Handout 4:
Basics of Diffraction

Chem 6850/8850

X-ray Crystallography

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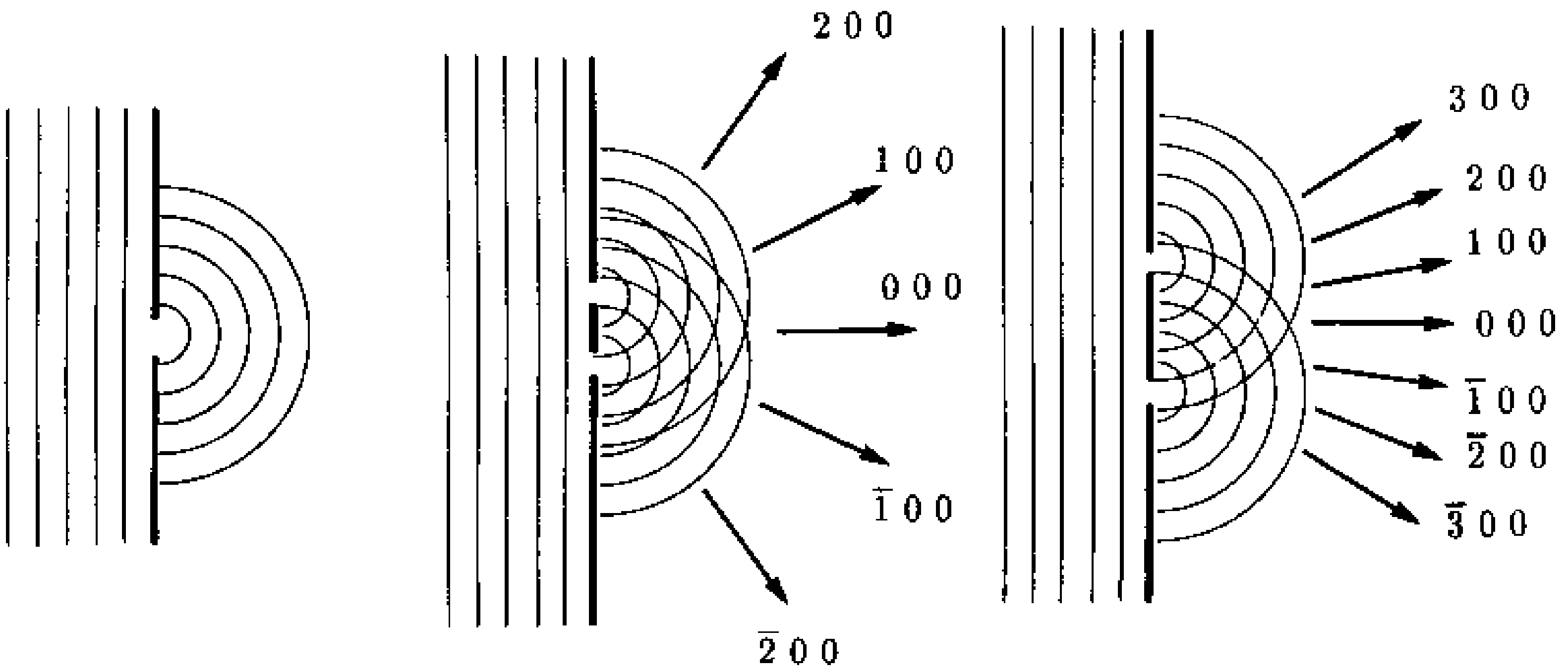
Diffraction

- **Definition (from “Cambridge Advanced Learner’s Dictionary”):**
  - **diffraction** noun [U] SPECIALIZED
    (a pattern caused by) a change in the direction of light, water or sound waves
  - **diffract** verb [T]
    to separate light into coloured strips or into light and dark strips
- **Definition (from “Merriam Webster’s Dictionary”):**
  - Main Entry: **dif·frac·tion**; Function: noun
    Etymology: New Latin *diffraction-, diffractio*, from Latin *diffringere* to break apart, from *dis- + frangere* to break
  - A modification which light undergoes in passing by the edges of opaque bodies or through narrow slits or in being reflected from ruled surfaces and in which the rays appear to be deflected and to produce fringes of parallel light and dark or colored bands; *also* : a similar modification of other waves (as sound waves)

X-ray diffraction

- **"Scattering of X-rays by the atoms of a crystal that produces an interference effect so that the diffraction pattern gives information on the structure of the crystal or the identity of a crystalline substance" (Webster's)**
  - remember that both light and X-rays are electromagnetic radiation – the only difference lies in the wavelength!
- **X-ray diffraction can be envisioned as an equivalent process to what happens when you shine light through a grating**
  - formulism obeys the same laws derived for the "slit experiments"

Diffraction of light by slits



"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

- Incoming light is a plane wave
- Slit apertures result in an outgoing spherical wave
- Interference determines the diffraction pattern

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Diffraction of light by masks

