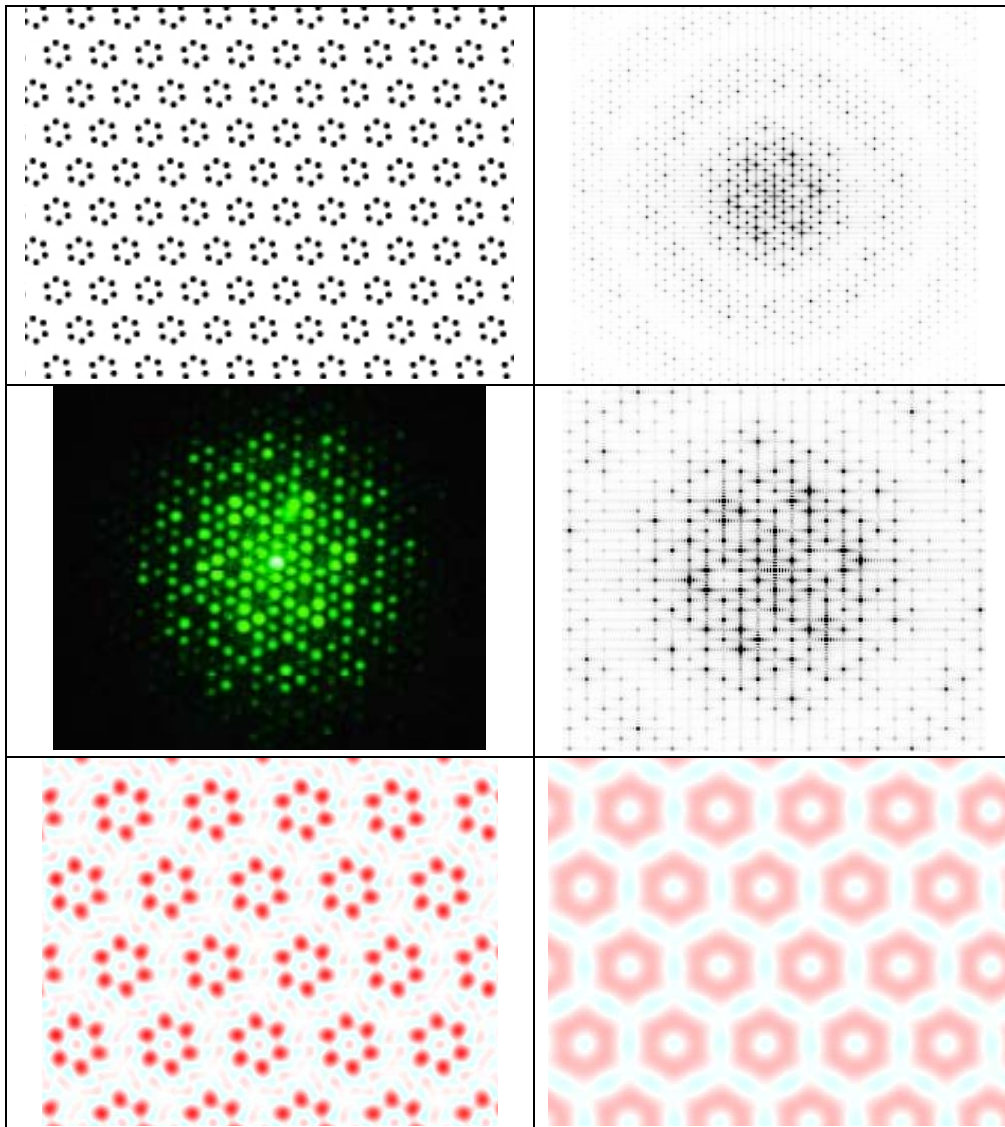_____

Experiments in Diffraction Using Optical Crystals and Computer Simulation

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Synopsis

The goal of this project was to develop a laboratory experiment on diffraction which integrated the following elements:

(a) existing and newly developed "optical crystals"

(b) graphics, tutorials, and simulations available on the web

(c) brief overview of some of the key concepts of diffraction and crystal structure, to provide context for the "hands-on" work with the optical crystals and computer simulations.

Most of the material is related to two-dimensional geometry and analysis, although some references are made to three-dimensional crystal geometry, where it's thought that these references would be helpful to allow the students to correlate the analytical or experimental results with real crystals and crystallographic techniques.

The intent of including the "overview" material is to re-familiarize students, who have had at least some background in optical physics and materials, with the nomenclature and mathematics relevant to the diffraction experiments. The information is presented assuming only general background or limited recall of these topics. It is not possible to provide a comprehensive treatment of all the necessary topics in a short paper, but references are provided for students who want more background.

The new optical crystal slides developed for this project are described in Appendix A. The patterns on these slides are designed to quickly demonstrate important concepts, by showing the effect of changing one feature at a time. For example, one slide which has four patterns of atoms of slightly different sizes, while the shape of the atom and the lattice geometry is the same. Another example is a slide which has four patterns of atoms of different shapes, while the size of the atoms is approximately the same, and again the lattice geometry is unchanged. See Figure S – 1 for the real space and diffraction pattern photographs from the slide with atoms of different shapes.

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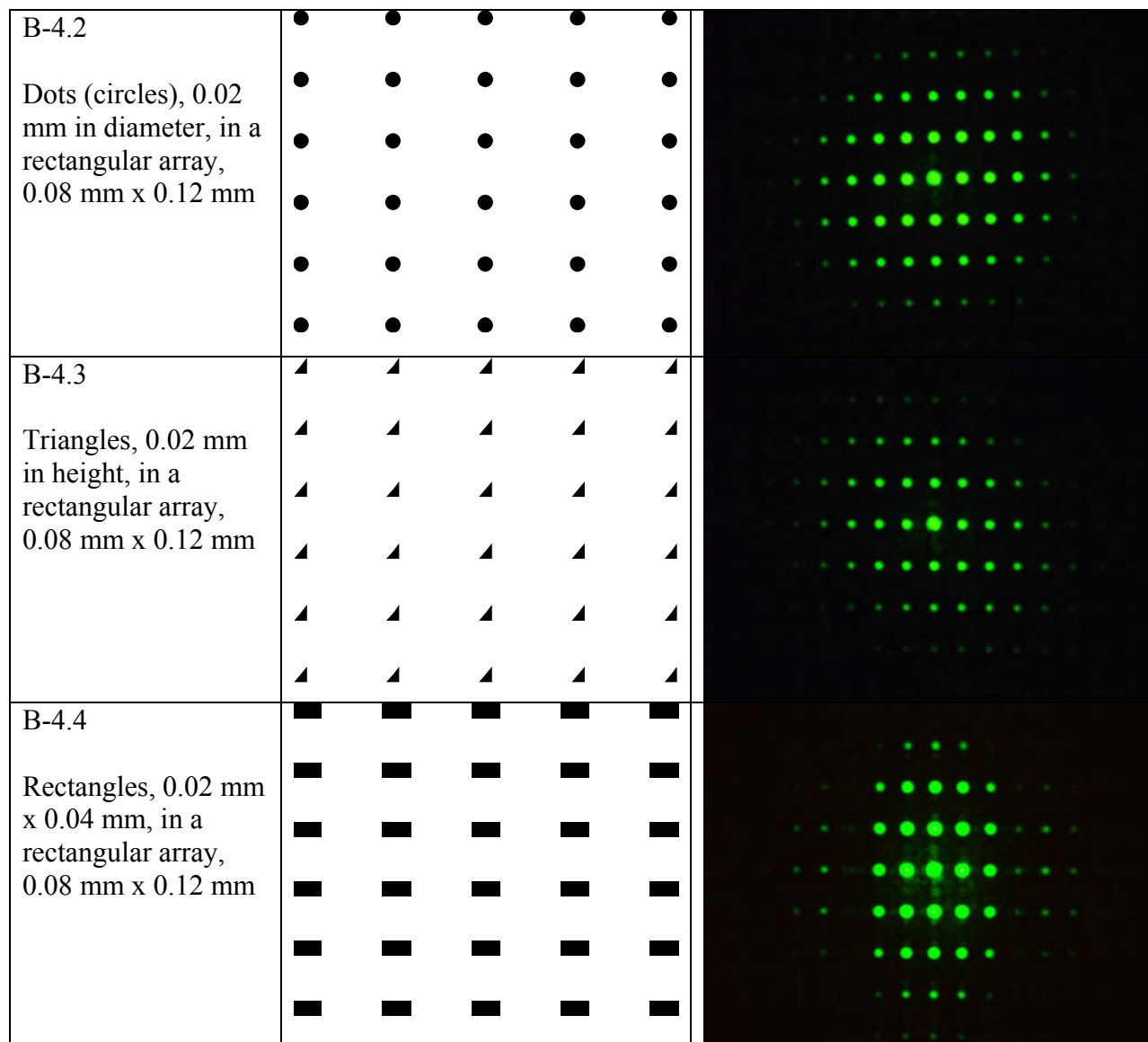|		
B-4.2 Dots (circles), 0.02 mm in diameter, in a rectangular array, 0.08 mm x 0.12 mm		
B-4.3 Triangles, 0.02 mm in height, in a rectangular array, 0.08 mm x 0.12 mm		
B-4.4 Rectangles, 0.02 mm x 0.04 mm, in a rectangular array, 0.08 mm x 0.12 mm		

Figure S – 1: Example of one of the new optical crystal slides developed for this project

The computer simulations provide even more flexibility than the optical crystals for the student to quickly investigate the effects of changing size or shape of the motif, or the lattice geometry, and other parameters. Figure S – 2 shows an example of how the computer simulation output is used to help demonstrate the relationship between the Fourier transforms of the motif and the lattice, and the "net" Fourier transform of the convolution of the motif and lattice.
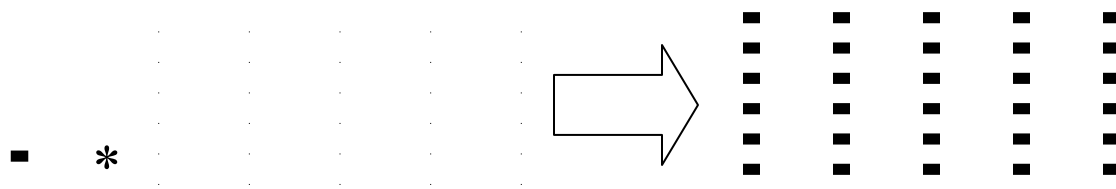
(Convolution of the motif and the lattice results in a crystal structure)
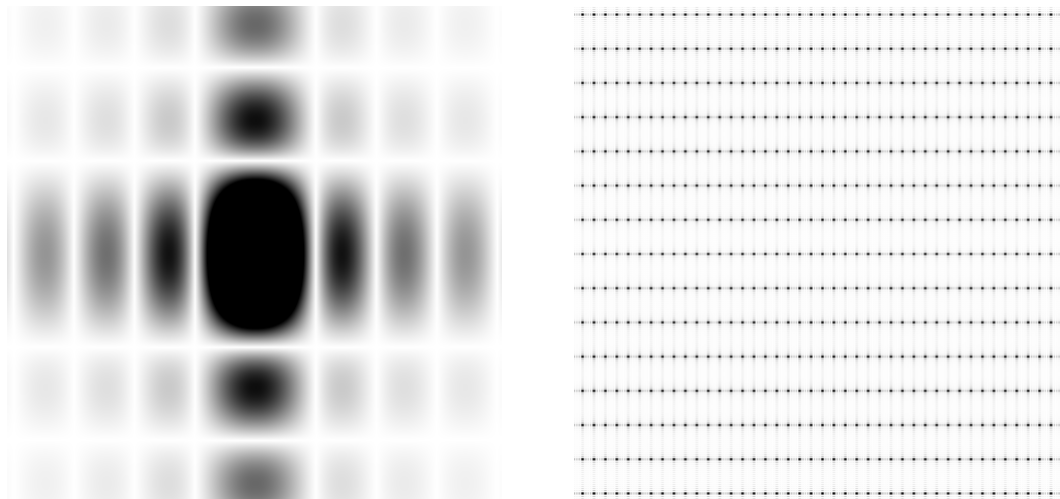
(The Fourier transforms of the motif and the lattice are multiplied to obtain the Fourier transform of the crystal structure)
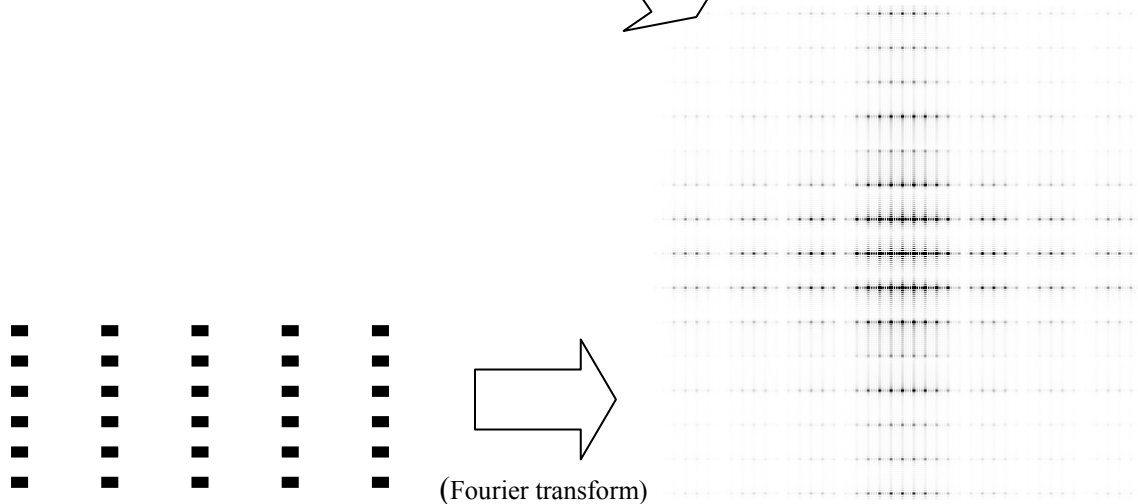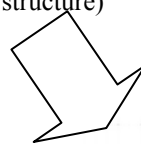
(Fourier transform)

Figure S – 2: Example of how the computer simulation output is used to demonstrate concepts (from Section 6 "Convolution")

Experiments in Diffraction Using Optical Crystals and Computer Simulation

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One of the important new features of this project was to integrate the use of the computer simulations with the use of the optical crystal slides. This was accomplished by using the same real space patterns for both the optical crystal slides and as input to the computer simulation - see Figure S – 3 as an example. Showing direct correlation between the observed results from the optical crystal slides and the calculated results from the computer simulation (and allowing the students to demonstrate this for themselves), provides the students both better understanding and confidence in the meaning of each.
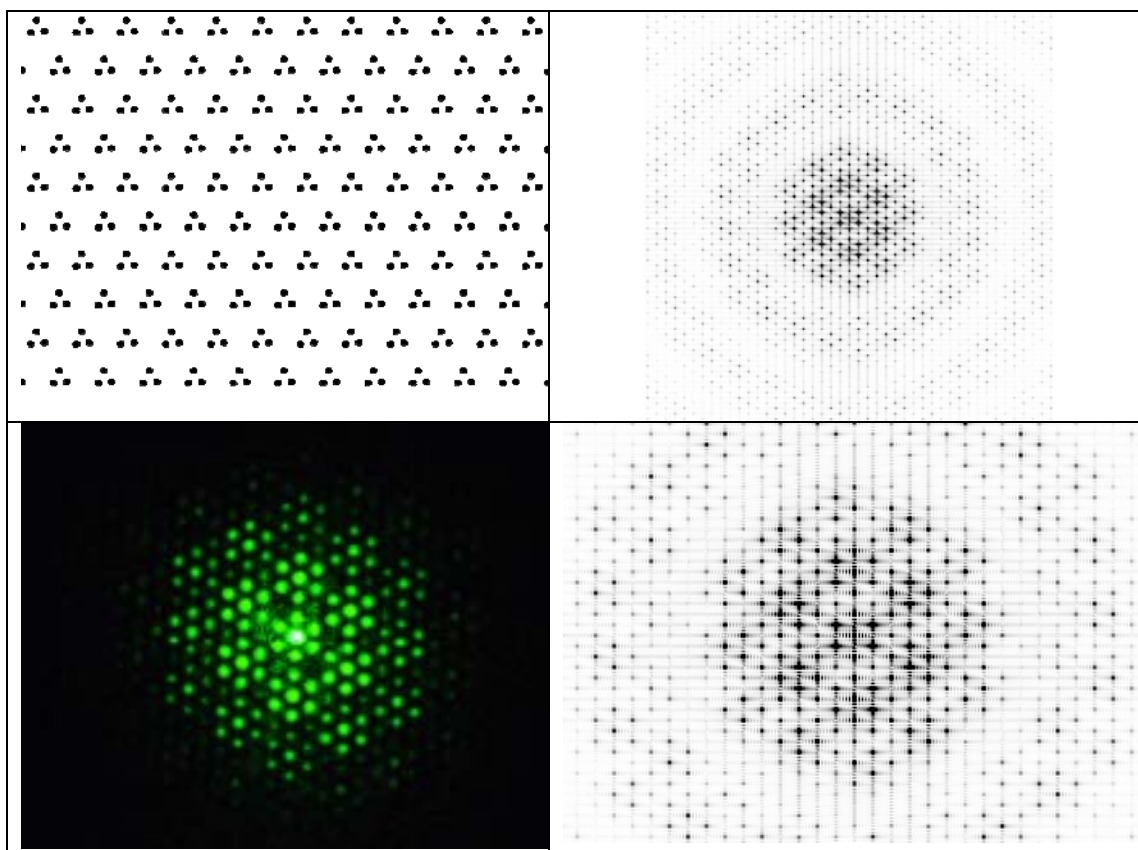

Figure S – 3: Example of how the computer simulation output and the optical crystal slides are integrated (from Section 8 "Symmetry of the Crystal Lattice and the Diffraction Pattern")

Overview

This project was to develop a laboratory experiment on diffraction. My goal in developing this project was to integrate some very useful and interesting interactive material available on the web, with some new slides (two-dimensional "optical crystals") developed by Robert Bachilla, Dr. Larry Sorensen, and myself over the past several months.

Robert and I started meeting with Dr. Sorensen in the fall of 2005, with the original goal of replacing the 1973 "optical crystals" that were being used in the Physics 575 laboratory class. The idea was not just to replace them, but also to expand the patterns, to be able to show additional concepts and to thereby allow the students to gain better and broader understanding of diffraction. In order to strategize what to show, we began researching literature and material on the web. The interactive programs on the web were so helpful, easy to use and yet powerful, that we began discussing how to integrate the web material with the "hands-on" laboratory work with the optical crystals.

Replacing the optical crystals turned out to be far more difficult than we had originally envisioned. The popularity of digital photography has resulted in decreased availability of high resolution "analog" photography materials. Robert Bachilla conducted extensive research into digital methods, but the dynamic range currently available via digital methods is still not sufficient to produce optical crystals usable with lasers. He was successful in finding a high resolution black and white film for generating slides, and his investigation and production was the subject of his Master's thesis last Fall. Several of his photographs are incorporated into this paper, and all of his slides will hopefully be used as part of the laboratory lesson plan.

At Dr. Sorensen's suggestion, I have also investigated commercial microfiche as a way to generate the optical crystals. While fewer and fewer options are commercially available for microfiche (again, due to the popularity of digital mediums for storage), this process was shown to be successful for generating optical crystals.

