The film is 5.00 cm from the crystal.

a) What is the wavelength of the radiation diffracted from the ($3\bar{1}0$) planes?
b) Where will the $3\bar{1}0$ reflection strike the film?

*3-2 A transmission Laue pattern is made of a cubic crystal in the orientation of Prob. 3-1. By means of a stereographic projection similar to Fig. 3-8, show that the beams diffracted by the planes ($2\bar{1}0$), ($2\bar{1}3$), and (211), all of which belong to the zone [$\bar{1}20$], lie on the surface of a cone whose axis is the zone axis. What is the angle ϕ between the zone axis and the transmitted beam?

3-3 Determine, and list in order of increasing angle, the values of 2θ and (hkl) for the first three lines (those of lowest 2θ values) on the powder patterns of substances with the following structures, the incident radiation being Cu $K\alpha$:

a) simple cubic ($a = 3.00$ Å),
b) simple tetragonal ($a = 2.00$ Å, $c = 3.00$ Å),
c) simple tetragonal ($a = 3.00$ Å, $c = 2.00$ Å),
d) simple rhombohedral ($a = 3.00$ Å, $\alpha = 80°$).

3-4 In Fig. 3-14, put $m = 10$. (a) Write down a complete list of the path differences, in wavelengths λ, between the ray scattered by each plane below the surface and the ray scattered by the surface plane, for a scattering angle of $2\theta_1$. What plane scatters a ray exactly out of phase with the ray scattered by the third plane below the surface? What is the path difference for these two rays? (b) Write down a similar list of path differences for rays scattered at an angle halfway between $2\theta_B$ and $2\theta_1$ in order to convince yourself that these rays do *not* cancel one another.

*3-5 In Fig. 3-14, assume that the incident beam is perfectly parallel, instead of convergent, and incident at the angle θ_B. Does broadening of the diffracted beam still occur? If so, derive the relation between t and B.

*3-6 Calculate the breadth B (in degrees of 2θ), due to the small crystal effect alone, of the powder pattern lines of particles of diameter 1000, 750, 500, and 250 Å. Assume $\theta = 45°$ and $\lambda = 1.5$ Å. For particles 250 Å in diameter, calculate the breadth B for $\theta = 10$, 45, and 80°.

3-7 Check the value given in Sec. 3-7 for the increase in breadth of a diffraction line due to the natural width of the $K\alpha$ emission line. [*Hint:* Differentiate the Bragg law and find an expression for the rate of change of 2θ with λ.]