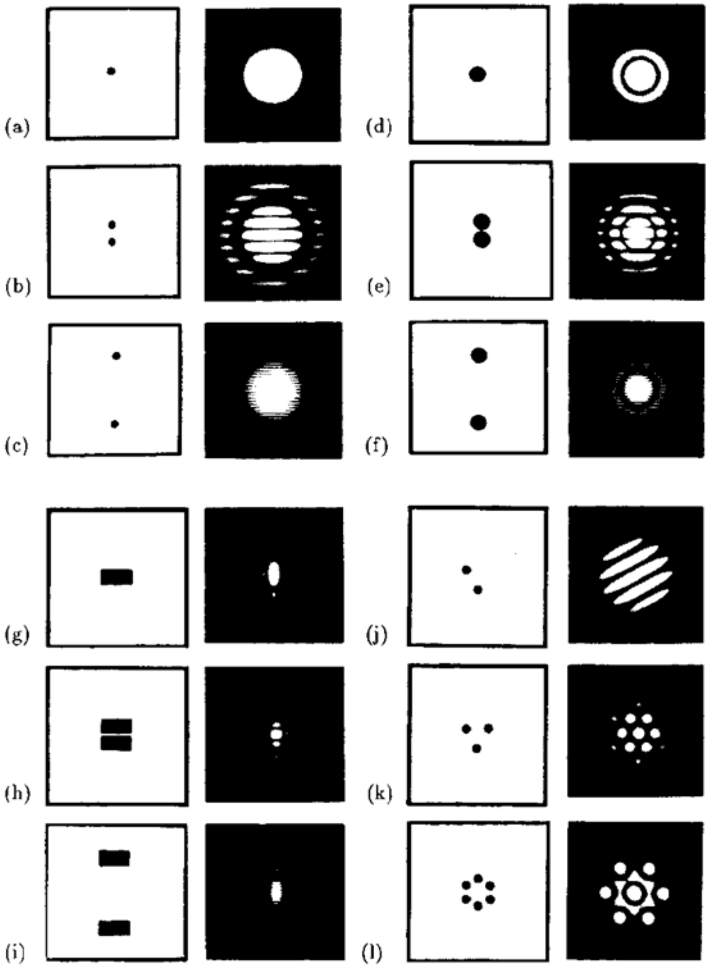
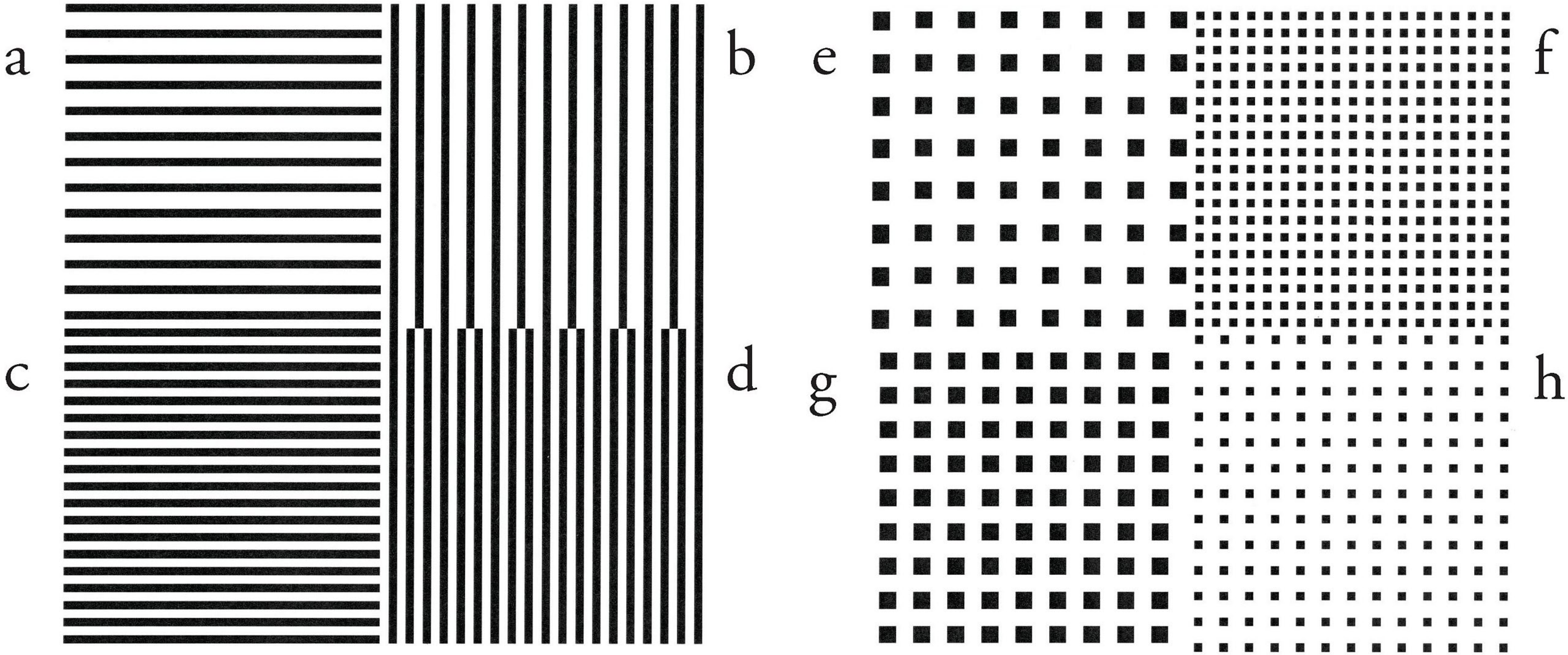