While Robert was photographing his patterns, he kindly photographed the patterns I had generated. I had developed a small number of patterns designed to quickly show some key concepts in diffraction – the effect of the atom and the lattice size and shape, and the effects of imperfections due to thermal effects or crystal "stacking errors". Robert was wonderful to work with throughout this project, and demonstrated skill and persistence in researching methods and producing several beautiful and interesting new sets of optical crystals.

I owe both Robert and Dr. Sorensen huge thanks for all of their help and patience as we worked together to generate materials for an updated 2-D Diffraction laboratory lesson. Throughout my Master's studies in the Application of Physics, I have been particularly fascinated with light, optics and diffraction, I think because the physics describing light is elegantly simple in theory and yet endlessly complex in real-life applications.

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Table of Contents

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1. Introduction

The purpose of this experiment is to gain a better understanding of the physics of diffraction by using optical crystals (two-dimensional patterns on slides), and computer simulations. Optical crystals allow you to use optical wavelengths to investigate the same physics pioneered by von Laue, W. H. Bragg and W. L. Bragg, and Davisson and Thomson, in their Nobel prizewinning experiments and analysis. There have been many Nobel Prizes awarded for discoveries related to diffraction, including:

> Von Laue, Nobel prize 1914, for his discovery of the diffraction of X-rays by crystals

> W. H. Bragg and W. L. Bragg, Nobel prize 1915, for their analysis of crystal structure by means of X-rays)

> Davisson and Thomson, Nobel prize 1937, for their experimental discovery of the diffraction of electrons by crystals

After briefly reviewing some of the basic physics of diffraction and of crystal geometry, we'll look at how the different structural elements of a crystal affect the diffraction pattern. Throughout the experiment, we'll use both the optical crystal slides and computer simulation programs to illustrate important concepts. These tools are brought together to directly compare the results of each in the section on dealing with symmetry.

Figure 1 - 1 below shows the arrangement used for producing the optical crystal slides. The optical crystal slides are intended to be used with lasers (although white light could be used; in addition, the slides can also be put under a microscope or into a projector to get a better look at the patterns). The slides show diffraction patterns similar to those which might be seen with X-rays or electron diffraction through real crystalline materials, but are a lot more practical to use in the lab.
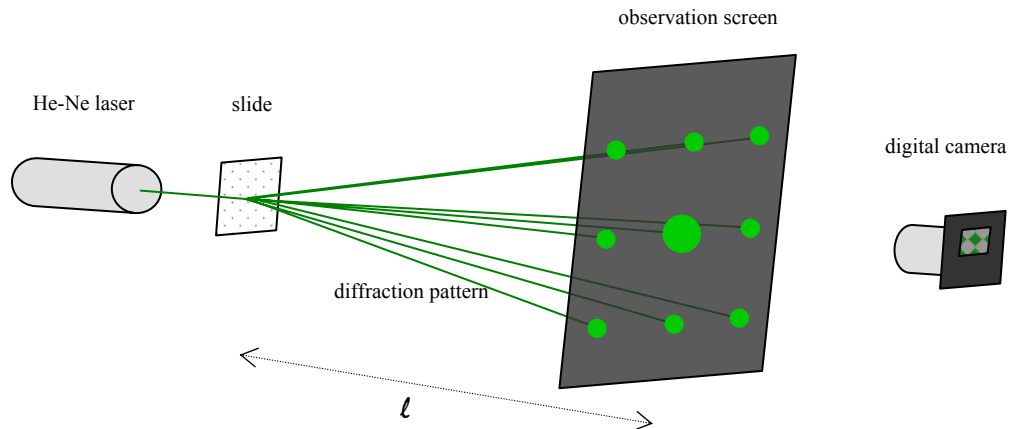

Figure 1 – 1: Arrangement for making the "optical crystal" slides (courtesy R. Bachilla)

2. Review of the Physics of Diffraction

Diffraction describes what happens when a wave interacts with an obstacle. Later on, we'll see that the mathematical description of the interaction can be extremely complex, but a simple, one-dimensional example is straightforward to describe mathematically and useful to review.

Recall that a general solution to the wave equation is

$$E\,(\mathbf{r},\,t) = E_0 * exp\,\{\,i\,(\mathbf{k}\cdot\mathbf{r}\text{-}\omega t)\,\}$$

or in one dimension:

$$E\,(x,\,t) = E_0 * exp\,\{\,i\,(kx\text{-}\omega t)\,\}$$

where E_0 is the maximum amplitude of the wave, $\mathbf{k}$ = the wave vector, which has a magnitude = $2\pi\,/\,\lambda$ and direction associated with the direction of movement of the wavefront, and ω is the angular velocity = 2π * frequency (in Hz) for the wave. λ is the wavelength of the incoming wave.

One useful way to visualize the interaction is by using Huygens construction, where a plane wave is treated as the envelope of the little spherical "wavelets" generated by each point on the wave front.
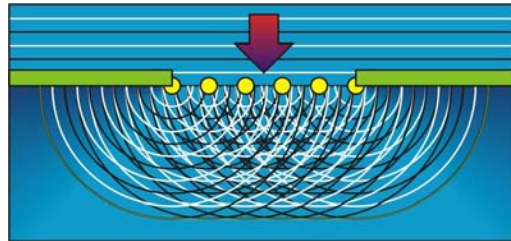

Figure 2 - 1: Diffraction through a single slit, using Huygens' construction (from Reference Website #9)

When the plane wave encounters a slit (of a size comparable to the wavelength of the plane wave), the spherical wavelets will form an interference pattern on the opposite side of the slit which will depend on the wavelength of the incoming wave, and the size of the slit. If, instead of a point, we visualize that the "wavelet" is generated by an infinitesimal volume element, dV, then the effect of the infinitesimal volume element on the wave movement is a function of the geometry at the volume element f $(\mathbf{r})$ * dV. For the example of a single slit (using the 1-D form of the equation), f (x) = 1 for the width of the slit, and f (x) = 0 otherwise. The wave diffracted from an infinitesimal volume element dV is equal to f $(\mathbf{r})$ * $exp\,\{\,i\,(\mathbf{k}\cdot\mathbf{r}\text{-}\omega t)\,\}$ dV . Every infinitesimal volume element inside the slit make a contribution to the diffraction pattern on the other side of the slit, so that:

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Diffracted electric field = $E(\boldsymbol{k}) = \sum f(\boldsymbol{r_1}) * exp\{i(\boldsymbol{k} \cdot \boldsymbol{r_1} - \omega t)\} dV_1 + f(\boldsymbol{r_2}) * exp\{i(\boldsymbol{k} \cdot \boldsymbol{r_2} - \omega t)\} dV_2 + \dots.$

or expressing the summation as an integral:

$$E(\boldsymbol{k}) = \int f(\boldsymbol{r}) * exp\{i(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)\} dV$$

Since the integration is carried out for the variable $\boldsymbol{r}$, the factor of $exp\{i(-\omega t)\}$ may be taken out of the integral. As a practical matter, diffraction experiments involve measurements of the intensity of diffracted beams (to determine the structure of molecules and crystal structure, generally, X-rays, but for this experiment, light waves), where the period of measurement is many orders of magnitude larger than the period of the waves. This means that the measurement ends up being the time average of the intensity of the diffracted waves, and the factor $exp\{i(-\omega t)\}$ may be dropped from the equation without losing information (it also makes the equations easier to write). This leaves:

$$E(\boldsymbol{k}) = \int f(\boldsymbol{r}) * exp\{i(\boldsymbol{k} \cdot \boldsymbol{r})\} dV$$

Also note that the diffraction pattern intensity $= |E(\boldsymbol{k})|^2 = |\int f(\boldsymbol{r}) * exp\{i(\boldsymbol{k} \cdot \boldsymbol{r})\} dV|^2$

What this means is that the diffraction pattern is the Fourier transform of the geometry of the obstacle(s) doing the diffracting. This is true for one, two, or three dimensions, and for different geometric arrangements, e.g. the electron distribution in an atom in a crystal lattice, or the arrangement of the atoms with respect to the crystal lattice, or the geometry of crystal lattice pattern itself.

Returning to the one dimensional example of a single slit, we use $f(x)$ instead of $f(\boldsymbol{r})$, and as noted above, $f(x) = 1$ inside the slit and $f(x) = 0$ elsewhere.
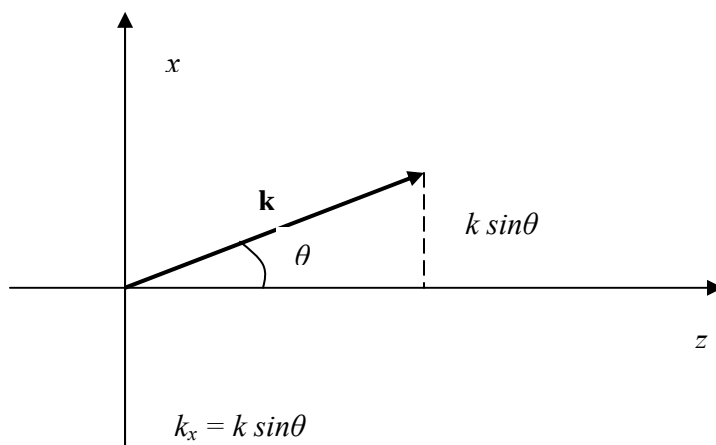

Figure 2 - 2: Geometry of the wave vector

With the geometry as shown in Figure 1 - 2, $k * r = k_x * x = k \sin\theta * x$, and the resulting diffraction pattern is given by:

$$E(k) = \int f(x) * exp\{ i*k*\sin\theta*x \} \, dx.$$

The integral should be evaluated from $-\infty$ to ∞, but in the case of a single slit, $f(x)$ is non-zero only for the width of the slit, $2 * X_0$. Since $f(x) = 1$ between $-X_0$ and X_0, the equation becomes:

$$E(k) = \int_{x = -X_0}^{x = X_0} exp\{ i*k*\sin\theta*x \} \, dx.$$

In one dimension, it simplifies the integral to show the diffraction function, normally shown as $E(k)$, as $E(\sin\theta)$. The magnitude of k is unchanged by diffraction, since the wavelength is unchanged, and the direction is dependent on θ or $\sin\theta$:

$$E(\sin\theta) = \int_{x = -X_0}^{x = X_0} exp\{ i*k*\sin\theta*x \} \, dx.$$

Using integral tables, this reduces to:

$$E(\sin\theta) = 2 * X_0 * (\sin\alpha / \alpha) \text{ where } \alpha = k * X_0 * \sin\theta.$$

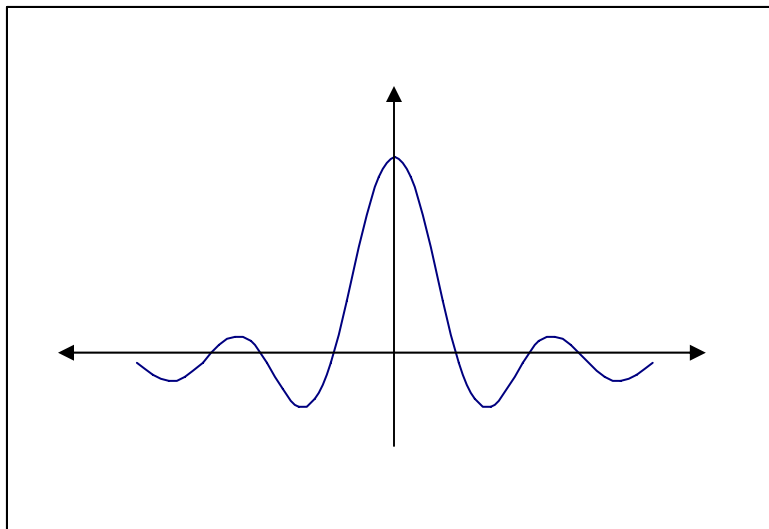The sin α / α function is also called the sinc α function, and has the form shown below:

Figure 2 – 3: Shape of the sinc function

As noted above, the intensity that is measured for a diffraction pattern is I $(\mathbf{k})$ = | E $(\mathbf{k})$ | ^{2}
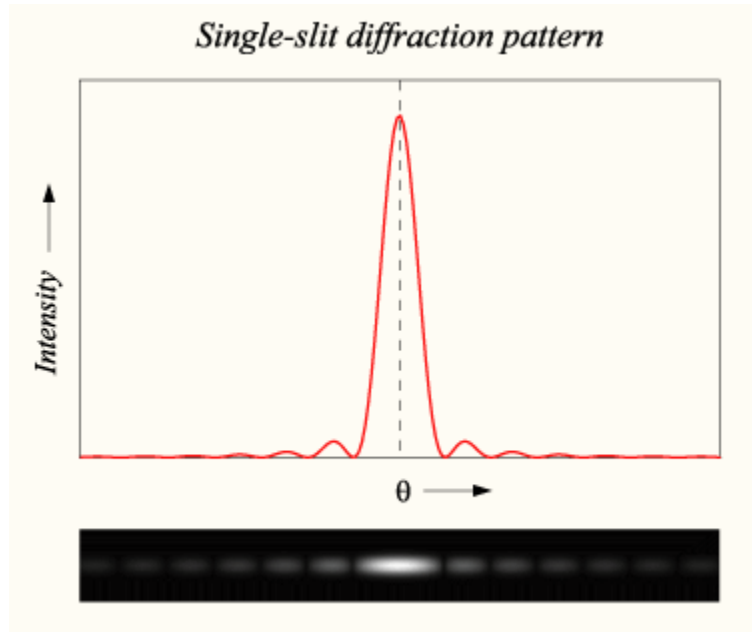(or | E $(sin\ \theta)$ | ^{2}), so a graph of intensity looks like this:

Figure 2 – 4: Graph and photograph showing the diffraction pattern from a single slit (from Reference Website #1)

Above is a photograph of the diffraction from a single slit, to compare with the intensity plot.

From previous experiments or classes, you probably remember that it doesn't matter whether you use a positive or negative object (e.g. a pinhole or a black dot) with a light source. This is called "Babbinet's Theorem." Whether the pattern is opaque on a translucent background, or translucent on a black (opaque) background, the diffraction patterns end up appearing the same, except at the origin in precisely the forward direction.   Most of the examples we'll use in the following sections are opaque dots or other representations of "atoms" instead of slits or pinholes, but situation is exactly analogous to what we've already described for a single slit.

For a simple two-dimensional example, see the discussion and the graphics illustrating the intensity of the diffraction pattern for a single atom, at the website:

http://www.mineralogie.uni-wuerzburg.de/crystal/teaching/basic_a.html

Notice that this website has links to a variety of interactive tools important for understanding diffraction. We'll refer to it again.

For more good examples, take a look at the program "Diffraction and Fourier Transform", which can be found at the following website:

http://lcr.epfl.ch/page37304-en.html

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Student exercise #1: Try the "Diffraction and Fourier Transform" program with a single dot of size = 10, then size = 70. Notice the inverse relationship of size between the dot and the radius of the first minimum of the diffraction pattern. You can also select a rectangular shape, or draw an arbitrary shape and see what the Fourier transform is for that shape.

To further demonstrate the effect of the size and shape of an "atom", use one of the "2D gas" slides. The size and shape of the diffraction pattern doesn't change if one or many randomly placed "atoms" are on a slide (assuming the size and shape of the "atom" doesn't change), but the intensity of the pattern is increased if more random "atoms" are used, making it easier to see the patterns in the lab. Notice how the diffraction pattern varies depending on the shape of the "atom." Also, use the slides to observe the reciprocal effect of different size "atoms" on the diffraction patterns.
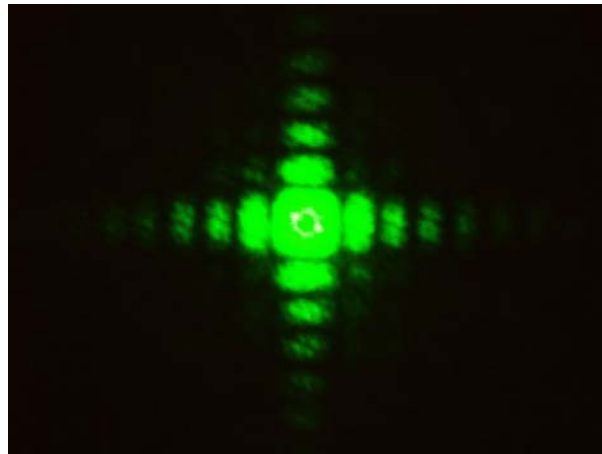

Figure 2 – 5: Diffraction pattern produced from a "gas" of large squares
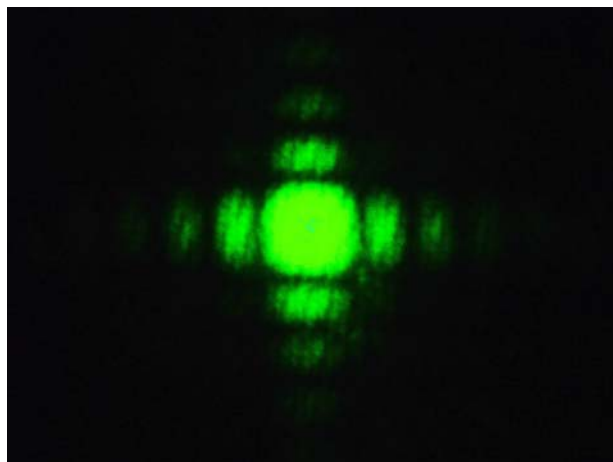

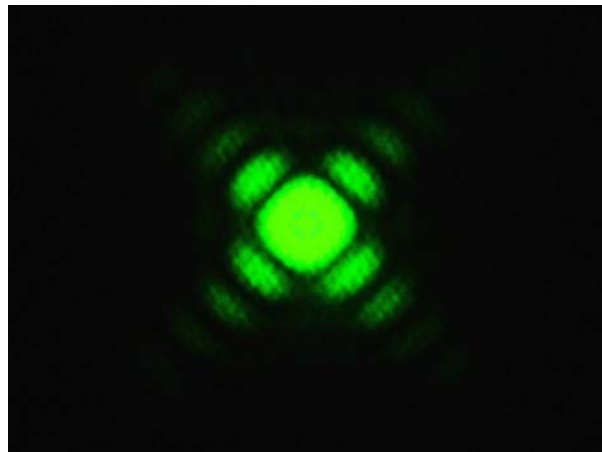Figure 2 – 6: Diffraction pattern produced from a "gas" of small squares

Figure 2 – 7: Diffraction pattern produced from a "gas" of large diamonds
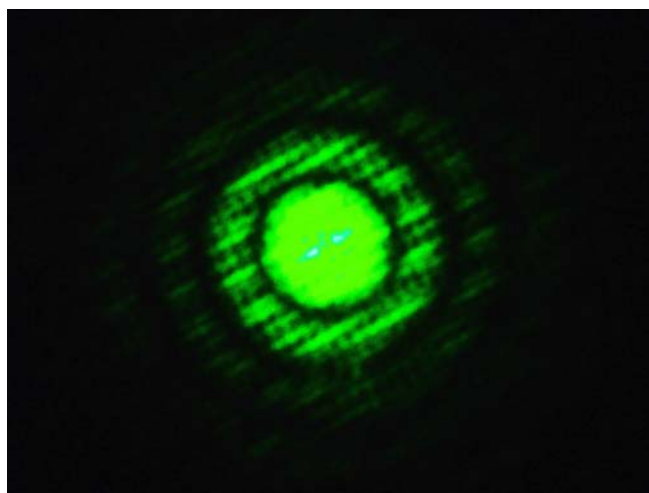

Figure 2 – 8: Diffraction pattern produced from a "gas" of dots
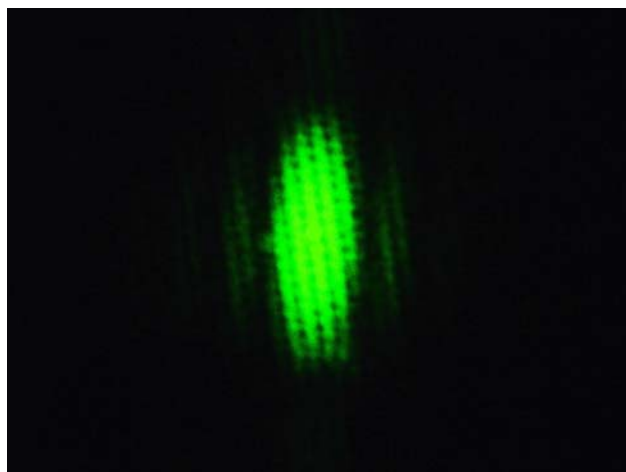

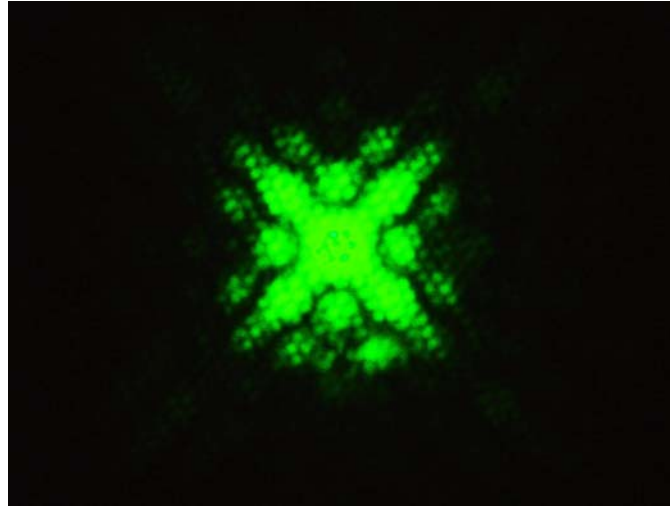Figure 2 – 9: Diffraction pattern produced from a "gas" of rectangles

Figure 2 – 10: Diffraction pattern produced from a "gas" of crosses (X's)

Some interesting notes related to the diffraction pattern, and the significance of the Fourier transform.

(A). the inverse of a Fourier transform (denoted FT $^{-1}$ below) of a function, is the function itself.

E (k) = FT f (x)
f (x) = FT $^{-1}$ E (k)

The example most people are familiar with is the use of the Fourier transform to decompose a periodic waveform, shown in the time domain, into its components in the frequency domain.
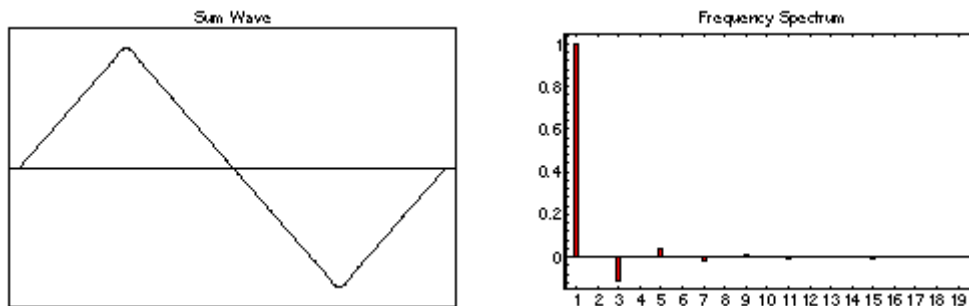

Figure 2 – 11: Fourier composition of a triangle wave (from Reference Website #13)

If you take the inverse Fourier transform of the function in the frequency domain, you will "recompose" the original waveform in the time domain.

(B). The position vector r and the wave vector k (where $|k| = 2\pi / \lambda$) are a Fourier transform pair, or conjugates, similar to time t and frequency ω.   Note that r and k are a spatial Fourier

transform pair, while t and ω are a temporal Fourier transform pair. An inverse relationship exists between the "width" of each of the variables of the pair. The bigger the slit, for example, the smaller the diffraction pattern, and vice versa. In the limit of the Dirac delta function (defined only at one point) representing a slit, the Fourier transform is infinitely broad. The Heisenberg uncertainty principle applies to the measurement (or even the definition) of position and momentum (remember that $\lambda = h / p$ where h is Planck's constant, and p is momentum - this equation is true for both photons and massive particles such as electron of the particles being diffracted):

$$\Delta x * \Delta p \geq \hbar / 2.$$

The inverse, or reciprocal relationship between real space, represented by x in one dimension or *r* in three dimensions, and "*k* space" or "momentum space," is something we'll observe over and over again as we study diffraction in more detail.

Student exercise #2: Explain in your own words why the diffracted intensity is the Fourier transform of the real structure for an "atom".

3. Crystal Geometry

A crystal is made up of atoms or molecules in a regular, periodic arrangement. As mentioned above, the diffraction pattern is given by the Fourier transform of:

>   a. the size and shape of the macroscopic crystal.
>   b. the geometry of the crystal lattice.
>   c. the arrangement of the atoms or molecules related to the "unit cell" of the crystal lattice.
>   d. the arrangement of the electrons in the atoms.

Although the diffraction pattern contains information about item a, it is rarely of interest, since other means exist for measuring macroscopic crystal size and shape. However, if the macroscopic crystal is small (or perhaps some kind of masking is used), then there is an effect on the diffraction pattern. The effect is the inverse of the "crystal building" exercise that you may have reviewed at this website:

http://www.mineralogie.uni-wuerzburg.de/crystal/teaching/basic_a.html

Or, you can generate a lattice and add a mask in real space using the "Diffraction and Fourier Transform" program at the following link:

http://lcr.epfl.ch/page37304-en.html

Both sites will let you see the effects of small crystal size or masking.

Of more practical interest to crystallographers are the effects of b, c, and d. In order to discuss these effects, we will first review crystal structure and nomenclature.

The crystal structure can be thought of as the combination of the crystal lattice (conceptually, a regular array of imaginary, infinitely small points) and a motif (conceptually, the unit or structure that is regularly repeated in space). Figure 2 – 1 shows three different crystal structures generated from the same rectangular lattice, but with different "motifs" (which could represent different types of atoms or molecules).
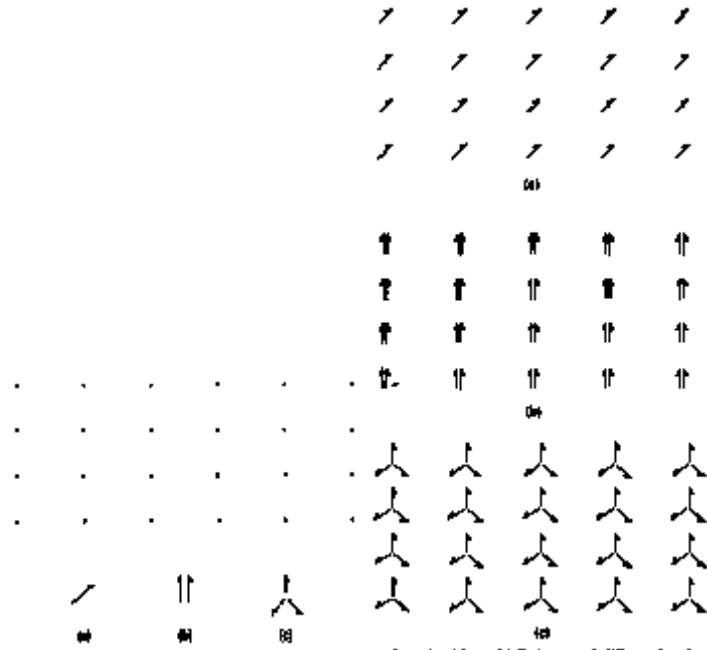
Figure 3 – 1: Rectangular lattice with different motifs. Crystal structure = lattice * motif (from Sherwood, pg. 60)

Crystal Lattice

One requirement of the crystal lattice structure is that it "fill space", that is, through whatever appropriate symmetry functions, all space can be filled with the lattice pattern with no gaps. For example, pentagons can't make up a plane lattice pattern, because there's no way to fill space with pentagons without any gaps. Appendix B is an extract from Reference 2 (Optics, Hecht and Zajac) which has an excellent discussion of two-dimensional patterns, lattices, and symmetry.

Some of the key concepts from Appendix B include:

   (a) You can choose an arbitrary point in the lattice and draw two lines to adjacent points to define the fundamental lattice vectors, **a** and **b** (in two-dimensions; the lattice vectors are **a**, **b**, and **c** in three dimensions). The angle between the lattice vectors is φ (in two-dimensions, for three dimensions, α, β, and γ are used)

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(b) The fundamental lattice vectors define a parallelogram (or parallelepiped in three dimensions) which we can call the "unit cell". While the choice of how to draw the fundamental lattice vectors may be arbitrary, conventions exist regarding the choice of the vectors and unit cell.

(c) The vectors are chosen so that the unit cell is generally primitive. A primitive unit cell is one where each unit cell is associated with a single lattice point.

(d) However, where it's appropriate to better represent the symmetry of lattice, a non-primitive unit cell is chosen. A non-primitive unit cell is associated with multiple lattice points.

(e) There are five plane lattices - these represent 4 lattice systems (oblique, square, hexagonal, and rectangular), each with a primitive unit cell, and with a non-primitive unit cell for the rectangular lattice system. The rectangular non-primitive unit cell is called a *centered* or *incentered* cell. Any two-dimensional lattice can be formed from one of these five plane lattices.

Lattice system	Lattice type	Conventional representation	Representative points
Oblique	Primitive	$a \neq b$ $\varphi > 90°$	(0, 0)
Square	Primitive	$a = b$ $\varphi = 90°$	(0, 0)
Hexagonal	Primitive	$a = b$ $\varphi = 120°$	(0, 0)
Rectangular	Primitive	$a \neq b$ $\varphi = 90°$	(0, 0)
	Centered	$a \neq b$ $\varphi = 90°$	(0, 0), (½, ½)

Figure 3 – 2: Plane lattices. (Based on Table 3.1, page 70, Sherwood)

More about Three-dimensional Crystal Lattices

As mentioned above and shown in Figure 2 - 3, the unit cell is defined with lattice vectors **a**, **b**, and **c**, and the angles between the lattice vectors are called α, β, and γ.
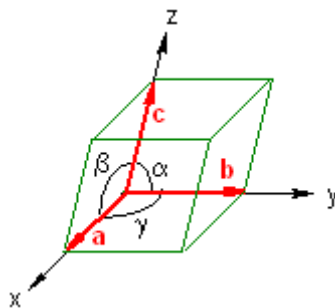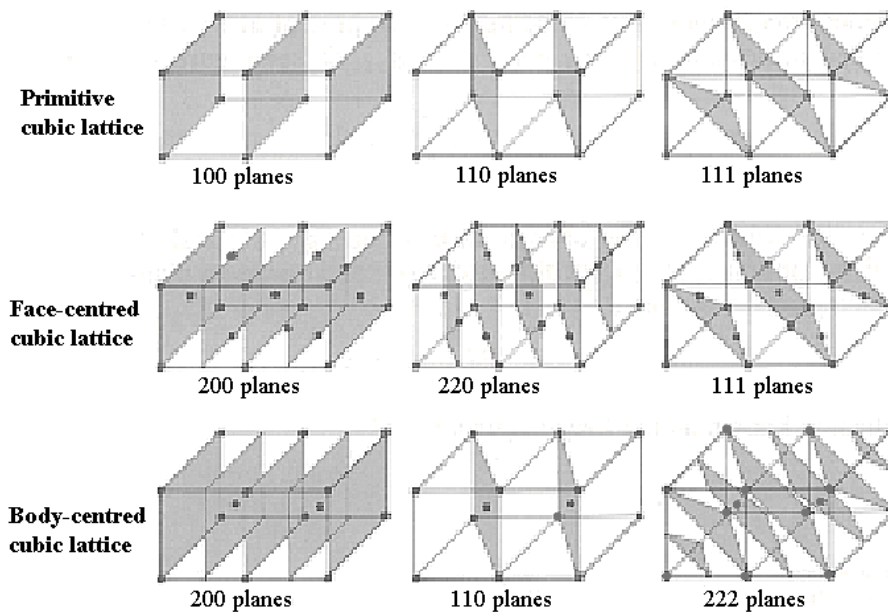

Figure 3 – 3: Geometry of the unit cell in three dimensions (from Reference Website #4)

There are 14 space lattice groups (known as the Bravais lattices). The 14 Bravais lattices are developed by combining one of the seven crystal systems (cubic, hexagonal, tetragonal, orthorhombic, monoclinic, and triclinic) with one of the lattice centerings (body-centered, face-centered, or centered on a single face).

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In general, any lattice point in a primitive unit cell can be described in terms of $\mathbf{r} = p\mathbf{a} + q\mathbf{b} + r\mathbf{c}$, with p, q, and r being integers. If the unit cell is non-primitive, p, q, and r may take on fractional values. The conventional way of referring to a lattice point is by the ordered triplet (p, q, r) for example, (0,1,2).

Later on, we'll need to reference lattice planes. Obviously, there are many planes that can be drawn through the regularly arranged points of a crystal lattice. In order to define which set of planes we're talking about, we'll use conventional "Miller Indices" (*hkl*). Miller Indices are defined as the reciprocals of the fractional intercepts which the plane makes with the lattice vectors.

Primitive cubic lattice	100 planes	110 planes	111 planes
Face-centred cubic lattice	200 planes	220 planes	111 planes
Body-centred cubic lattice	200 planes	110 planes	222 planes

Miller indices for three types of cubic lattices.

Figure 3 - 4: Examples of Miller indices (from Reference Website #10)

Note that (*hkl*) is a set of planes, and [*hkl*] is a direction. Refer to the following website if you're interested in more information about Miller indices:

http://en.wikipedia.org/wiki/Miller_index

The Unit Cell or "Motif" of the Crystal

As described above, a unit cell may be primitive (each unit cell associated with a single lattice point) or non-primitive (unit cell is associated with more than one lattice point). The simplest possible case is a primitive unit cell with a single element "motif" – for example, the "motif" of slide B-3 (see Appendix A) is single dot. However, the contents of the unit cell may be extremely complex, as shown in Figure 3 – 5.
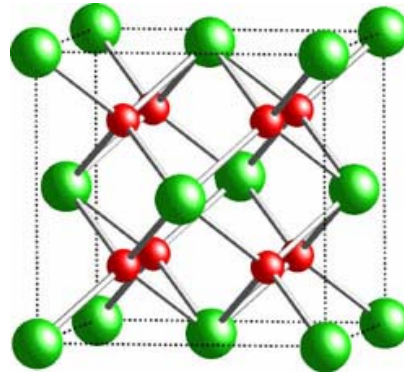
Figure 3 - 5: Unit cell of fcc plutonium dioxide (from Reference Website #12).

The contents of the unit cell may include many different atoms and molecules. Analysis of the unit cell requires different information than the analysis of crystal lattice, as discussed in the following sections.

4. Analysis of the Crystal Lattice Using Diffraction Techniques

If we neglect for the moment the contents of the unit cell and just consider the diffraction effects from the lattice points, we can consider each of the lattice points as a perfect point scatterer (i.e. as a delta function). To calculate the intensity maxima of the resulting diffraction patterns, either Bragg's Law or the von Laue equations may be used, with identical results.

Bragg's Law relates the distance between lattice planes, d_{hkl}, and the wavelength of the incoming wave, λ, with the scattering angle, θ. The lattice planes are treated as planes of reflection, and it's important to note that the spacing of importance in Bragg's Law is between the lattice planes, rather than between the atoms themselves. See the geometry in the diagram below.
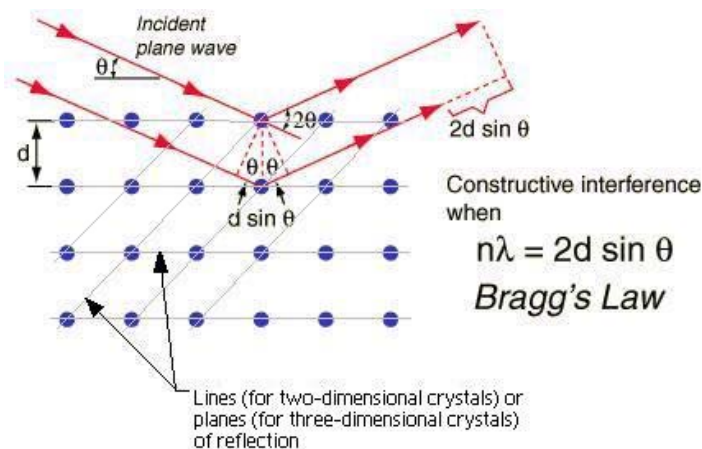

Figure 4 – 1: Geometry for Bragg's Law (based on a sketch from Reference Website #11)

For a three-dimensional crystal, the lattice planes which "reflect" will change as the crystal is rotated, and therefore the diffraction pattern will change.

The von Laue equations can be derived from the Fourier transform relationship between the real space lattice and the reciprocal space lattice (modeling each as an infinite array of delta functions), and may be written as:

$\Delta k * \mathbf{a} = 2\,h\,\pi$
$\Delta k * \mathbf{b} = 2\,k\,\pi$
$\Delta k * \mathbf{c} = 2\,l\,\pi$

Where Δk is the difference between the incoming and the diffracted wave vectors (k_{in}, k_{diff}), and **a, b,** and **c** are the lattice vectors described above (for primitive unit cells) or appropriate unit vectors which will comprise a primitive unit cell, if the unit cell is not intrinsically primitive. As before, h, k, and l are integers. Solutions of Δk that satisfy all three equations represent diffraction maximums.

It can be shown that solutions to the above Laue equations are of the form:

$\Delta k = n * 2\,\pi\,(h\,a* + k\,b* + l\,c*)$

Where a* , b*, and c* are defined to be the normals to the planes formed by the b and c axes, the a and c axes, and the a and b axes, respectively, and n is an integer.

Defining **G** to be the reciprocal lattice vector

$\mathbf{G}_{hkl} = h\,\mathbf{a}* + k\,\mathbf{b}* + l\,\mathbf{c}*$

Which is perpendicular to the (hkl) set of planes in the real lattice, and has a magnitude

$|\mathbf{G}_{hkl}| = 1 / d_{hkl}$

$|\Delta k| = n * 2\,\pi\,|\mathbf{G}_{hkl}| = n * 2\,\pi / d_{hkl}$

since $\Delta k = k_{in} - k_{diff}$, and $|k_{in}| = |k_{diff}| = 2\,\pi / \lambda$
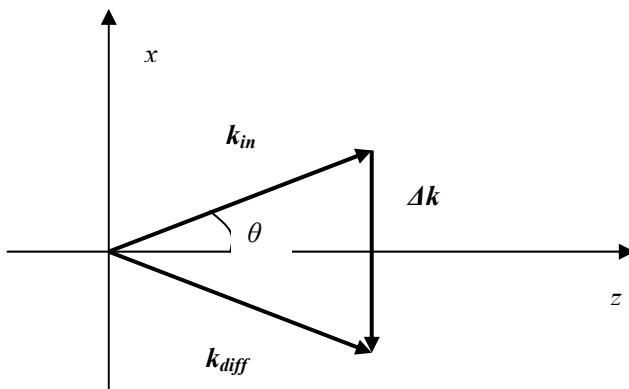
Figure 4 – 2: Geometry of the incoming and diffracted wave vectors, including the scattering angle θ

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$| \Delta \mathbf{k} | = 2 * | \mathbf{k}_{diff} | \sin \theta = 4 \pi \sin \theta / \lambda$

$4 \pi \sin \theta / \lambda = n * 2 \pi / d_{hkl}$

$2 d_{hkl} \sin \theta = n * \lambda$

A detailed tutorial on the real vs. reciprocal lattice can be found at this website:

http://www.matter.org.uk/diffraction/Default.htm

The tutorial allows you to experiment by changing the dimensions of the real lattice to observe the effect on the reciprocal lattice.