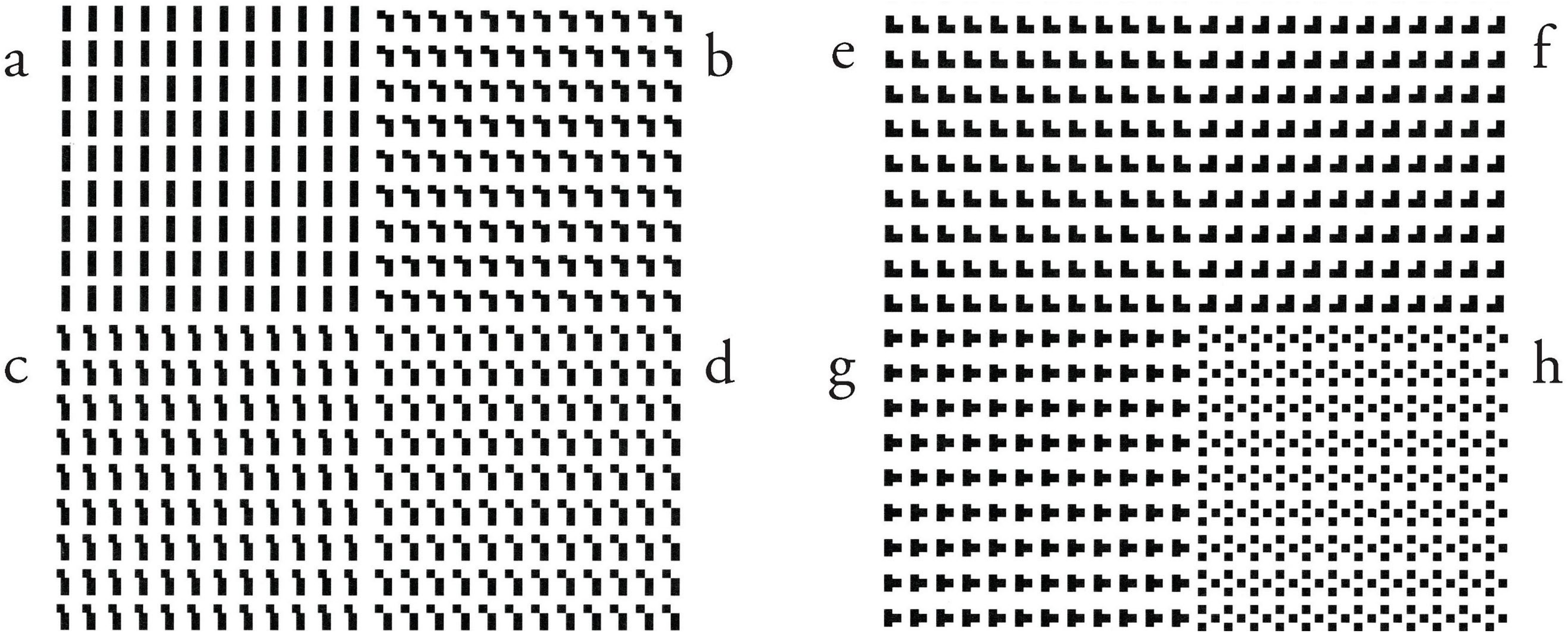
FIGURE 3.7. Examples of diffraction patterns from a variety of masks. The mask with the holes in it is to the left and its diffraction pattern is to the right. The diffraction pattern of (a) a single round hole in a mask, (b) two round holes, and (c) two round holes further apart. Note that in (b) and (c) the diffraction pattern is sampled (in lines) with a spacing that is inversely proportional to the distance between holes in the mask. The diffraction effects when the sizes of the holes in the masks are increased are shown in (d), (e), and (f). The holes are larger than in (a), (b), or (c), but the spacings between their centers are the same. Recall that the experimental diffraction pattern is now more compact, illustrating the reciprocal relationship between the size of an object and its diffraction pattern. Since the spacings of holes in the masks are the same in (a), (b), and (c), and in (d), (e), and (f), the distances between sampling regions are also the same. The effect of changing the shape of the holes in the mask is shown in (g), (h), and (i), where the holes are rectangular in shape. Again, the reciprocal relationship between dimensions in real space and in the diffraction pattern is shown. The wider part of the hole gives a narrower diffraction pattern. The spacings between holes are the same as in (a) to (f). Finally, the effect of different arrangements of holes on the diffraction pattern. In (j) there are two holes in the mask, and the resulting diffraction pattern is similar to that in (b), although one mask is rotated with respect to the other. In (k) the effect of three holes, equivalent to three superpositions of the diffraction pattern in (j), each at 120° to each other is seen. In (l) the diffraction pattern of six holes is shown. (Reprinted from G. Harburn, C. A. Taylor and T. R. Welberry: *Atlas of Optical Transforms*. Copyright © 1975 by G. Bell & Sons Ltd. Used by permission of the authors and the publisher, Cornell University Press.)

“Crystal Structure Analysis for Chemists and Biologists”, Glusker, Lewis and Rossi, VCH, 1994.