5. Analysis of the Contents of the Unit Cell

This section discusses the effects of items c and d in the list at the beginning of Section 3: the placement of the atoms or molecules with respect to the lattice points and the arrangement of the electrons with respect to their associated atoms. While the geometry of the crystal lattice will affect the geometry of the diffraction pattern spacing, or reciprocal lattice, the contents of the unit cell will affect the relative intensity of the diffraction maxima. Specifically, the observed diffraction pattern from an actual crystal will show partial or complete "extinctions" compared to a "ideal" pattern which could be calculated from an infinite real lattice made up of perfect point scatterers, or delta functions. The variation in intensity of the diffraction pattern maxima provides the information about the unit cell structure.

Analysis of the unit cell contents begins with consideration of how a single electron scatters an incoming wave of electromagnetic radiation. From experimental results, two types of scattering have been identified, Thomson scattering and Compton scattering.

Thomson scattering can be understood from classical electromagnetic wave theory, assuming that the electron doing the scattering is free to move, and being accelerated by the incoming radiation, acts as a source of radiation itself. Classical electromagnetic wave theory shows that the average magnitude of the electric field vector of the scattered waves, compared to the magnitude of the incident electric field is:

$E_{scat} / E_{in} = [e^2 / (4 \pi \varepsilon_0 r m c^2)] * [(1 + \cos^2 2\theta) / 2]$

Where e is the electron charge, ε_0 is the permittivity of free space (a constant equal to 8.854 x 10-12 F/m), m is the electron mass, r is the distance between the electron and where the field is sampled, c is the speed of light, and θ is the Bragg or scattering angle.

With this classical analysis, the principal of superposition holds, and so the contribution of each electron in the unit cell can be added up to find the net effect on the diffraction pattern:

_____

$(E_{scat})_{tot} = (E_{scat})_A + (E_{scat})_B + \ldots$

Defining the electron scattering factor $f_e = e^2 / (4 \pi \varepsilon_0 \, r \, m \, c^2)$, the superposition principle leads to the result:

$E_{scat} / E_{in} = \sum_n f_e \; exp \; \{ \; i * \varphi * n \; \}$

If, instead of considering discrete electrons, we consider an electron density function, $\rho(r)$, continuous over some volume, and sum together the contribution the contribution from infinitesimal volume elements, we get the integral form of the summation, rather than the discrete form:

$E (\Delta \boldsymbol{k}) = \int_{\text{unit cell}} f_e \, \rho(\boldsymbol{r}) * exp \; \{ \; i \; (\Delta \boldsymbol{k} \cdot \boldsymbol{r}) \; \} \; d\mathbf{V}.$

Since the diffraction pattern is sampled at the reciprocal lattice points, *hkl*, it's useful to define a discrete "Structure Factor", E_{hkl}, (where the intensity of a given point is $| \, E_{hkl} \, |^2$):

$E_{hkl} = V \int_0^1 \int_0^1 \int_0^1 \rho(x,y,z) \; exp \; \{ \; 2\pi * i \; (hx+ky+lz) \; \} \; dx \; dy \; dz$

To "back out" the contents of the unit cell, the function $\rho(x,y,z)$ must be determined:

$\rho(x,y,z) = (1 / V) \sum_h \sum_k \sum_l E_{hkl} \; exp \; \{ \; -2\pi * i \; (hx+ky+lz) \; \}$

This numerical calculation is called Fourier Synthesis, and it can require thousands of calculations to determine the electron density function for a single point (*x*, *y*, and *z*). A complete structure analysis for a complicated molecule can require millions or hundreds of millions of calculations, and wasn't practical for complicated molecules until high speed computers were available.

Since the intensity ($| \, E_{hkl} \, |^2$) of the diffraction pattern is all we can see with our eyes, or record with a CCD or using photographic methods, the phase information associated with E_{hkl} is lost. Therefore, it is impossible to directly solve for $\rho(x,y,z)$ using the observed diffraction pattern and the last equation given above. This is referred to as the "Phase problem", and to work around it, crystallographers generally use approximation and iteration (except for some small, simple molecules), to determine the unit cell contents.

One final note is that Compton scattering, which uses the Quantum Mechanical concept of electromagnetic radiation being carried in packets as photons, and a "billiard ball" model of the collision of the photon with the electron, does not result in discrete diffraction effects, but rather

overall background scattering. In the collision of the photon with the electron, momentum is conserved, but the wavelength of the input radiation is changed. There is no well-defined phase relationships between the radiation being scattered from different electrons in the assembly, and with no well-defined phase relationship, the superposition principle discussed above for Thomson scattering, doesn't hold. Sometimes Compton scattering is referred to as incoherent scattering, and Thomson scattering as coherent scattering.

6. Convolution

We've discussed that the diffraction pattern is the Fourier transform of the real space geometry of the crystal, and that this is true whether we're talking about the geometry of the overall crystal (shape function), the crystal lattice (infinite lattice), or the contents of the unit cell (motif).

f(obstacle) = f(motif) * [f(infinite lattice) x f(shape function)]
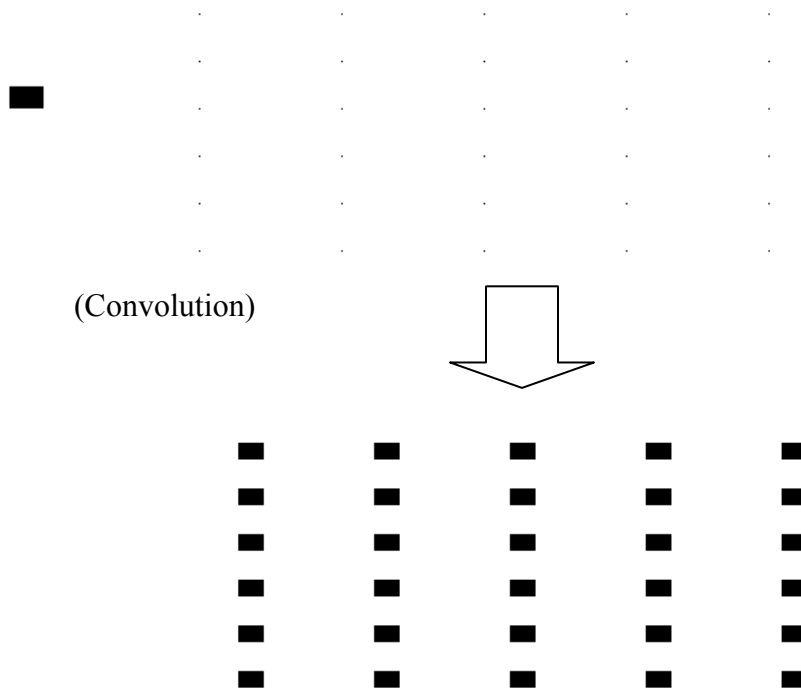
(Convolution)

Figure 6 – 1: Convolution of a single rectangle (motif) with a lattice, results in a lattice of rectangles.

Fourier transform

a

1/a
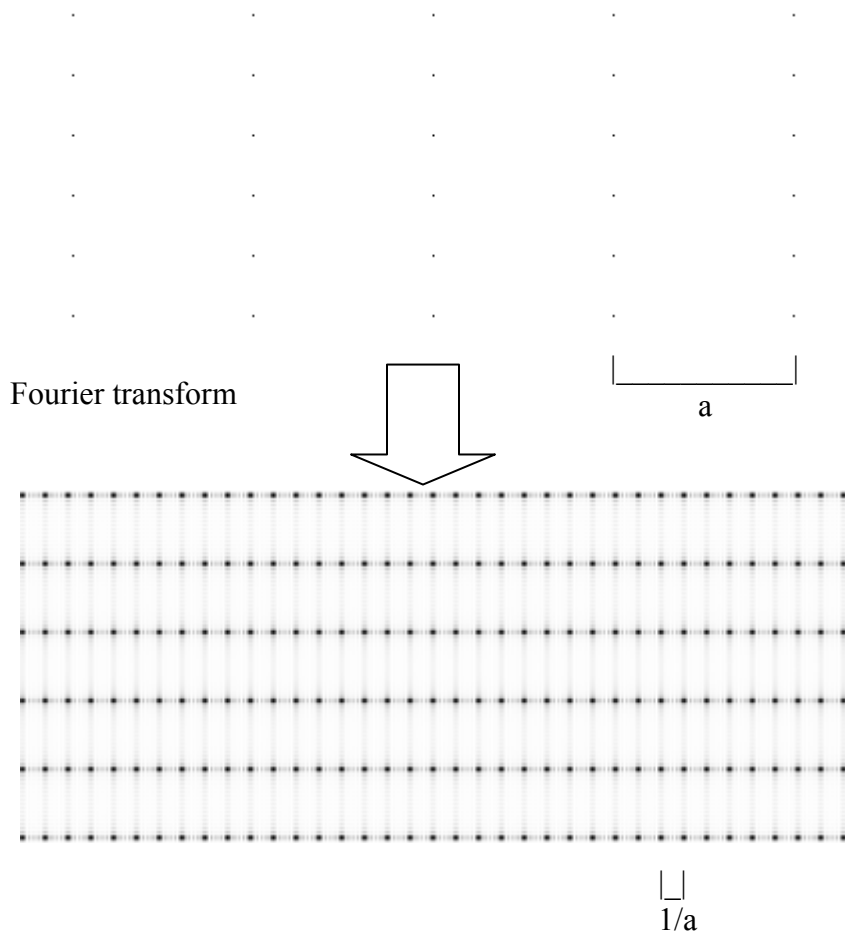
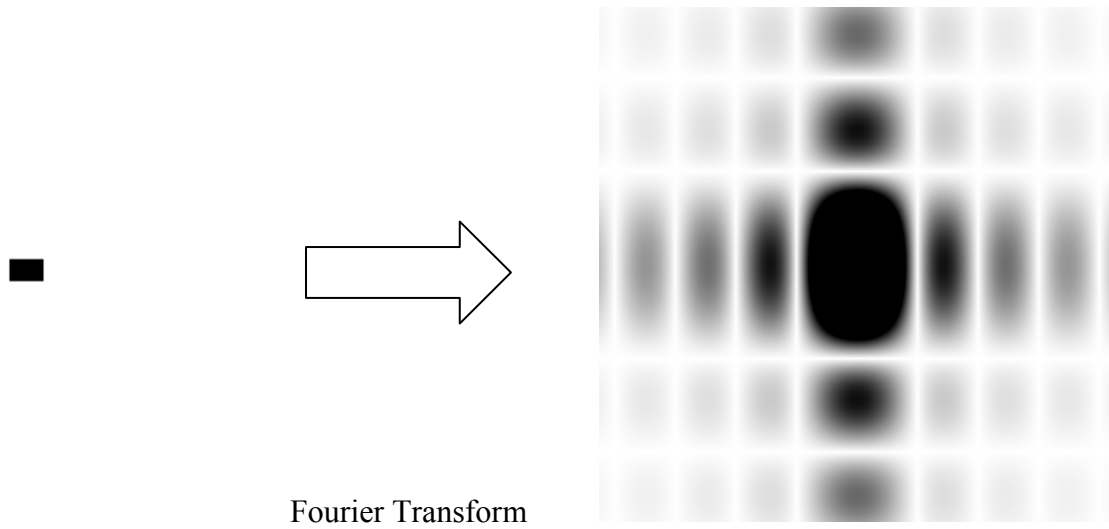Figure 6 – 2: The Fourier transform operation on a real lattice (top) yields the reciprocal lattice (bottom)

Fourier Transform

Figure 6 – 3: The Fourier transform of a single rectangle yields the pattern on the right.

Fourier transform
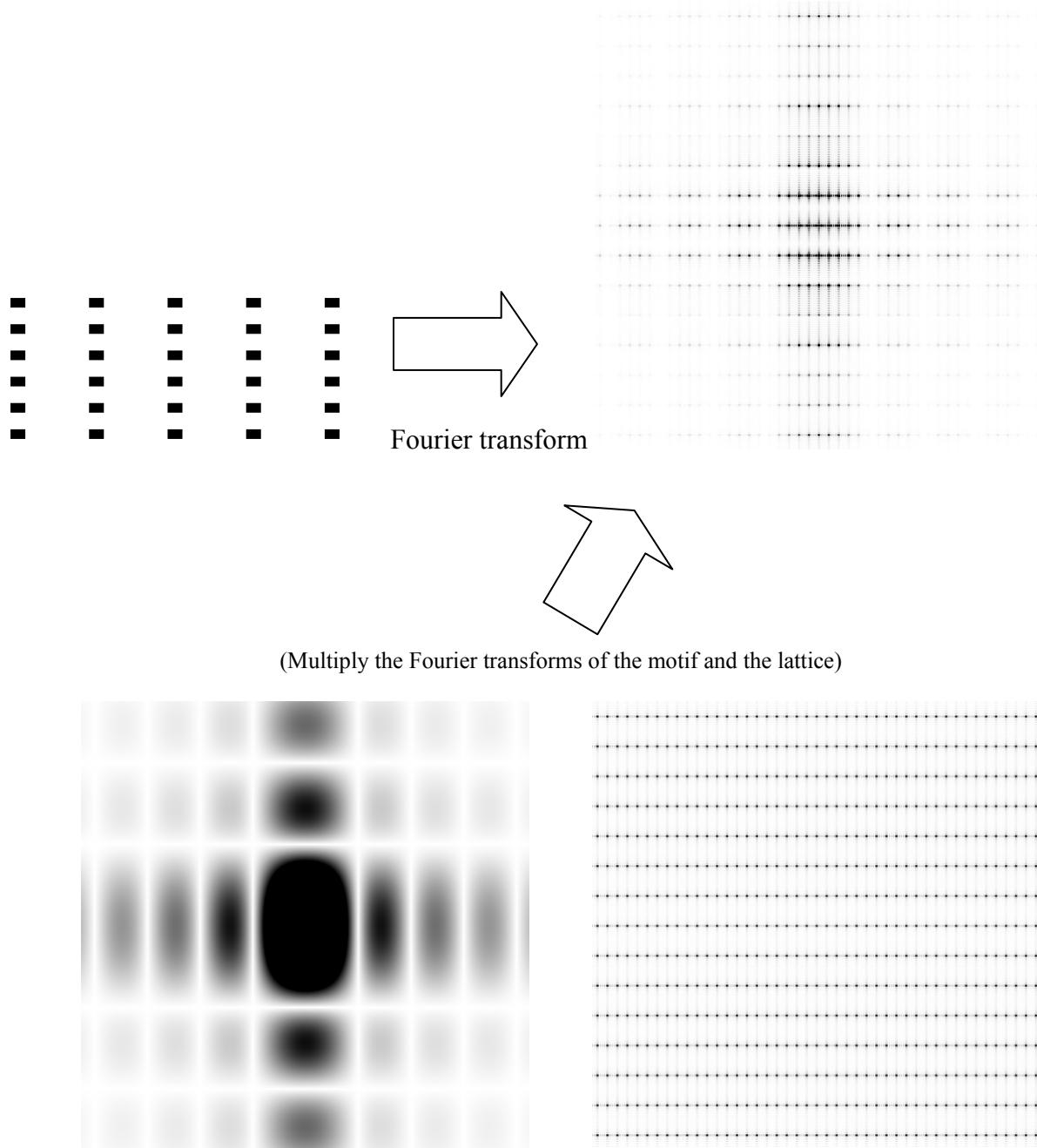
(Multiply the Fourier transforms of the motif and the lattice)

Figure 6 – 4: The Fourier transform of the lattice of rectangles is shown in the upper right hand corner. It is the product of the Fourier transform of the rectangle and the Fourier transform of the lattice.

The above figures show pictorially that the Fourier transform of the convolution of the motif with the lattice is the product of the individual transforms of the motif and the lattice. More generally:

Diffraction pattern amplitude F(sinθ) = T f(motif) x [Tf(infinite lattice) * Tf(shape function)]

Recall the definition and view an animated example of the convolution theorem by visiting this website:

http://mathworld.wolfram.com/Convolution.html

The effect on convolution can be seen in the diffraction pattern as an "enveloping" of the transform of the infinite lattice (idealized with perfect point scatterers) with the transform of the motif (assumes the transform of the shape function isn't affecting the result).

See a graphical example at this website:

http://www.mineralogie.uni-wuerzburg.de/crystal/teaching/conv_a.html

Below are some additional pictorial examples, from the "Diffraction and Fourier Transform" program at the following website:

http://escher.epfl.ch/fft/
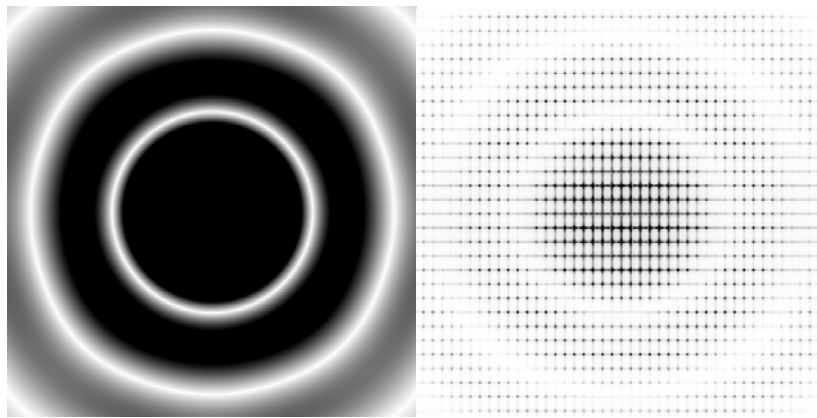
Figure 6 – 5: Fourier Transform of a single dot, and of a rectangular array of dots
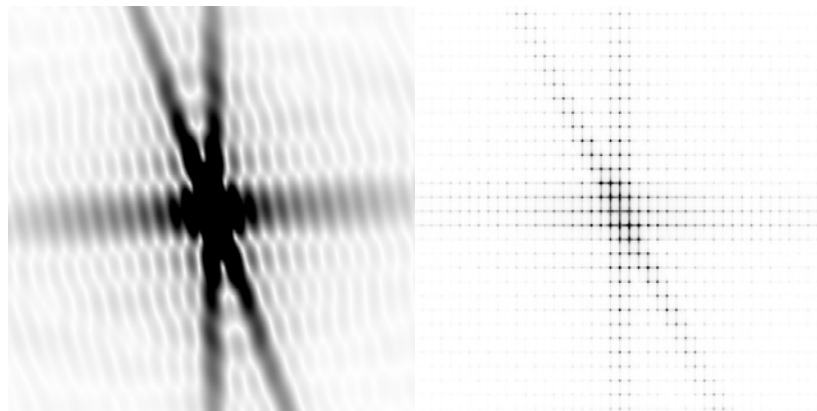
Figure 6 – 6: Fourier Transform of a single right triangle, and of a rectangular array of right triangles

7. The Effect of Wavelength - the Ewald Sphere

The Ewald sphere is a geometric construction which shows the relationships between the wavelength of the incident radiation, λ, the diffraction pattern (reciprocal lattice), and the scattering angle, $\boldsymbol{\theta}$. For simplicity, we'll discuss a two-dimensional representation of the Ewald sphere (a circle). See Figure 7 - 1 below, which is similar to Figure $4-2$ in showing the relationship between the incoming and diffracted wave vectors $\boldsymbol{k}_{in}$ and $\boldsymbol{k}_{diff}$, and the scattering angle, $\boldsymbol{\theta}$.
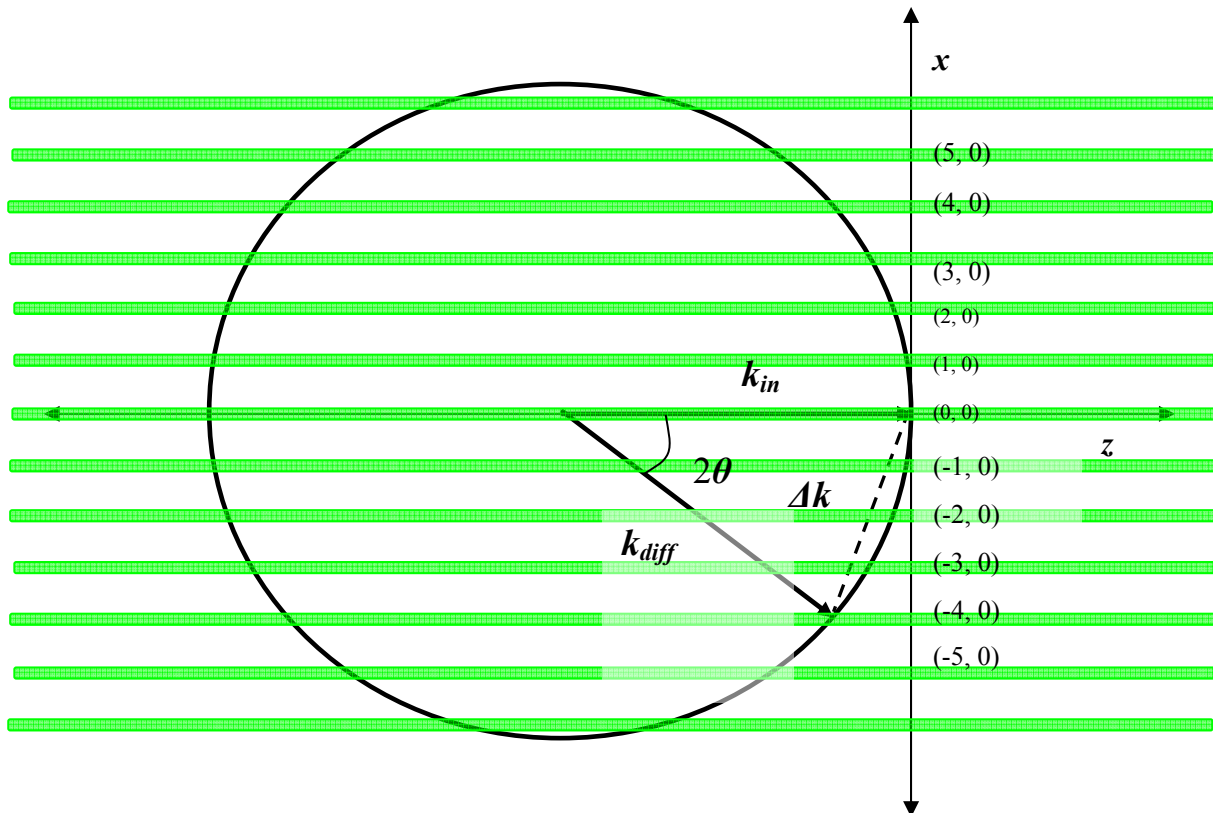

Figure $7-1$: Two-dimensional representation of the Ewald sphere – a circle.

The Ewald circle is generated using the following steps:

1) Starting at the origin of the reciprocal lattice, a circle (or sphere, in three dimensions) is drawn with radius equal to the magnitude of the $\boldsymbol{k}_{in}$ and $\boldsymbol{k}_{diff}$ vectors (remember that $\boldsymbol{k}_{in}$ and $\boldsymbol{k}_{diff}$ have the same magnitude, equal to $2\,\pi\,/\,\lambda$).

2) The origin of the circle is determined by the direction of the incoming wave vector, k_{in}. The head of the k_{in} vector is at the origin of the reciprocal lattice, and the tail defines the origin of the circle.

The significance of the Ewald circle (or sphere) is that diffraction maximums occur where the lattice points intersect the circle, because the intersection indicates that the Bragg condition is satisfied.

Note that in Figure 7 – 1, the reciprocal lattice geometry is represented by the long green rods parallel to the z axis, where the z axis is the direction of the incoming wave vector. This is intended to represent the diffraction geometry of the two-dimensional optical crystals that we've been using in this experiment. Recall the statement in Section 2, that the Fourier transform of a delta function is infinitely broad. The optical crystals can be considered a delta function in the axis parallel to the incoming wave vector.

While the optical crystal slides are a simplification of "real crystals", it should be noted that crystallographers often use thin samples of material for structural analysis, with the result that reciprocal lattice points are elongated, and diffraction occurs even when the Bragg condition is not exactly satisfied. See the diagram at the following website for a graphical representation of this situation:

http://www.microscopy.ethz.ch/ED-Ewald.htm

To get a better sense of the three-dimensional Ewald sphere, run the "Ewald sphere animation" at the following website:

http://lcr.epfl.ch/page37304-en.html

The animation shows the reciprocal lattice rotating about the reciprocal lattice origin, while the incoming wave vector and the Ewald sphere remain stationary. A number of experimental methods for analyzing crystals involve rotating the crystal and capturing the resulting diffraction patterns on film (or with a CCD). In the animation you'll see yellow arrows indicating the intersections of the Ewald sphere with the reciprocal lattice – these are where the diffraction maximums would be recorded.

More animations are shown at the following website:

http://www.science.uva.nl/research/cmp/goedkoop/group/docs/fluctuations/scans.html

The animations on this website are interesting because they show different experimental methods for recording diffraction patterns.

Student exercise #4: Draw the reciprocal lattice geometry in both the x and the y axes, for the 0.12mm x 0.08mm real lattice (the geometry used in several of the optical crystal slides), using wavelengths equal to the red and green lasers (use an appropriate scale). What is the effect of

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8. Symmetry of the Crystal Lattice and the Diffraction Pattern

Please refer again to Appendix B for a detailed description of the symmetry operations, the 17 space groups, and standard notation for describing each of the 17 space groups. Following are some of the key concepts related to these points:

(a)   There are 6 symmetry operations:

Proper rotation
Reflection
Inversion = rotation + reflection
Screw rotation = rotation + translation
Glide = reflection + translation
Improper rotation = rotation + inversion

(b)   The 17 space groups represent all the possible symmetries in two dimensions.   As mentioned earlier, symmetry operations on the unit cell are used to fill space to form a complete crystal lattice.

(c)   The standard notation for describing the 17 space groups is as follows:
first letter is the lattice type, either a *p* (primitive cell) or *c* (centered rectangular).
the next three characters may be either numbers or letters, to indicate the following symmetries:
m (mirror),
g (glide),
1 (none),
and a digit *n* to indicate the *n*-fold rotation (*n* = 2, 3, 4, 6).

For example, a "p2" notation indicates a primitive cell with 2-fold rotation and no mirrors or glides, whereas the "p4gm" notation indicates a primitive cell with 4-fold rotation, and mirror axes oriented 45° to a glide. Similar notation and classification methods are used for three dimensional crystals.

Use the slides in the binder to view the diffraction pattern of each one of the 17 space groups. Notice that each one of the 17 space groups has been generated with a "motif" of right triangles and dots. For reasons of consistency, all of the examples in this section are of the dot motif.
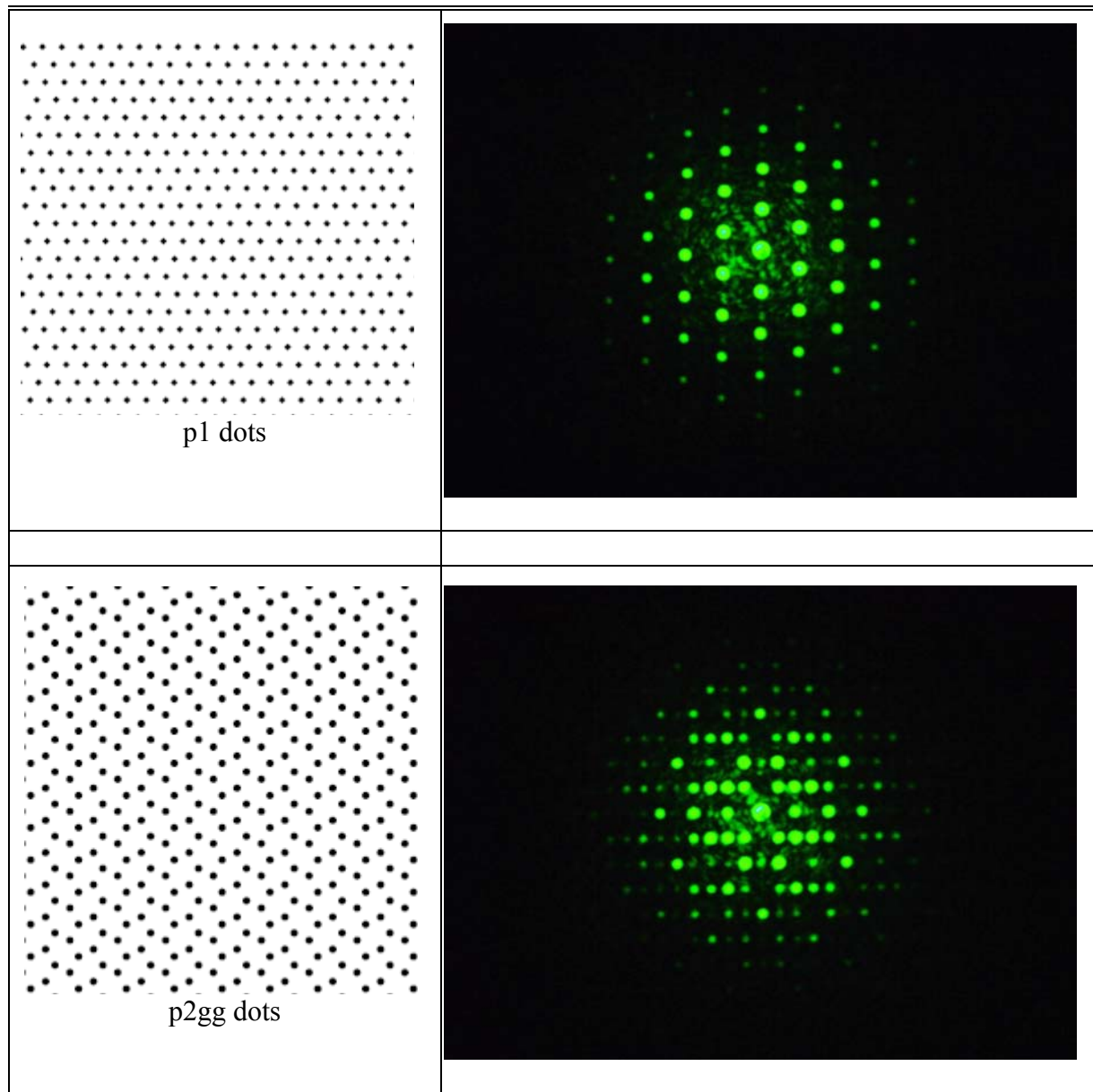
Figure 8 – 1: Real space patterns and photographs of diffraction patterns (not to scale) for the p1 and the p2gg space groups.

Notice the symmetry of the diffraction pattern compared to the real space lattice. Also notice the complete and partial "extinctions" in the diffraction pattern. Crystallographers use this information to determine the structure of three-dimensional crystals - the diffraction pattern from an unknown sample can be compared to characteristics of known samples.

Let's say, for example, you were trying to determine the real space structure associated with the diffraction pattern shown in Figure 8 – 2.

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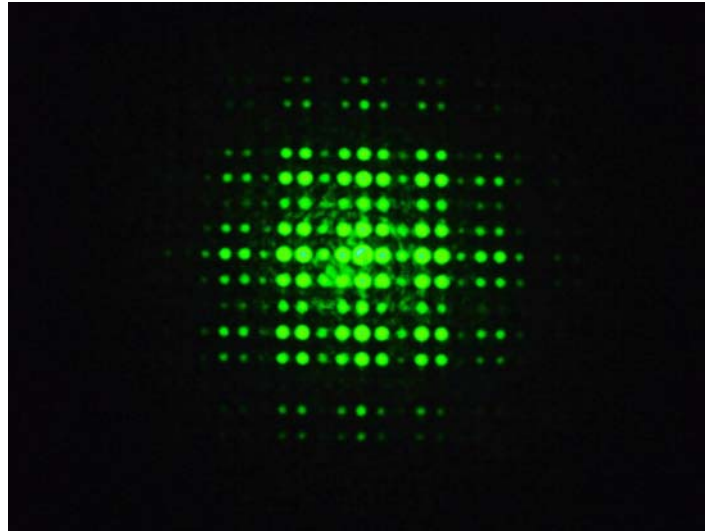
Figure 8 – 2: Photograph of the diffraction pattern from an unknown optical crystal

By examining the symmetry of the diffraction pattern, you may be able to determine that the symmetry of the real space pattern is even, perhaps 2 or 4. You may have noticed from previous examples that the symmetry of the diffraction pattern has the same, or one degree higher, symmetry as the real space pattern. The reason for this is shown below.

Another way to write the Structure Factor discussed in Section 5 is:

$$F_{hkl} = \sum_j f_j \exp\left(2\pi i\,(h_j + ky_j + lz_j)\right)$$

For some given reciprocal lattice point *hkl*, and a point *–h, -k, -l* which is centrosymmetrically related:

$$F_{hkl} = \sum_j f_j \exp\left(2\pi i\,(h_j + ky_j + lz_j)\right)$$

$$F_{(-h,-k,-l)} = \sum_j f_j \exp\left(-2\pi i\,(h_j + ky_j + lz_j)\right)$$

$$F_{hkl}{}^* = F_{(-h,\,-k,\,-l)}$$

$$|F_{hkl}| = |F_{(-h,\,-k,\,-l)}|$$

Since the intensity of each point is equal to $|F_{hkl}|^2$, we will observe centrosymmetry of the diffraction pattern, even if the lattice is not centrosymmetric.

One way to determine the real space structure of the unknown optical crystal in Figure 8 – 2 would be to use computer simulation to try to match the diffraction pattern shown. The following website allows you to quickly generate and view the diffraction patterns for the unit cells and lattices generated from the 17 space groups (using "JFourier2" under Java applets):

http://jcrystal.com/steffenweber

However, an even more powerful tool is the Diffraction and Fourier Transform (DFT) program at this website:

http://lcr.epfl.ch/page37304-en.html

This program allows you to generate simple patterns using the graphical tools included with the program, or to load in a pattern developed from any graphics program as long as it has been saved as a *png, *.gif, or *.jpg file type (use the "Advanced" button to open and save files). Also at the website above is a program "Escher Web Sketch" that allows you to build your own patterns ("decorate" any of the 17 space groups with the motif of your choosing).

The following figures show the output of the DFT program, together with real space pattern (used to make the optical crystal slide and as input to the DFT program), and the photograph of the diffraction pattern from the optical crystal slide.
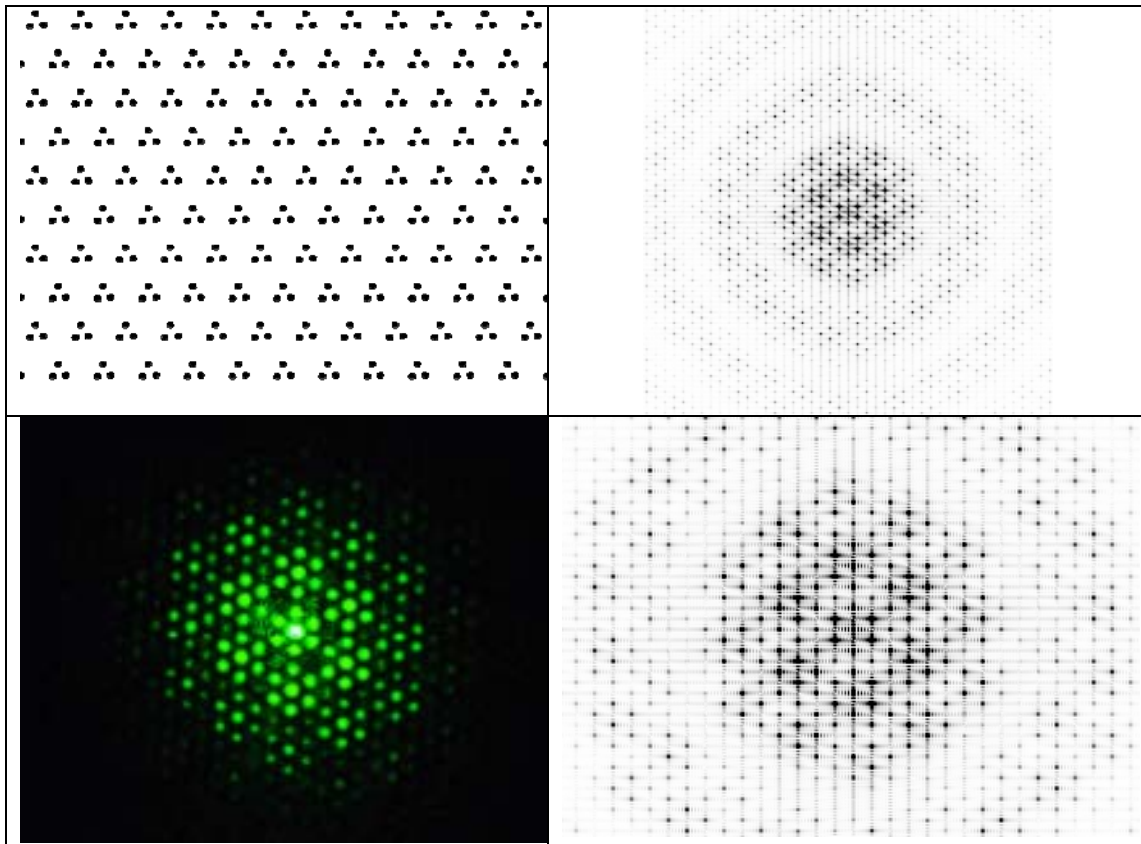
Figure 8 – 3: Clockwise from upper left: the real space pattern for the p3 space group, the calculated diffraction pattern, the calculated diffraction pattern magnified, and the photograph of the p3 diffraction pattern.
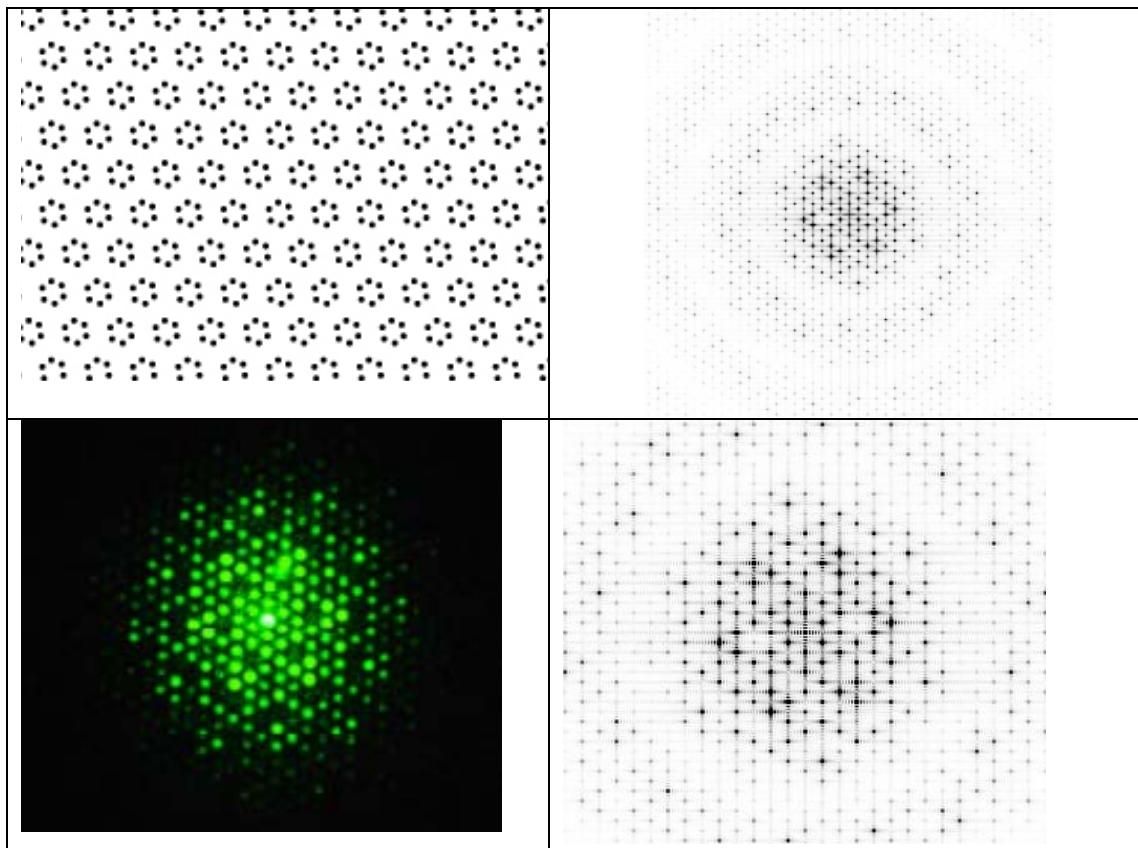
_____

Figure 8 – 4: Clockwise from upper left: the real space pattern for the p6 space group, the calculated diffraction pattern, the calculated diffraction pattern magnified, and the photograph of the p6 diffraction pattern.