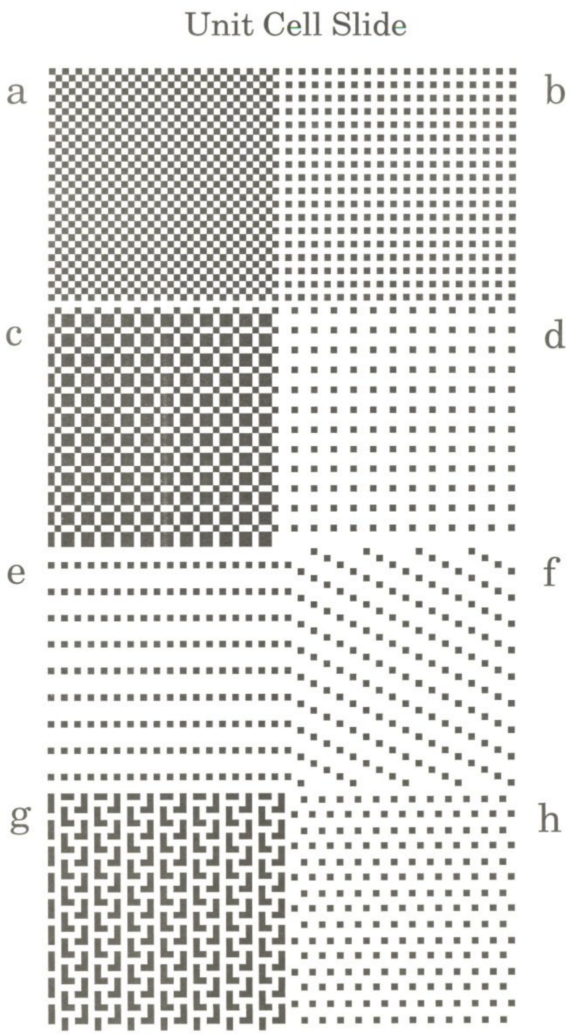
Diffraction – Discovery Slide



Diffraction Intensities – VSEPR Slide



Diffraction by unit cell arrays



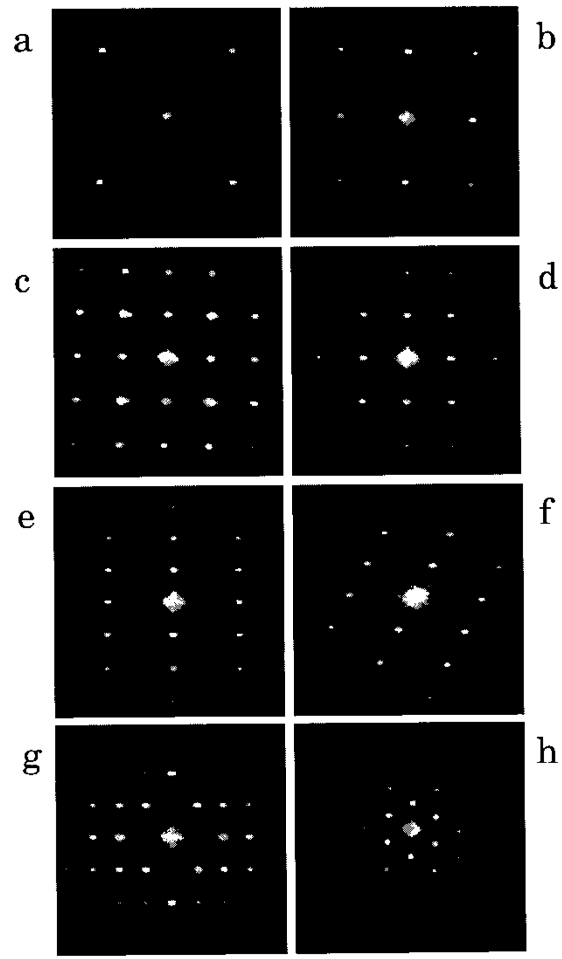
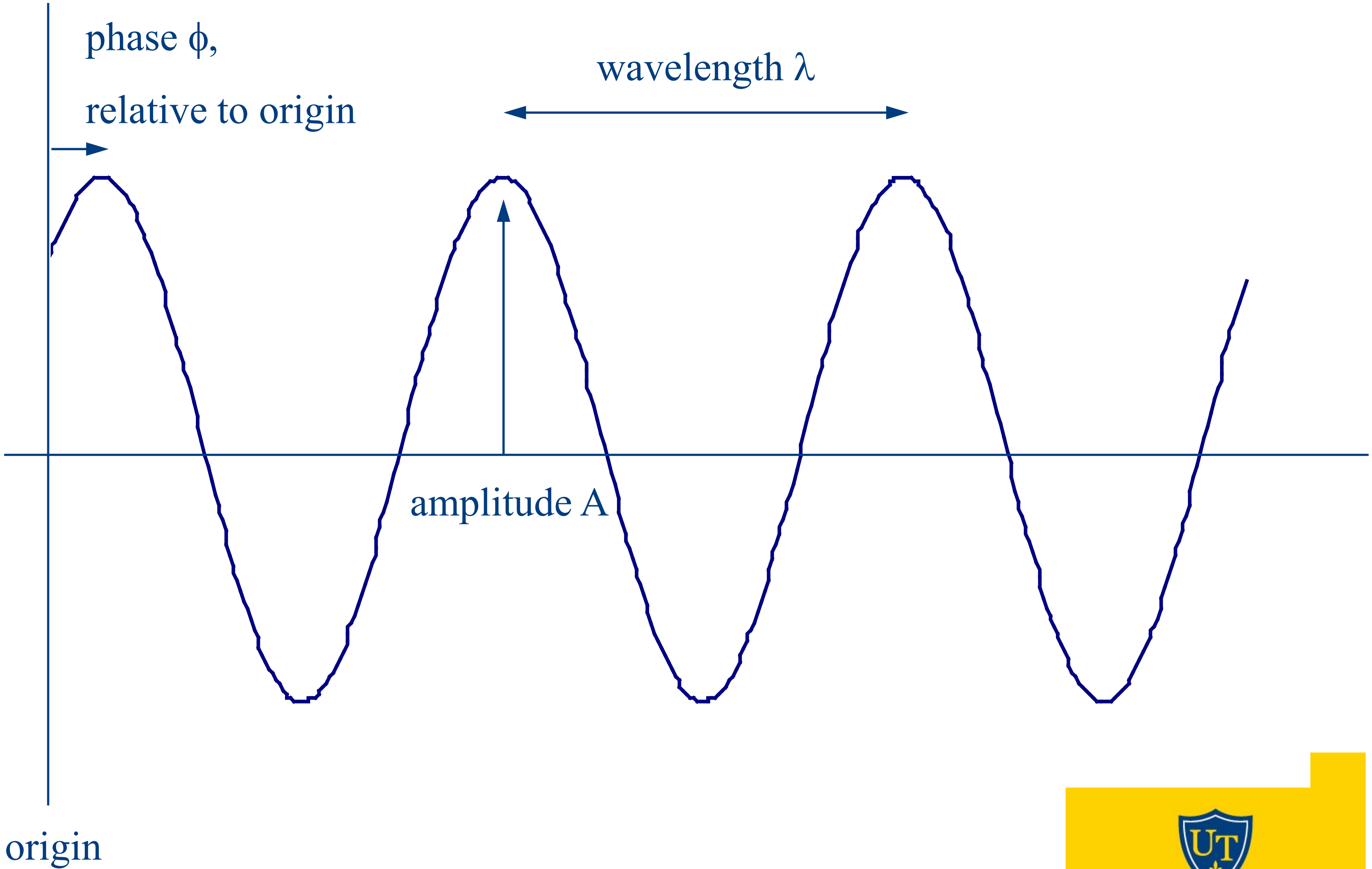


Figure 2 (left). Some two-dimensional unit cells. (a)centered 2x2 pixel square; (b)2x2 pixel square; (c)3x3 pixel square with two different spot sizes; (d)3x3 pixel square; (e)2x4 pixel rectangle; (f) monoclinic, 2x4 pixel with ~63º angle; (g) 4x5 pixel rectangle with glide; (h)hexagonal array, equivalent to a 5.28x5.28 pixel with 60º angle(actual size is 22x22 pixels in a 300 in^{-1} grid). Beside each array is a unit cell (see text). For ease of viewing, these portions of the masks are considerably expanded from the actual masks (see text for true size).

Figure 3 (right). Diffraction patterns corresponding to the arrays in Figure 2a-h. The patterns were obtained with a 5mW, 670-nm diode laser.

Waves



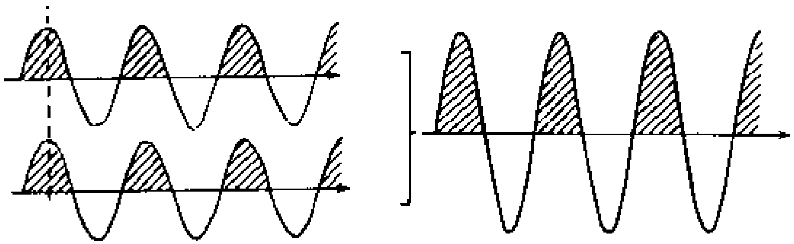
Wave equations

- **A wave can be described by a cosine function**
  - amplitude is position dependent (x)
  - amplitude is time dependent (t)

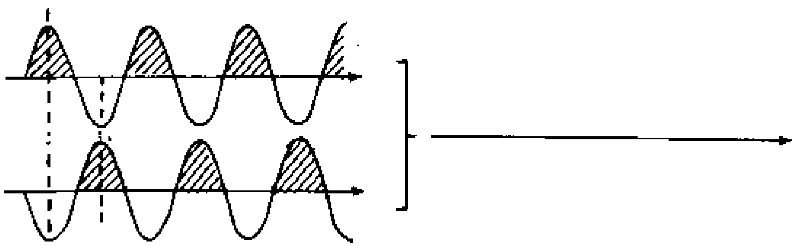
    $\Rightarrow A = \cos(kx - \omega t)$

- **Two parallel waves will interact with each other**
  - called interference
  - constructive interference if waves are in phase
  - destructive interference if waves are exactly out of phase
- **The interaction between waves can be envisioned by addition of their wave equations**

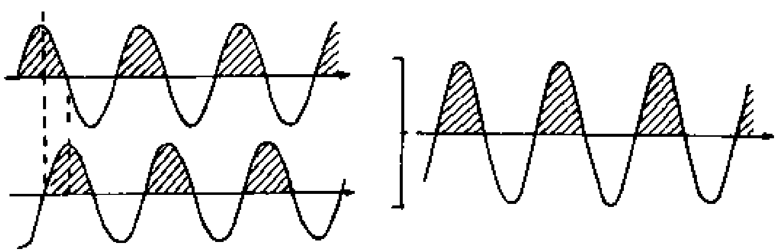
Adding wave functions



in phase
(constructive
interference)



out of phase
(destructive
interference)



partially out of phase

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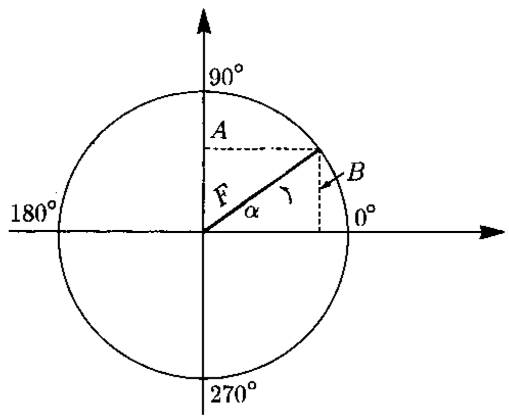
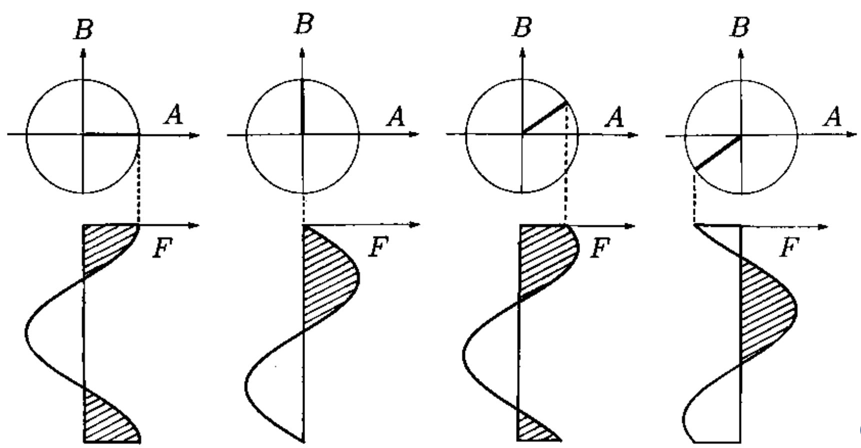
Vector description





- **How do we add two cosine functions with different frequencies and phases?**
  - Point-by-point (or graphical) addition possible, but time consuming
- **It is convenient to describe a wave by a vector moving on a circle**
  - We know how to do math with vectors!
  - $\mathbf{F} = |\mathbf{F}| \cdot (\cos(\alpha t) + i \cdot \sin(\alpha t)) = |\mathbf{F}| \cdot \mathbf{e}^{i\alpha t}$

“Crystal Structure Analysis for Chemists and Biologists”, Glusker, Lewis and Rossi, VCH, 1994.

Interference

- **For waves with the same frequency and amplitude, we see constructive interference when two waves have a phase difference of $n\lambda$, where ($n \in \mathbb{Z}$)**
  - called “in phase”
- **Destructive interference is observed for a phase difference of $(n + ½)\lambda$, where ($n \in \mathbb{Z}$)**
  - called “out of phase”
- **A phase difference can result from a path difference**
  - happens in the slit experiments
  - the same thing happens when X-rays are diffracted by a crystal

Laue equations

- In 1912, Max von Laue realized that the path differences PD_1, PD_2 and PD_3 for waves diffracted by atoms separated by one unit cell translation have to be a multiple of the diffraction wavelength for constructive interference
  - $PD_1 = h\,\lambda$, $PD_2 = k\,\lambda$, $PD_3 = l\,\lambda$
  - $h, k, l \in \mathbb{Z}$
- He showed that these three conditions have to be fulfilled simultaneously