The calculated diffraction patterns shown in the above figures were generated from the "Magnitude" view of the FT using the DFT program. Particularly in the magnified view of the calculated diffraction pattern, you can see the close match between it and the photograph of the diffraction pattern.

Back to the earlier discussion about symmetry of the diffraction pattern, notice that both the p3 and p6 diffraction patterns shown above have 6-fold symmetry. The patterns are distinctly different however, with respect to the partial and full extinctions of the diffraction maxima.

Student exercise #5: Using the Diffraction and Fourier Transform program, calculate the diffraction patterns for the p2mm, p2gg, p4mm, and p4gm space groups. Using these results, identify the space group associated with Figure 8 – 2, and Figure 8 – 5, below.
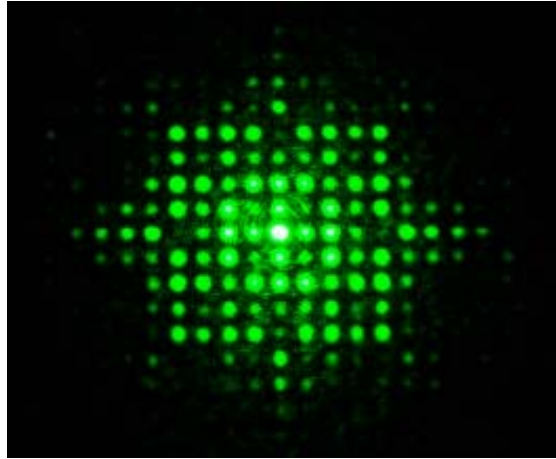
Figure 8 – 5: Photograph of the diffraction pattern from another unknown optical crystal

More features of the Diffraction and Fourier Transform Program

The Diffraction and Fourier Transform program calculations can be graphically displayed in a variety of ways, including Complex, Real Part, Imaginary Part, Magnitude, and Phase options.
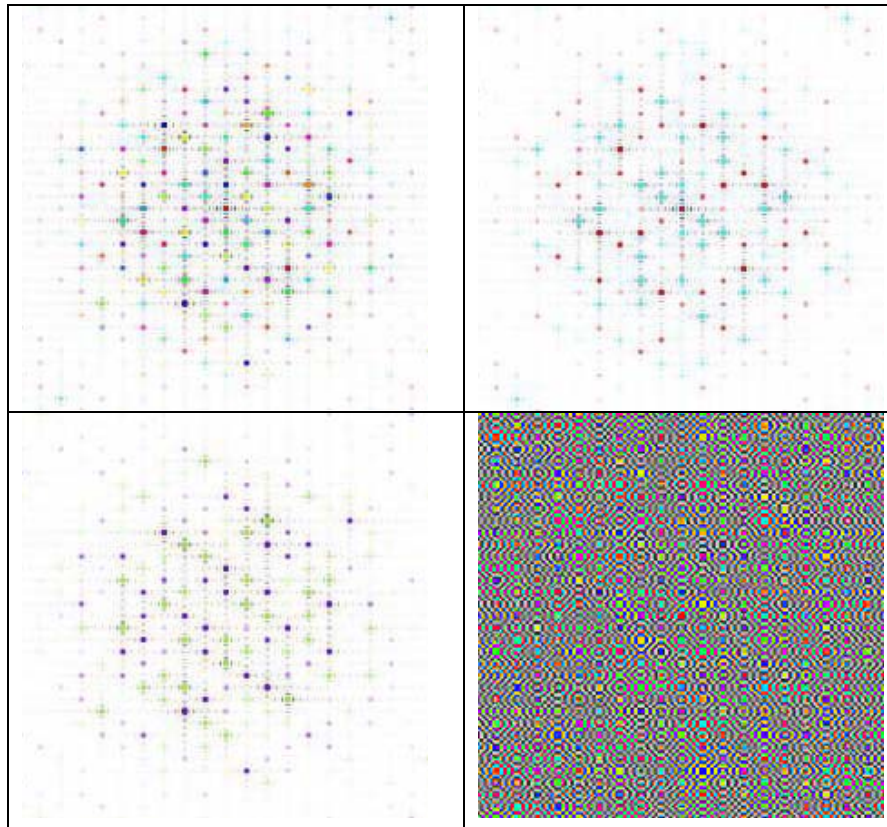

Figure 8 – 6: Clockwise from upper left: output of the DFT program for the p6 space group, using the Complex, Real Part, Imaginary Part, and Phase options. Magnitude is shown in Figure 8 – 4.

The "Magnitude" option is comparable to what your eye, a CCD, or the camera "sees" (remember that the diffraction pattern intensity = $| E (k) |^2$). The other options can be understood by referring back to the diffraction pattern equation in Section 2:

$$E (k) = \int f (r) * exp \{ i (k \cdot r) \} dV$$

The "Complex" option is the complete solution to the equation, "Real Part," "Imaginary Part" and "Phase" are self-explanatory. Performing the "FFT-1" (inverse Fourier Transform) on each option is interesting, in particular for the "Magnitude" option, because the program output graphically shows the "Phase problem" discussed in Section 5.

The Diffraction and Fourier Transform program also allows you to place a mask on either the real space lattice (simulates the effect of a small, finite crystal) or on the calculated diffraction pattern (simulates the effects of limited size of the recording device, as an example).

The effect of small crystal size was discussed briefly in Section 3 – for very small crystals, there will be noticeable subsidiary maxima between the main diffraction maxima.

The effect of placing a mask on the calculated diffraction pattern and performing the inverse Fourier Transform is to lose resolution on the calculation of the real space geometry. This is an intuitively obvious result – less available data results in a less precise calculation.
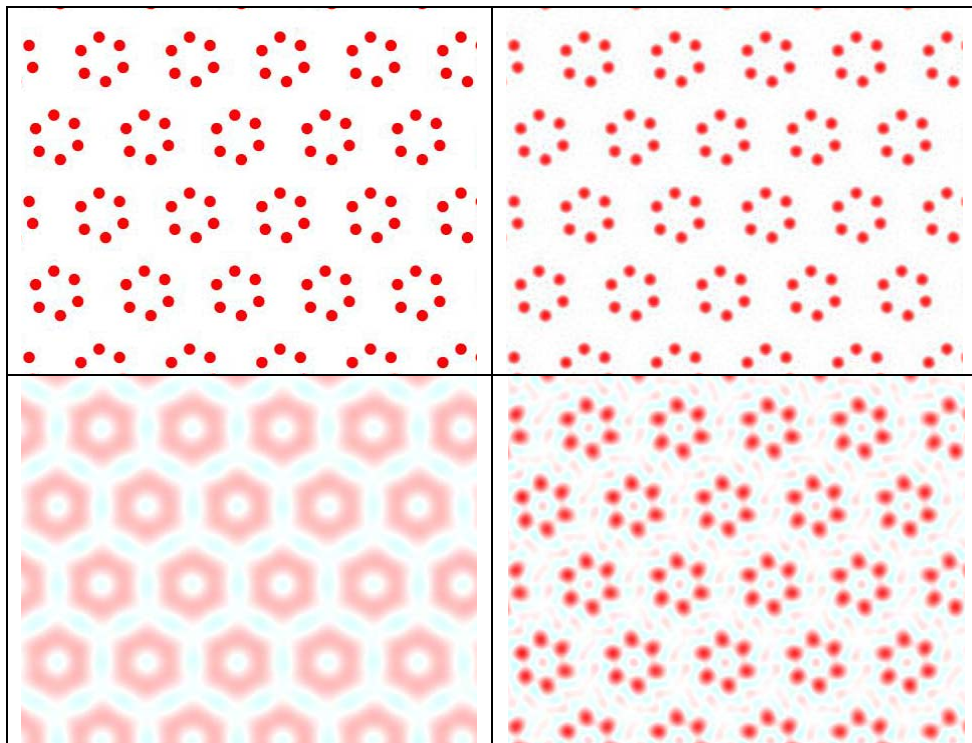

Figure 8 – 7: Clockwise from upper left – each picture shows the effect of placing successively smaller masks on the calculated "Complex" diffraction pattern of the DFT program, and performing the inverse Fourier Transform (for the p6 space group). The original real space pattern is shown in Figure 8 – 4.

9. Conclusion

Diffraction describes what happens when a wave interacts with an obstacle. The diffraction pattern which results from this interaction contains information about the structure of the obstacle - the diffraction pattern amplitude is the Fourier transform of the geometry of the obstacle.

When the obstacle is a crystal, each component of the crystal geometry can be important for understanding the diffraction pattern. A crystal is made up of ordered arrays of atoms or molecules. The geometry of the array, or lattice, determines the geometry of the reciprocal lattice, while the arrangement of the atoms and molecules (the contents of the unit cell), determines the enveloping function for the reciprocal lattice. If the crystal is very small, the finite size of the crystal can also affect the diffraction pattern - there will be noticeable subsidiary maxima between the main peaks of the diffraction pattern.

The diffraction pattern is affected by the wavelength of the incoming wave. This effect can be understood by using the Ewald sphere (or circle in two dimensions), a simple geometrical construction relating the wavelength of the incoming wave with the scattering angle and the reciprocal lattice.

The symmetry of the crystal can be analyzed by observing the symmetry of the diffraction pattern (the diffraction pattern has the same, or one degree higher, symmetry as the real space pattern), and by observing the full or partial extinctions of the diffraction peaks in the diffraction pattern. Analysis of the full and partial extinctions is beyond the scope of this paper. See the texts in the References section (for example, Sherman) for more information if desired.

Most of the discussion and experiments in the preceding sections focused on two-dimensional geometries - in most cases, there is a direct analogy to three dimensions.
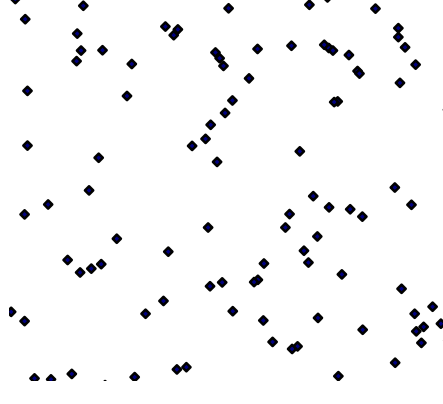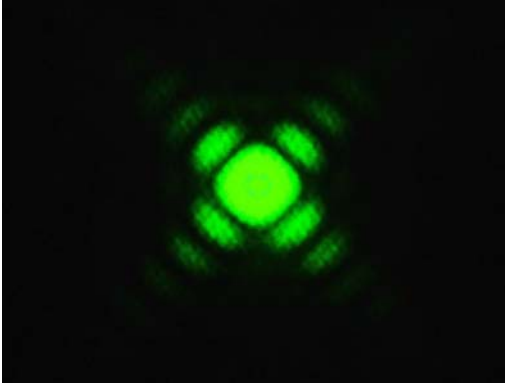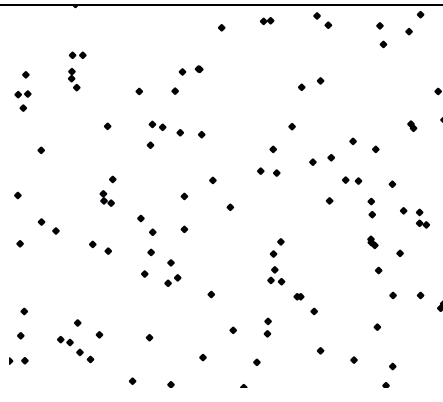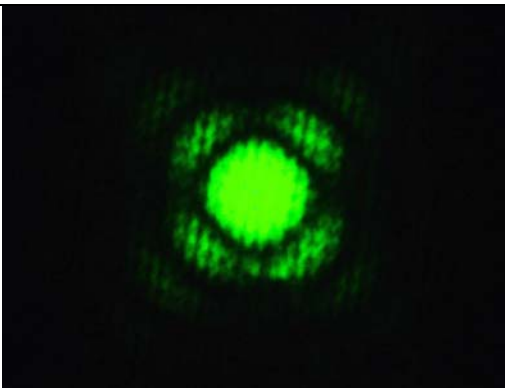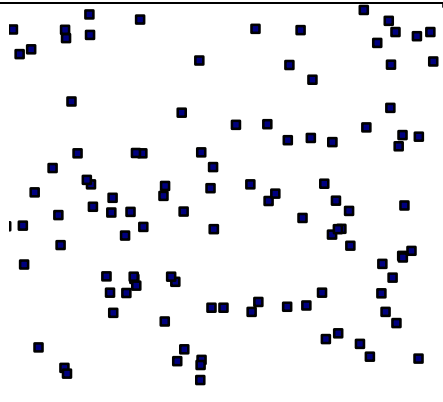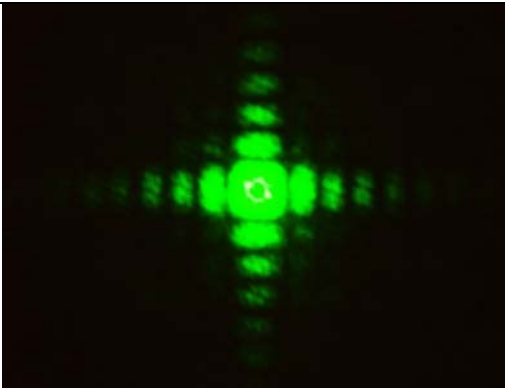
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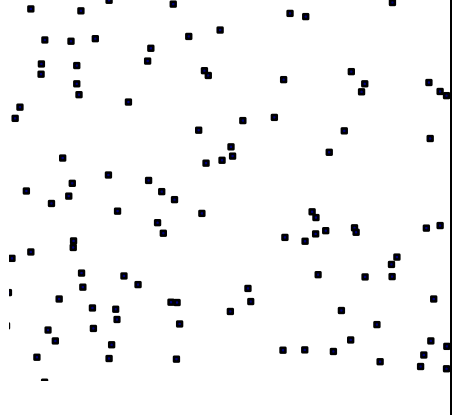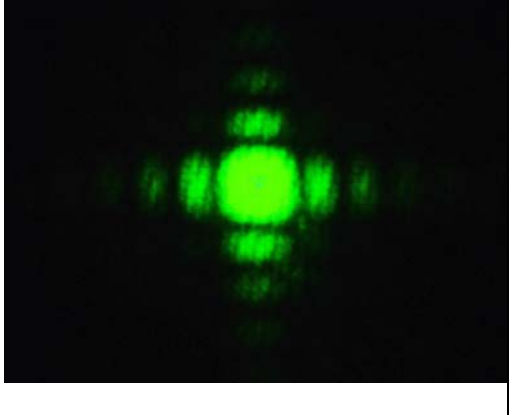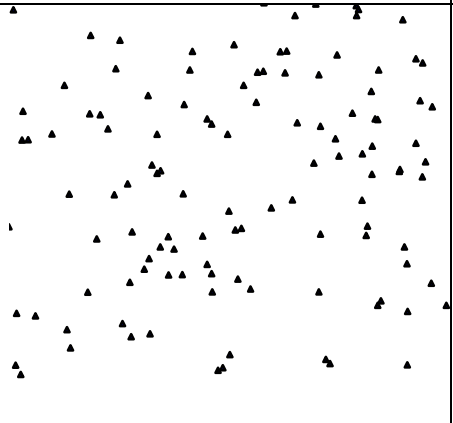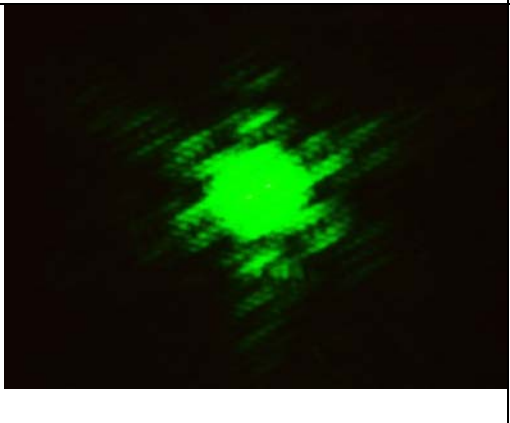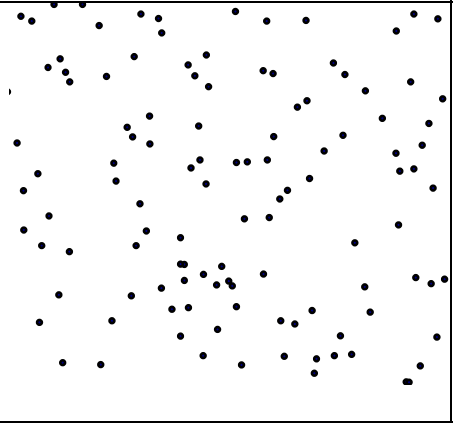
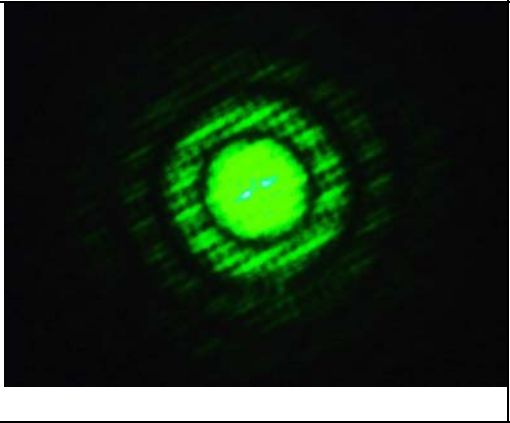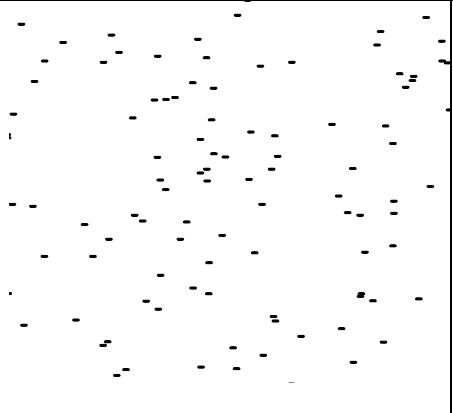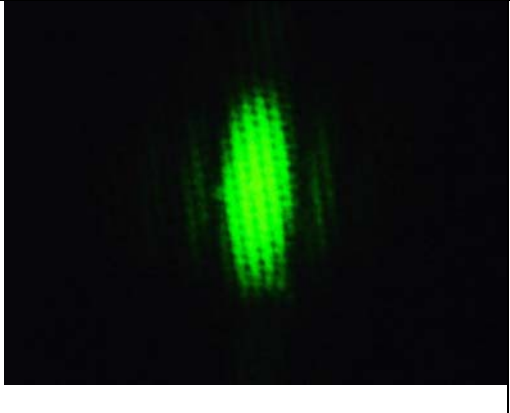## Websites