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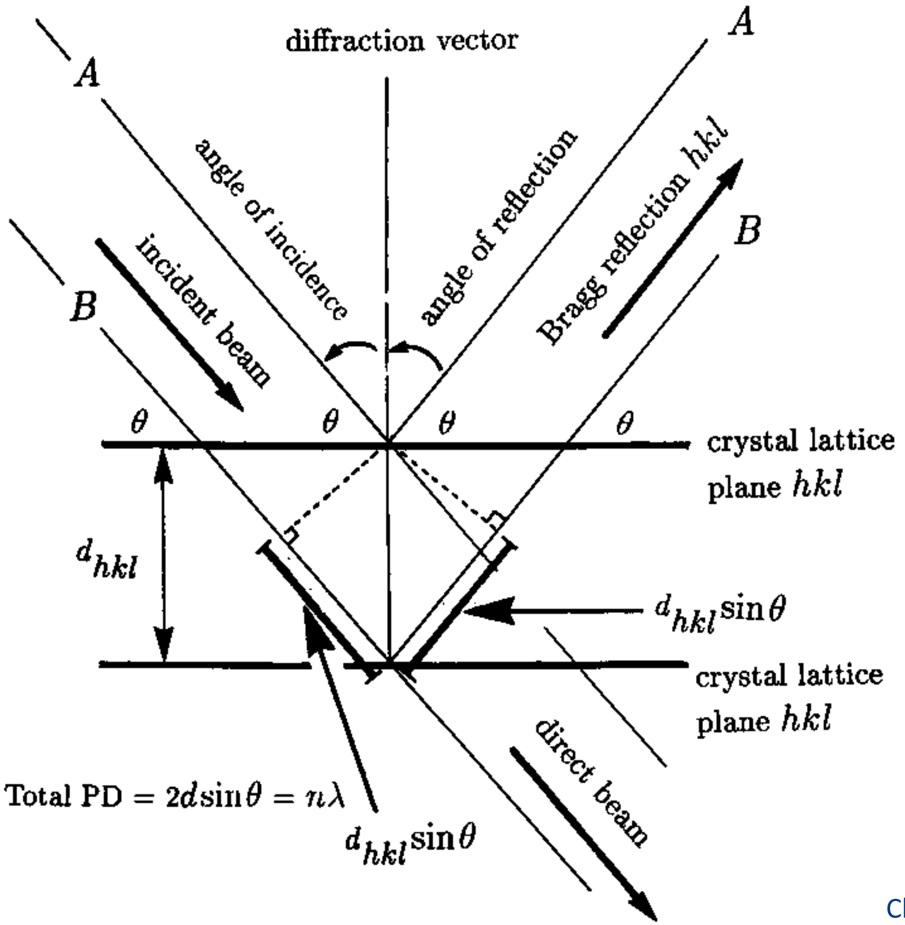
Bragg's law - 1913



- **Reflection of X-rays from parallel lattice planes**
  - families of planes have equal spacing
- **Constructive interference when PD = $n\lambda$**
- **The Laue equations can be rewritten as $2d_{hkl}\sin\theta_{hkl} = n\lambda$**

"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

Equivalence of Bragg and Laue formulations

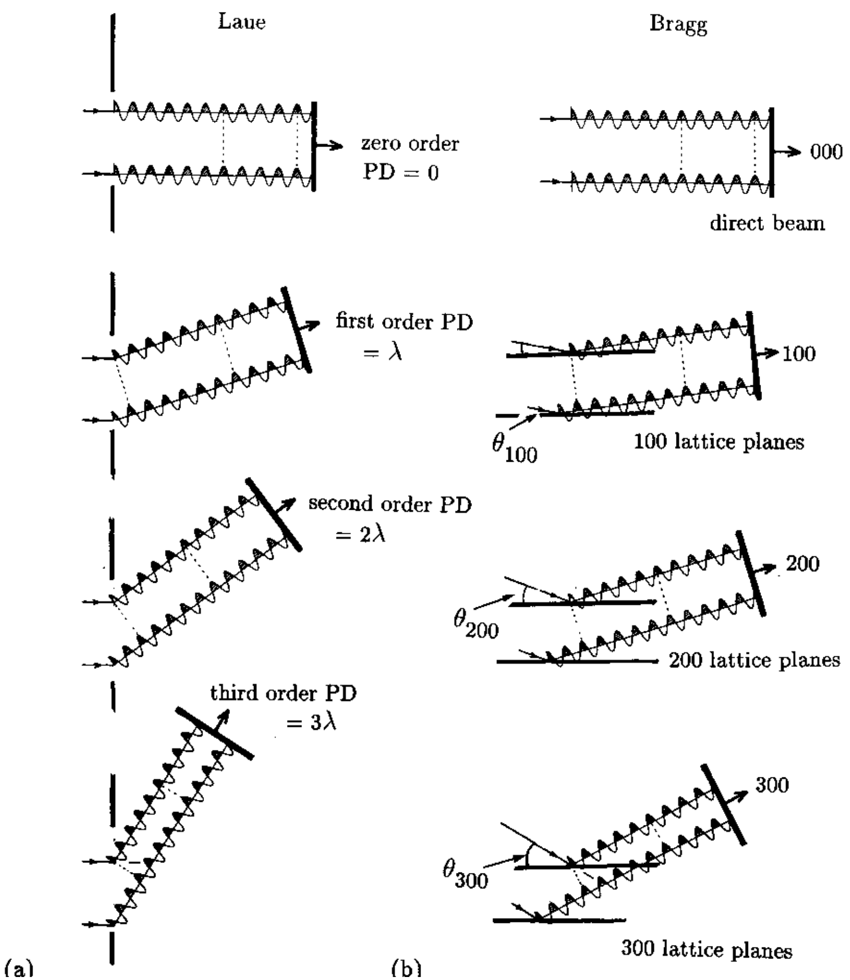


FIGURE 3.9. Conditions for diffraction. (Left) Max von Laue considered the path difference between a scattered and another wave scattered one unit cell away. If the difference is an integral number of wavelengths, reinforcement occurs, and a stronger diffracted beam is observed. Examples are shown for the direct beam, the first, second and third orders. (Right) W. L. Bragg realized that these same conditions could be considered as reflection from lattice planes. In addition, he realized that the orders of reflection [0,1,2,3] are equal to the indices $h00$ of the lattice planes causing that Bragg reflection. Note that the direction of a Bragg reflection is inclined at an angle $2\theta_{hkl}$ to the direct beam. (a) Laue considerations of path differences and (b) Bragg considerations of reflections from lattice planes. In both cases the overall result (diffraction) is the same.

"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

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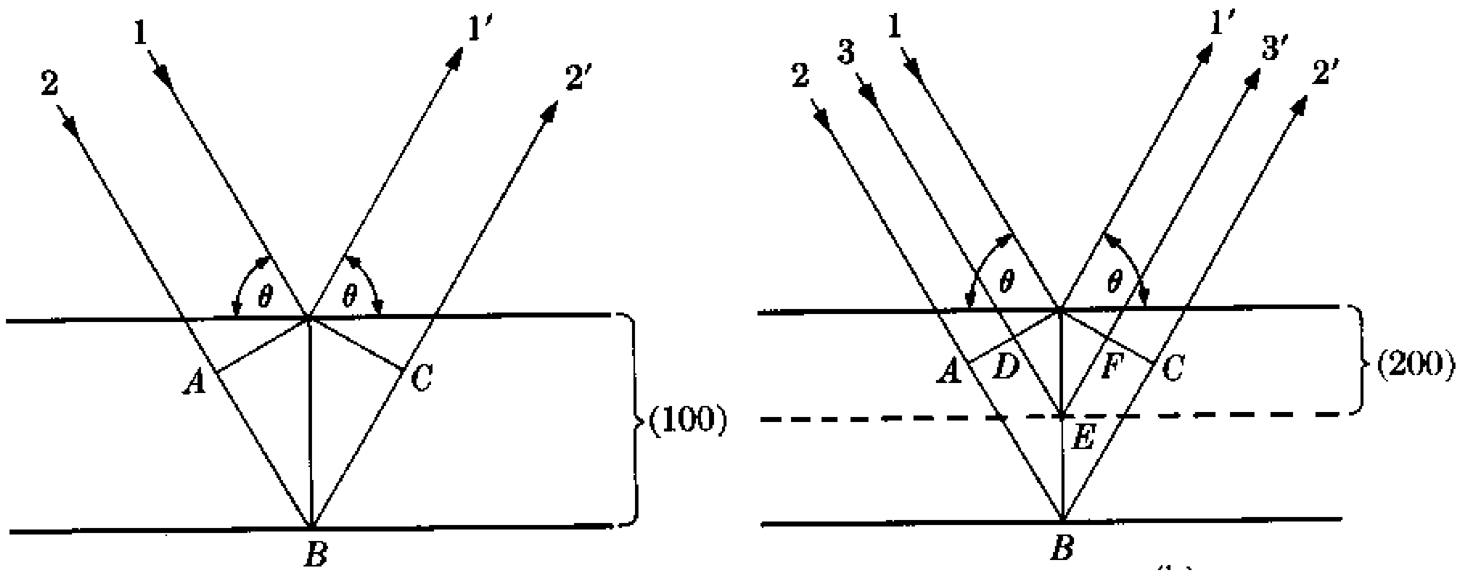
Indexing of lattice planes

"Elements of X-ray Diffraction", Cullity and Stock, Prentice Hall College Div., 3rd edition, 2001.



- **In contrast to face indexing, the absolute values of h, k and l matter when describing lattice planes**
  - there are twice as many 200 planes as 100 planes
- **Plane spacing is described by d_{hkl}**
  - $d_{100} = 2d_{200}$

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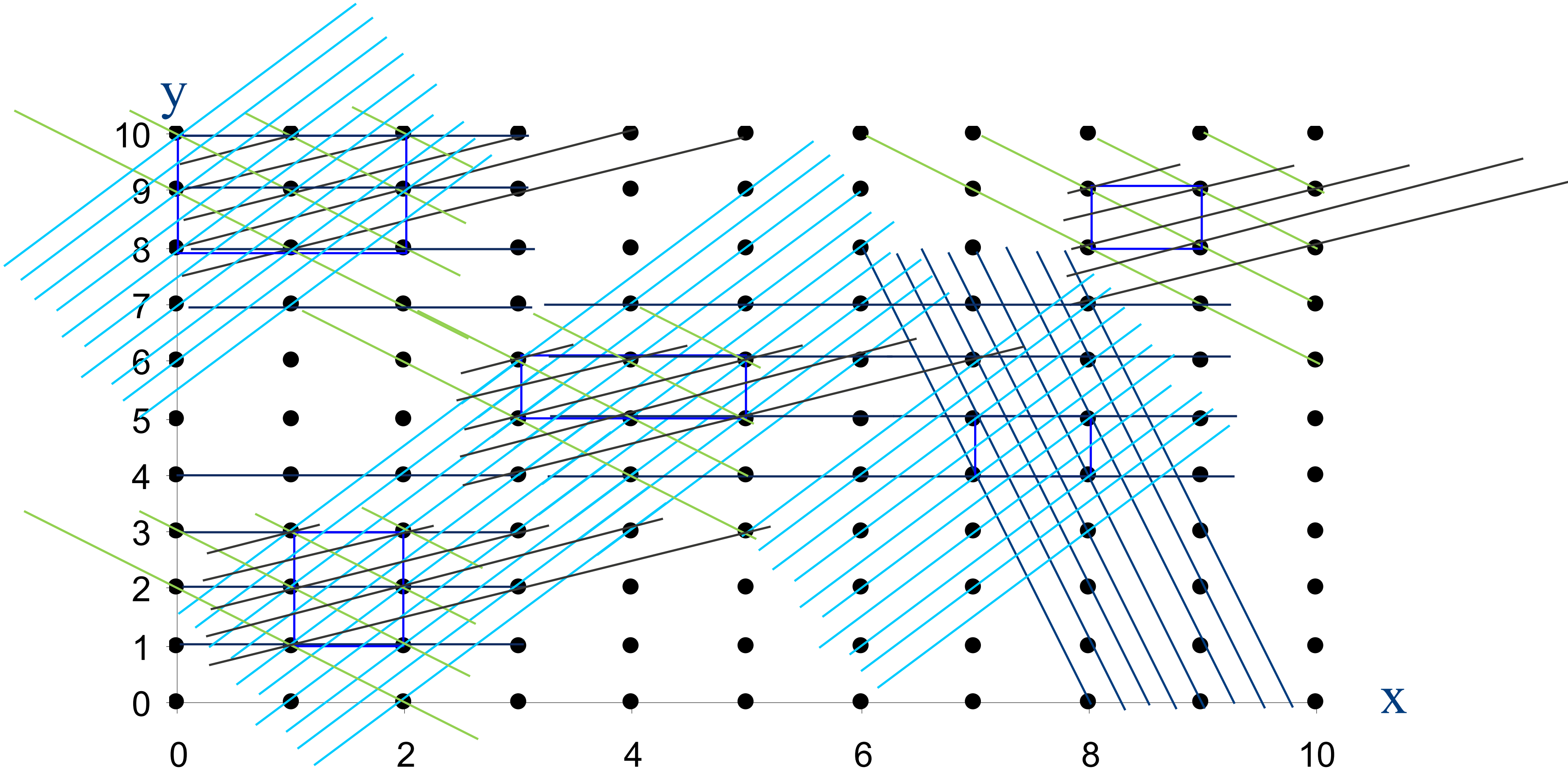
Miller indices