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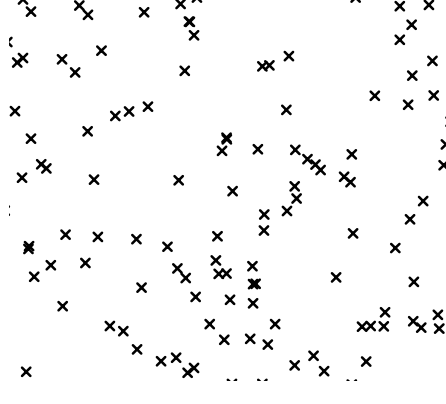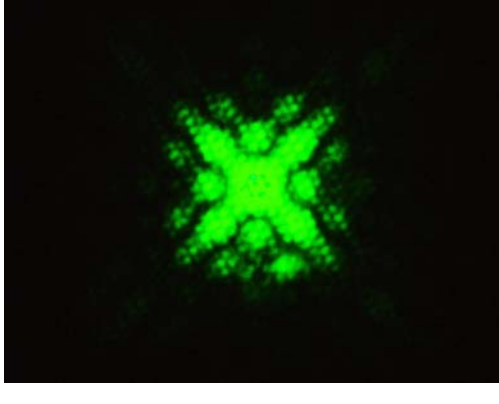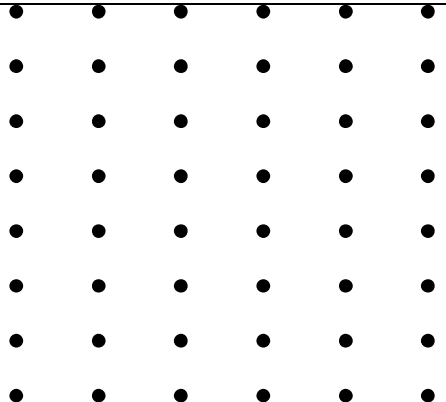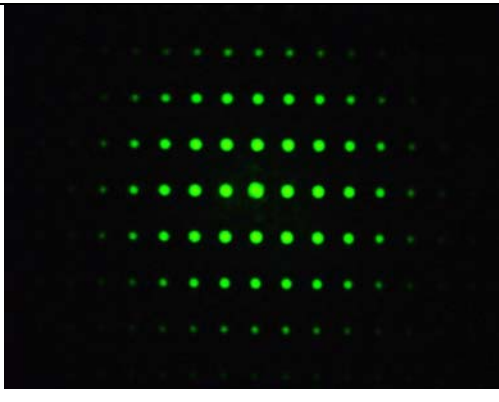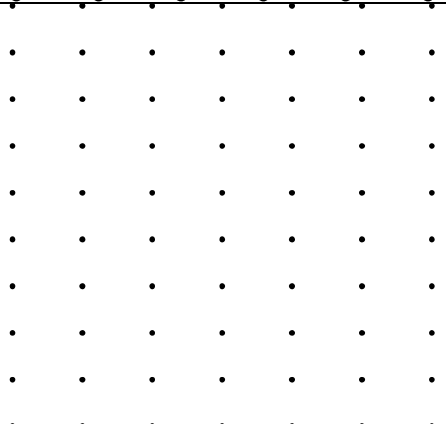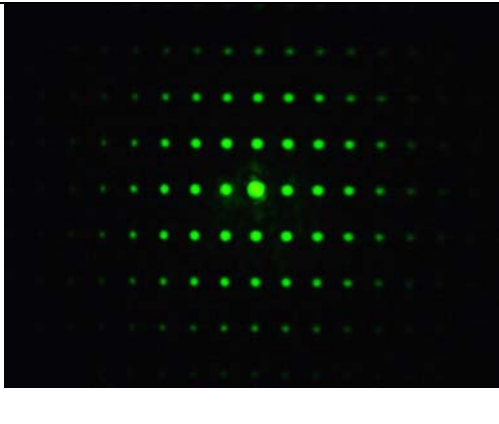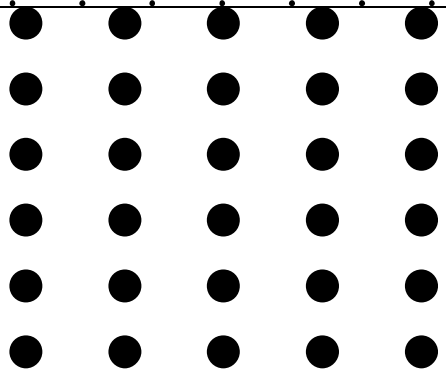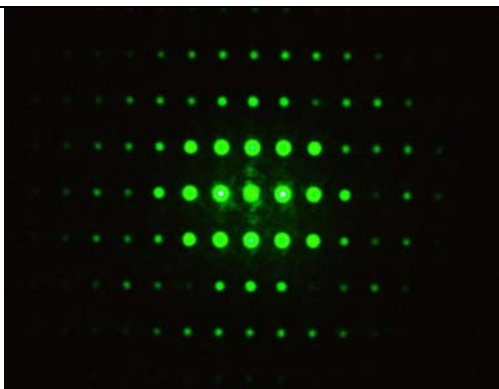
Appendix A – The "B" Numbered Slides

B-1.1 A gas of large diamonds		
B-1.2 A gas of small diamonds		
B-1.3 A gas of large squares		

B-1.4 A gas of small squares		
B-2.1 A gas of triangles		
B-2.2 A gas of dots		
B-2.3 A gas of rectangles		
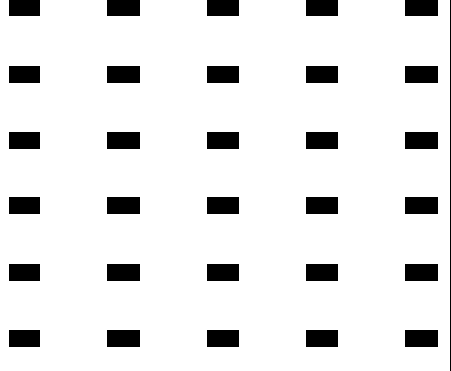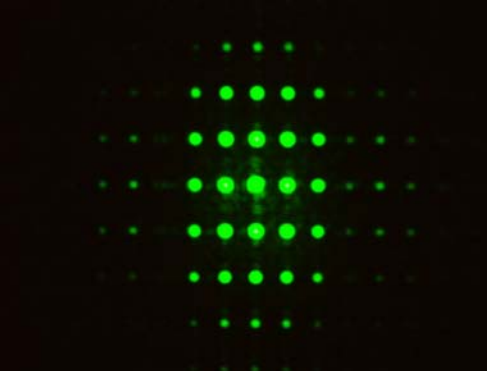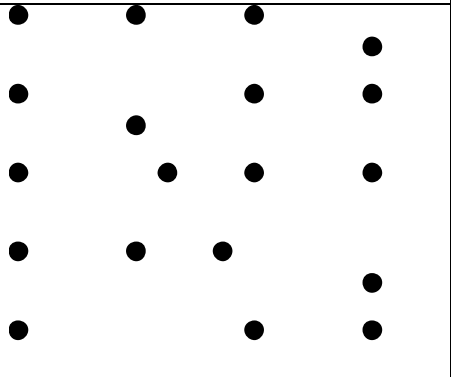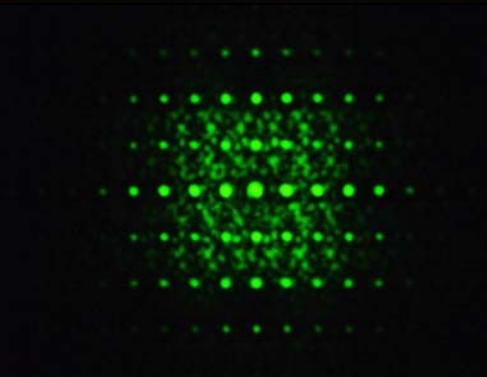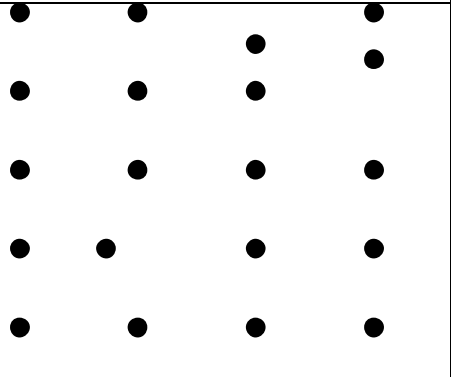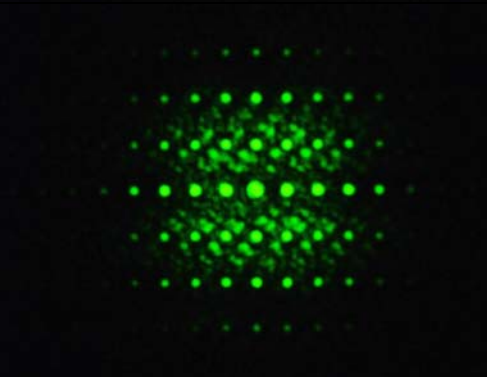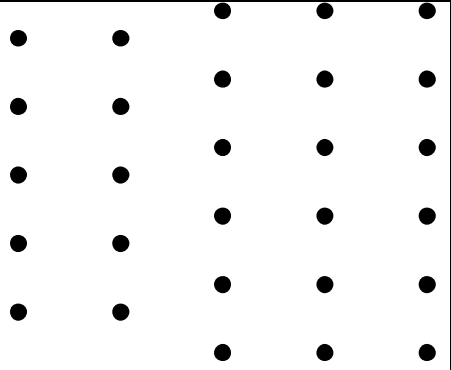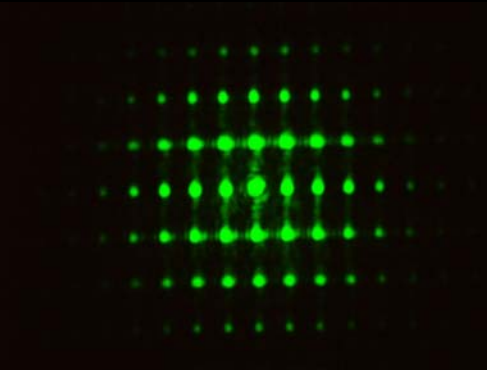
B-2.4 A gas of crosses		
B-3.1 Dots (circles), 0.02 mm in diameter, in a rectangular array, 0.08 mm x 0.12 mm		
B-3.2 Dots (circles), 0.01 mm in diameter, in a rectangular array, 0.08 mm x 0.12 mm		
B-3.3 Dots (circles), 0.04 mm in diameter, in a rectangular array, 0.08 mm x 0.12 mm		
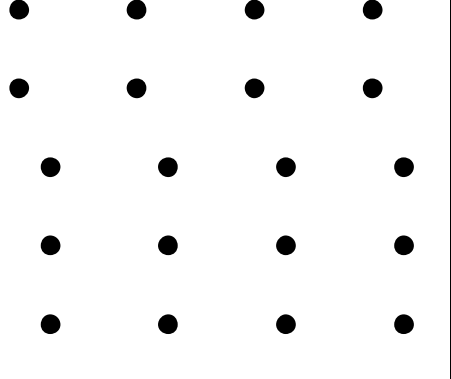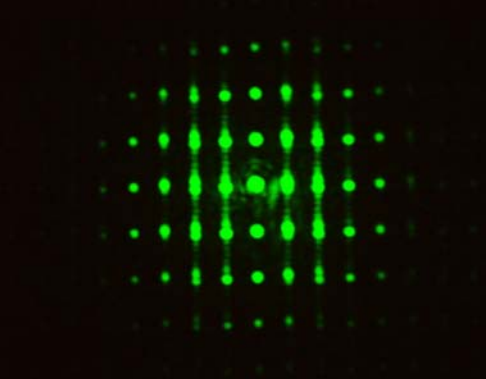
B-3.4 Dots (circles), 0.03 mm in diameter, in a rectangular array, 0.08 mm x 0.12 mm		
B-4.1 Squares, 0.02 mm each side, in a rectangular array, 0.08 mm x 0.12 mm		
B-4.2 Dots (circles), 0.02 mm in diameter, in a rectangular array, 0.08 mm x 0.12 mm		
B-4.3 Triangles, 0.02 mm in height, in a rectangular array, 0.08 mm x 0.12 mm		

B-4.4 Rectangles, 0.02 mm x 0.04 mm, in a rectangular array, 0.08 mm x 0.12 mm		
B-5.1 Dots (circles), 0.02 mm in diameter, in a rectangular array, 0.08 mm x 0.12 mm, with approximately 40% of the dots displaced from nominal position		
B-5.2 Dots (circles), 0.02 mm in diameter, in a rectangular array, 0.08 mm x 0.12 mm, with approximately 20% of the dots displaced from nominal position		
B-5.3 Dots (circles), 0.02 mm in diameter, in a rectangular array, 0.08 mm x 0.12 mm, with vertical stacking errors		

B-5.4 Dots (circles), 0.02 mm in diameter, in a rectangular array, 0.08 mm x 0.12 mm, with horizontal stacking errors		

Appendix B – Extract from TBD "Two-dimensional patterns, lattices, and symmetry"

2.1 Approaches to the study of crystal structures

In Chapter 1 we developed an understanding of simple crystal structures by first considering the ways in which atoms or ions could pack together and then introducing smaller atoms or ions into the interstices between the larger ones. This is a pragmatic approach as it not only provides us with an immediate and straightforward understanding of the atomic/ionic arrangements in some simple compounds, but also suggests the ways in which more complicated compounds can be built up.

However, it is not a systematic and rigorous approach, as all the possibilities of atomic arrangements in all crystal structures are not explored. The rigorous, and essentially mathematical, approach is to analyse and classify the geometrical characteristics of quite general two-dimensional patterns and then to extend the analysis to three dimensions to arrive at a completely general description of all the patterns to which atoms or molecules or groups of atoms or molecules might conform in the crystalline state.

These two distinct approaches—or strands of crystallographic thought—are apparent in the literature of the nineteenth and early twentieth centuries. In general, it was the metallurgists and chemists, such as Tammann[*] and Pope[*], who were the pragmatists, and the theoreticians and geometers, such as Fedorov[*] and Schoenflies[*], who were the analysts. It might be thought that the analytical is necessarily superior to the pragmatic approach because its generality and comprehensiveness provides a much more powerful starting point for progress to be made in the discovery and interpretation of the crystal structures of more and more complex substances. But this is not so. It was, after all, the simple models of sodium chloride and zinc blende of Pope (such as we also constructed in Chapter 1) that helped to provide the Braggs[*] with the necessary insight into crystal structures to enable them to make their great advances in the interpretation of X-ray diffraction photographs. In the same way, 40 years later, the discovery of the structure of DNA by Watson and Crick was based as much upon structural and chemical knowledge and intuition, together with model building, as upon formal crystallographic theory.

However, a more general appreciation of the different patterns into which atoms and molecules may be arranged is essential, because it leads to an understanding of the important concepts of symmetry, motifs and lattices. The topic need not be pursued rigorously—in fact it is unwise to do so because we might quickly 'lose sight of the wood for the trees!' The essential ideas can be appreciated in two dimensions, the subject of

[*] Denotes biographical notes available in Appendix 3.

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this chapter. The extension to three dimensions (Chapters 3 and 4) which relates to 'real crystal structures', should then present no conceptual difficulties.

2.2   Two-dimensional patterns and lattices

Consider the pattern of Fig. 2.1(a), which is made up of the letter **R** repeated indefinitely. What does **R** represent? Anything you like—a 'two-dimensional molecule', a cluster of atoms or whatever. Representing the 'molecule' as an **R**, an *asymmetric* shape, is in effect representing an *asymmetric* molecule. We shall discuss the different types or elements of symmetry in detail in Section 2.3 below, but for the moment our general everyday knowledge is enough. For example, consider the symmetry of the letters **R M S. R** is asymmetrical. **M** consists of two equal sides, each of which is a reflection or mirror image of the other, there is a **mirror line** of symmetry down the centre indicated by the letter m, thus **M**$_{\leftarrow m}$. There is no mirror line in the **S**, but if it is rotated 180° about a point in its centre, an identical **S** appears; there is a **two-fold rotation axis** usually called a **diad axis** at the centre of the **S**. This is represented by a little lens-shape ✿ at the axis of rotation: **S**.

In Fig. 2.1(a) **R**, the repeating 'unit of pattern' is called the **motif**. These motifs may be considered to be situated at or near the intersections of an (imaginary) grid. The grid is called the **lattice** and the intersections are called **lattice points**.

Let us now draw this underlying lattice in Fig. 2.1(a). First we have to decide where to place each lattice point in relation to each motif: anywhere will do—above, below, to one side, in the 'middle' of the motif—the only requirement is that the *same* position with respect to the motif is chosen every time. We shall choose a position a little below the motif, as shown in Fig. 2.1(b). Now there are an infinite number of ways in which the
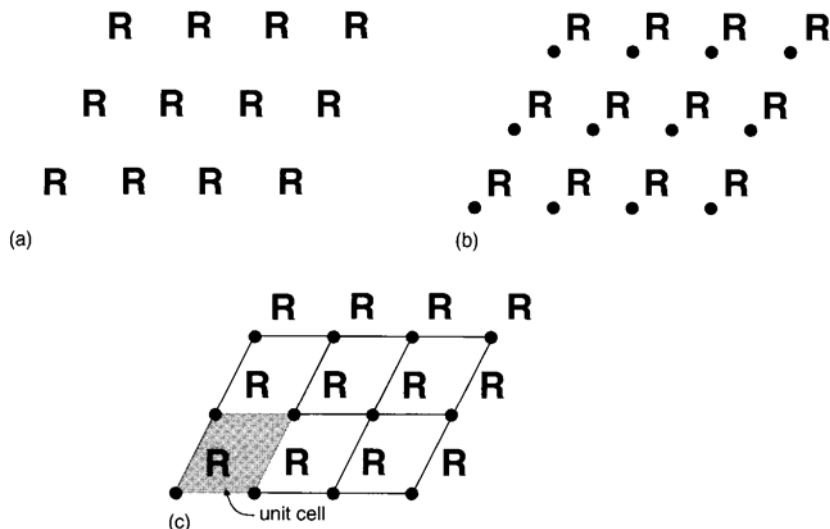
Fig. 2.1.   (a) A pattern with the motif **R**, (b) with the lattice points indicated and (c) the lattice and a unit cell outlined (Drawn by K. M. Crennell).