- **Any lattice plane can be described by its intersection points with the three-unit cell axes**
- **Miller indices are the reciprocal of the intercepts**
  - integers h, k and l refer to reciprocals of intercepts on a, b and c
- **Identify planes *adjacent* to origin**
  - planes through the origin cannot be described, as the intercept would be zero
- **A plane running parallel to an axis has an intercept of ∞, this corresponds to a Miller index of 0**

Examples of lattice planes



- **Any lattice plane can be described by three integers called Miller indices h, k and l**

Some examples of Miller indices

“Elements of X-ray Diffraction”, Cullity and Stock, Prentice Hall College Div., 3rd edition, 2001.

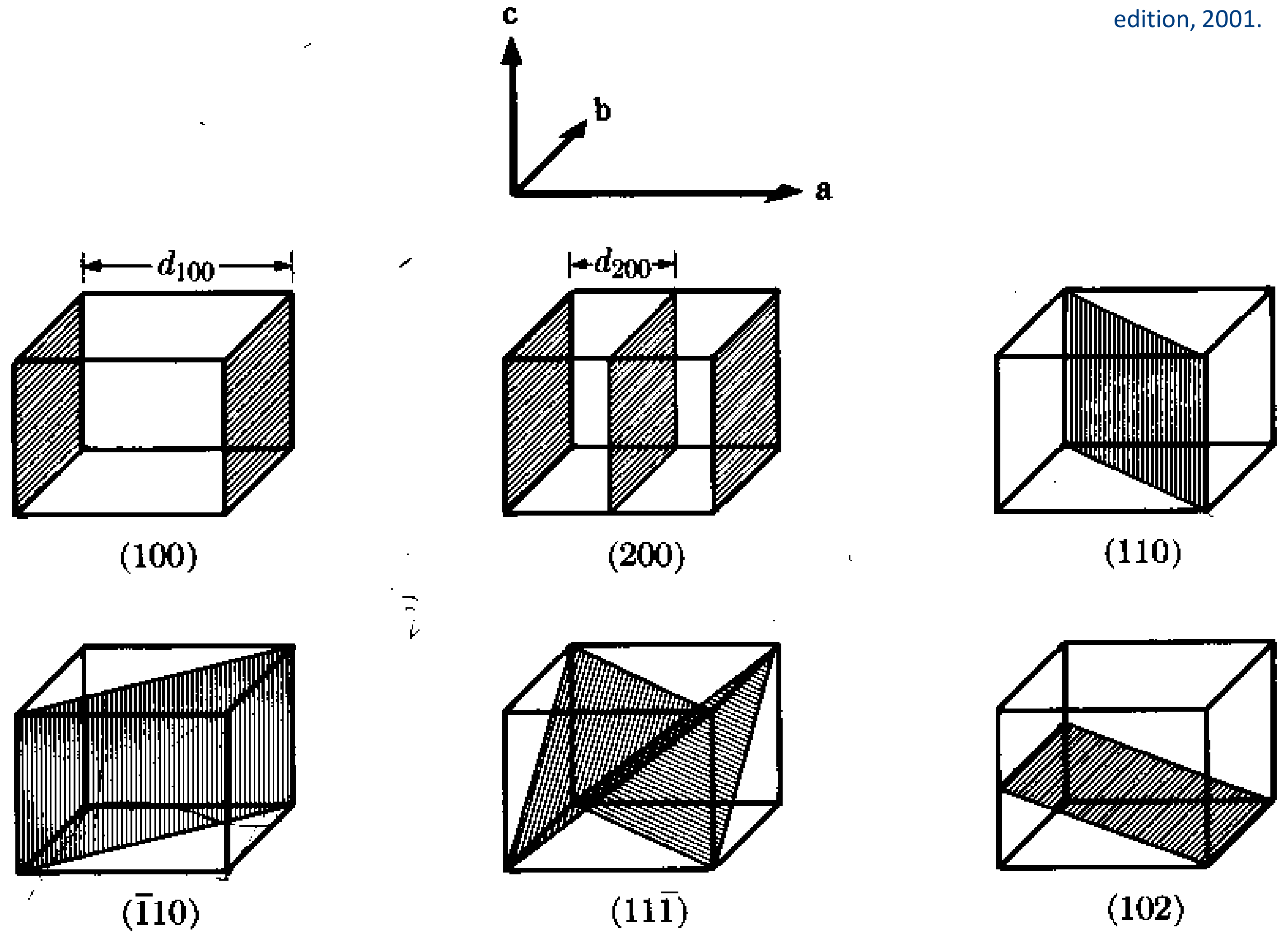


Fig. 2–10 Miller indices of lattice planes. The distance d is the plane spacing.