2.2 Two-dimensional patterns and lattices 43

lattice points may be 'joined up' (i.e. an infinite number of ways of drawing a lattice or grid of lines through lattice points). In practice, a grid is usually chosen which 'joins up' adjacent lattice points to give the lattice as shown in Fig. 2.1(c), and a unit cell of the lattice may also be outlined. Clearly, if we know (1) the size and shape of the unit cell and (2) the motif which each lattice point represents, including its orientation with respect to the lattice point, we can draw the whole pattern or build up the whole structure indefinitely. The unit cell of the lattice and the motif therefore define the whole pattern or structure. This is very simple: but observe an importance consequence. Each motif is identical and, for an infinitely extended pattern, the environment (i.e. the spatial distribution of the surrounding motifs, and their orientation) around each motif is identical. This provides us with the definition of a lattice (which applies equally in two and three dimensions): *a lattice is an array of points in space in which the environment of each point is identical.* Again it should be stressed that by environment we mean the spatial distribution and orientation of the surrounding points.

Like all simple definitions (and indeed ideas), this definition of a lattice is often not fully appreciated; there is, to use a colloquial expression, 'more to it than meets the eye!' This is particularly the case when we come to three-dimensional lattices (Chapter 4), but, for the two-dimensional case, consider the patterns of points in Fig. 2.2 (which should be thought of as extending infinitely). Of these only (a) and (d) constitute a lattice; in (b) and (c) the points are certainly in a *regular* array, but the surroundings of each point are *not* all identical.

Figures 2.2(a) and (d) represent two two-dimensional lattice types, named **oblique** and **rectangular**, respectively, in view of the shapes of their unit cells. But what is the distinction between the oblique and rectangular lattices? Surely the rectangular lattice is just a special case of the oblique, i.e. with a 90° angle?

(a)   (b)

(c)   (d)
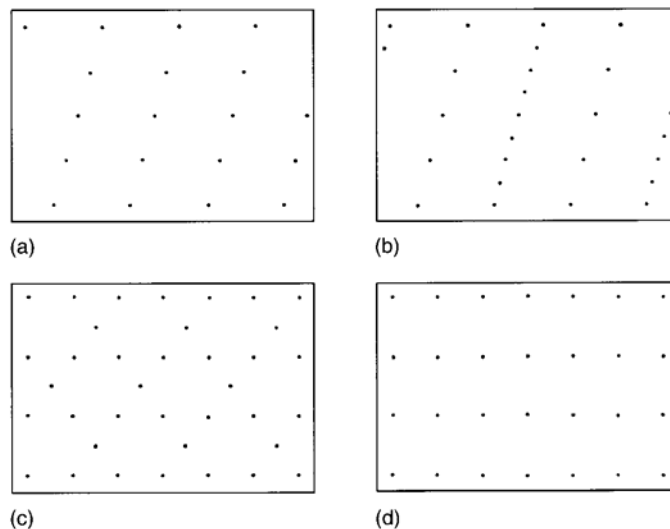
Fig. 2.2. Patterns of points. Only (a) and (d) constitute lattices.

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The distinction arises from different symmetries of the two lattices, and requires us to extend our everyday notions of symmetry and to classify a series of symmetry elements. This precise knowledge of symmetry can then be applied to both the motif and the lattice and will show that there are a limited number of patterns with different symmetries (only seventeen) and a limited number of two-dimensional lattices (only five).

2.3   Two-dimensional symmetry elements

The clearest way of developing the concept of symmetry is to begin with an asymmetrical 'object'—say the **R** of Fig. 2.1—then to add successively mirror lines and axes of symmetry and to see how the **R** is repeated to form different patterns or groups. The different patterns or groups of **R**s which are produced correspond, of course, to objects or projections of molecules (i.e. 'two-dimensional molecules') with different symmetries which are not possessed by the **R** alone.

The patterns or groups which arise and which as explained below are of concern in crystallography are shown in Fig. 2.3. On the left are the patterns of **R**s, in the centre are decorative motifs with the same symmetry, and on the right are projections of molecules. Figure 2.3(1) shows the **R** 'on its own' and, as an example, the asymmetrical projection of the CHFClBr molecule. Figure 3.2(2) shows 'right-' and 'left'-handed **R**s reflected in the 'vertical' mirror line between them. This pair of **R**s has the same mirror symmetry as the projection of the *cis*-difluoroethene molecule. Now add another 'horizontal' mirror line as in Fig. 2.3(3). A group of four **R**s (two right- and two left-handed) is produced. This group has the same symmetry as the projection of the ethene molecule.

The **R** may be repeated with a diad (two-fold rotation) axis, as in Fig. 2.3(4). The two **R**s (both right handed) have the same symmetry as the *trans*-difluoroethene molecule. Now look back to the group of **R**s in Fig. 2.3(3); notice that they also are related by a diad (two-fold rotation axis) at the intersection of the mirror lines: the action of reflecting the **R**s across two perpendicular mirror lines 'automatically' generates the two-fold symmetry as well. This effect, where the action of two symmetry elements generates another, is quite general as we shall see below.

Mirror lines and diad axes of symmetry are just two of the symmetry elements that occur in two dimensions. In addition there are three-fold rotation or **triad** (3) axes (represented by a little triangle, ▲), four-fold rotation or **tetrad** (4) axes (represented by a little square, ■), and six-fold (6) or **hexad** axes (represented by a little hexagon, ⬤). Asymmetrical objects are represented as having a one-fold or **monad** (1) axis of symmetry (for which there is no little symbol)—which means in effect that one 360° rotation brings the object into coincidence with itself.

Figure 2.3(5) shows the **R** related by a triad (three-fold) axis. The projection of the trifluoroalkylammonia molecule also has this same symmetry. Now add a 'vertical' mirror line as in Fig. 2.3(6). Three more left-handed **R**s are generated, and at the same time the **R**s are mirror related not just in the vertical mirror line but also in two lines inclined at 60° as shown; another example of additional symmetry elements (in this case mirror lines) being automatically generated.

This procedure (of generating groups of **R**s which represent motifs with different symmetries) may be repeated for tetrad (four-fold) axes (Fig. 2.3(7)); plus mirror lines

2.3   Two-dimensional symmetry elements   45

(Fig. 2.3(8)); for hexad (six-fold) axes (Fig. 2.3(9)); plus mirror lines (Fig. 2.3(10)). Notice that not only do these axes of symmetry 'automatically' generate mirror lines at 90° (for tetrads) and 60° (for hexads) but also 'interleaving' mirror lines at 45° and 30° as well.

(1)   R   bromochlorofluoroethene   1

(2)   Я R   cis-difluoroethene   m
          m

(3)   Я R   ethene   2mm
          Я Я
          m

(4)   R   trans-difluoroethene   2
          Я

(5)   R   trifluoralkylammonia   3
          Я   ▲
          Я

Fig. 2.3.   (continued)

Experiments in Diffraction Using Optical Crystals and Computer Simulation
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Fig. 2.3.   The ten plane point groups showing left to right, the symmetry which arises based on an asymmetrical object **R**; examples of motifs; examples of molecules and ions (drawn as projections) and the point group symbols. (Drawn by K. M. Crennell, 1999.)

The ten arrangements of **R**s (and the corresponding two-dimensional motifs or projections of molecules) are called the **ten two-dimensional crystallographic or plane point groups**, so called because all the symmetry elements—axes (perpendicular to the page) and mirror lines (in the page)—pass through a point. The ten plane point groups are labelled with 'shorthand' symbols which indicate, as shown in Fig. 2.3, the symmetry elements present: 1 for a monad (no symmetry), *m* for one mirror line, *mm* (or 2*mm*) for two mirror lines (plus diad), 2 for a diad, 3 for a triad, 3*m* for a triad plus three mirror lines, 4 for a tetrad, 4*mm* for a tetrad plus four mirror lines, 6 for a hexad and 6*mm* for a hexad plus six mirror lines (the extra '*m*' in the symbols referring to the 'interleaving' mirror lines).

Now, in deriving these ten plane point groups we have ignored groups of **R**s with five-fold (**pentad**), seven-fold (**heptad**) etc. axes of symmetry with and without mirror lines. Such plane point groups are certainly possible and are widely represented in nature—the pentagonal symmetry of a starfish for example. However, what makes the ten plane point groups in Fig. 2.3 special or distinctive is that *only* these combinations of axes and mirror lines can occur in regular repeating patterns in two dimensions as is explained in Sections 2.4 and 2.5 below. Hence they are properly called the two-dimensional *crystallographic* point groups as indicated above. Patterns with pentagonal symmetry are necessarily non-repeating, non-periodic or 'incommensurate' and consequently have in the past been rather overlooked by crystallographers. However, with the realization that groups of atoms (or viruses) can form 'quasi crystals' with five-fold symmetry elements (see Section 4.8), the study of non-periodic two-dimensional patterns has become of increasing interest and importance (see Section 2.8). A simple way at this stage of 'seeing the difference' is to compare, for example, the arrangement of six lattice points equally spaced around a central lattice point (hexagons) with the arrangement of five 'lattice' points equally spaced around a central point (pentagons). In the former case the arrangement of points can be put together to form a lattice (a pattern or *tiling* of hexagons with 'no gaps' and 'no overlaps'). In the latter case the points cannot be put together to form a lattice—there are always 'gaps' or 'overlaps' between the tiling of pentagons. Try it and see!

2.4   The five plane lattices

Having examined the symmetries which a two-dimensional motif may possess we can now determine how many two-dimensional or plane lattices there are. We will do this by building up patterns from the ten motifs in Fig. 2.3 with the important condition that the symmetry elements possessed by the single motif must also extend throughout the whole pattern. This condition is best understood by way of a few examples. Consider the asymmetrical motif **R** (Fig. 2.3(1)); there are no symmetry elements to be considered and the **R** may be repeated in a pattern with an oblique (i.e. the most asymmetrical) arrangement of lattice points. Now consider the motif which possesses one 'vertical' mirror line of symmetry (Fig. 2.3(2)). This mirror symmetry must extend throughout the whole pattern from motif to motif which means that the lattice must be rectangular. There are two possible arrangements of lattice points which fulfil this requirement: a simple rectangular lattice and a centred rectangular lattice as shown in Fig. 2.4(a).

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The oblique *p*-lattice   *p*2

The rectangular *p*-lattice   *p*2*mm*

The rectangular *c*-lattice   *c*2*mm*

The square *p*-lattice   *p*4*mm*

The hexagonal *p*-lattice   *p*6*mm*

(a)

(b)
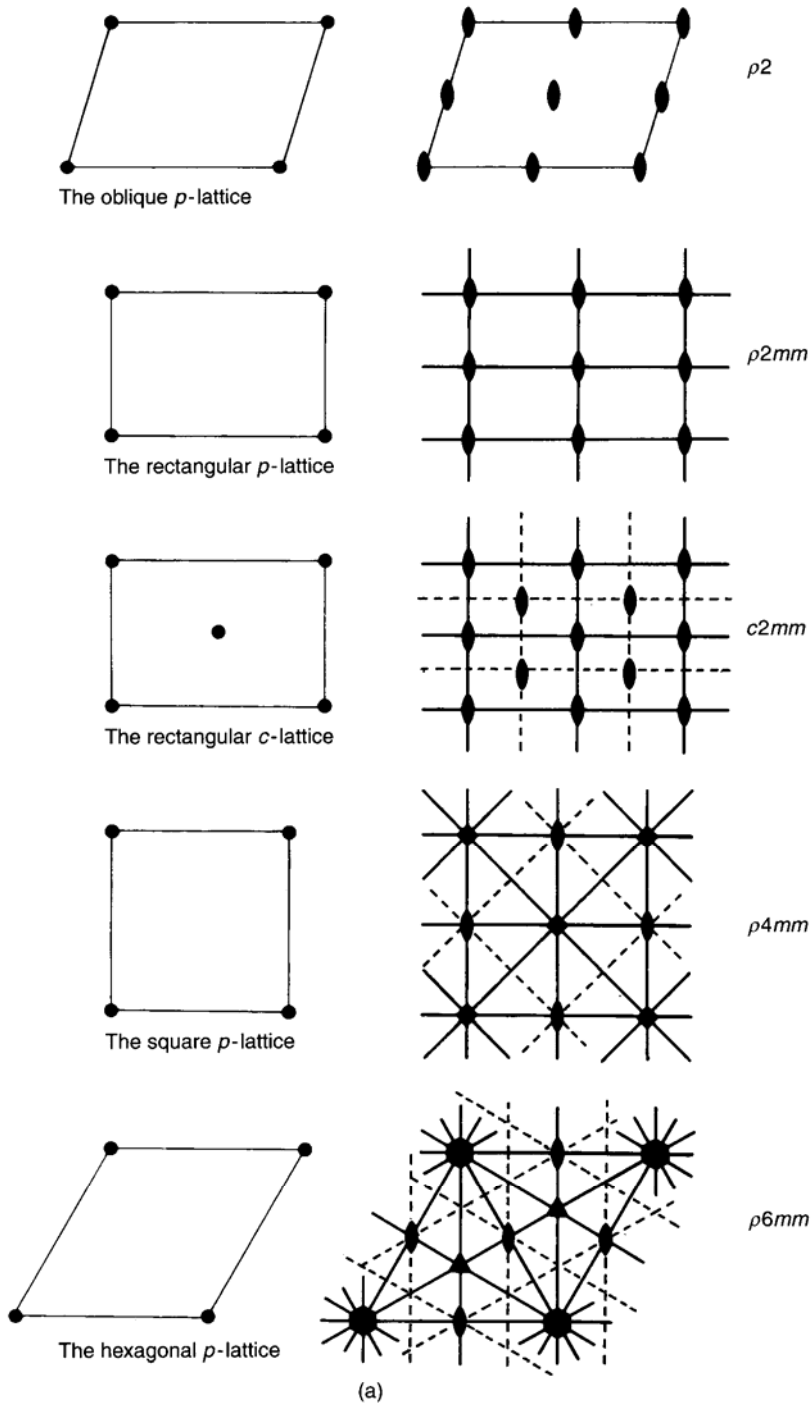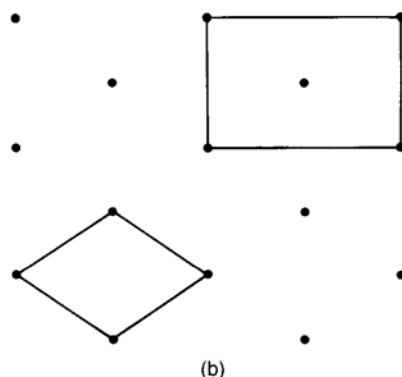
Fig. 2.4. (a) Unit cells of the five plane lattices, showing the symmetry elements present (heavy solid lines indicate mirror lines, dashed lines indicate glide lines) and their plane group symbols (from *Essentials of Crystallography*, by D. McKie and C. McKie, Blackwell, 1986). (b) The rectangular *c* lattice, showing the alternative primitive (rhombic *p* or diamond *p*) unit cell.

These rectangular lattices also possess 'horizontal' mirror lines of symmetry corresponding to the motif with the two sets of mirror lines as shown in Fig. 2.3(3). Now consider the motifs with tetrad (four-fold) symmetry (Figs 2.3(7) and (8)). This four-fold symmetry must extend to the surrounding motifs which means that they must be arranged in a square pattern giving rise to a square lattice (Fig. 2.4(a)).

Altogether, five two-dimensional or plane lattices may be worked out, as shown in Fig. 2.4(a). They are described by the shapes of the unit cells which are drawn between lattice points—oblique *p*, rectangular *p*, rectangular *c* (which is distinguished from rectangular *p* by having an additional lattice point in the centre of the cell), square *p* and hexagonal *p*. Notice again that additional symmetry elements are generated 'in between' the lattice points as shown in Fig. 2.4(a) (right). For example, in the square lattice there is a tetrad at the centre of the cell, diads halfway along the edges and vertical, horizontal and diagonal mirror lines as well as the tetrads situated at the lattice points.

All two-dimensional patterns must be based upon one of these five plane lattices; no others are possible. This may seem very surprising—surely other shapes of unit cells are possible? The answer is 'yes', a large number of unit cell shapes are possible, but the pattern of lattice points which they describe will always be one of the five of Fig. 2.4(a). For example, the rectangular *c* lattice may also be described as a rhombic *p* or diamond *p* lattice, depending upon which unit cell is chosen to 'join up' the lattice points (Fig. 2.4(b)). These are just two alternative descriptions of the *same* arrangement of lattice points. So the choice of unit cell is arbitrary: *any* four lattice points which outline a parallelogram can be joined up to form a unit cell. In practice we take a sensible course and mostly choose a unit cell that is as small as possible—or 'primitive' (symbol *p*)— which does not contain other lattice points within it. Sometimes a larger cell is more useful because the axes joining up the sides are at 90°. Examples are the rhombic or diamond lattice which is identical to the rectangular centred lattice described above and, to take an important three-dimensional case, the cubic cell (Fig. 1.6(c)) which is used to describe the ccp structure in preference to the primitive rhombohedral cell (Fig. 1.7(c)).
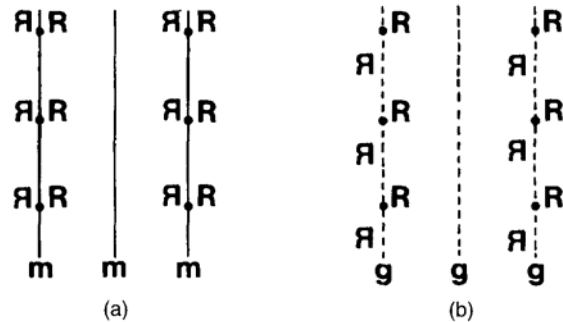
Fig. 2.5. Patterns with (a) reflection symmetry and (b) glide-reflection symmetry. The mirror lines (*m*) and glide lines (*g*) are indicated.

Now as there are ten point group symmetries which a motif can possess, it may be thought that there are therefore only ten different types of two-dimensional patterns, distributed among the five plane lattices. However, there is a complication: the combination of a point group symmetry with a lattice can give rise to an additional symmetry element called a **glide line**. Consider the two patterns in Fig. 2.5, both of which have a rectangular lattice. In Fig. 2.5(a) the motif has mirror symmetry as in Fig. 2.3(2); it consists of a pair of right- and left-handed **R**s. In Fig. 2.5(b) there is still a reflection—still pairs of right- and left-handed **R**s—but one set of **R**s has been translated, or glided half a lattice spacing. This symmetry is called a **reflection glide** or simply a **glide line of symmetry**. Notice that glide lines also arise automatically in the centre of the unit cell of Fig. 2.5(b) as do mirror lines in Fig. 2.5(a). Glide lines are, of course, as familiar to us as mirror lines; they represent the pattern of our footprints in the snow when we walk in a straight line!

The presence of the glide lines also has important consequences regarding the symmetry of the motif. In Fig. 2.5(a) the motif has mirror symmetry but in Fig. 2.5(b) it does not: the pair of right- and left-handed **R**s is asymmetric. It is the repetition of the translational symmetry elements—the glide lines—that determines the overall rectangular symmetry of the pattern. The glide lines which are present in the five plane lattices are shown (in addition to the axes and mirror lines of symmetry) in Fig. 2.4(a).

2.5   The seventeen plane groups

Glide lines give seven more two-dimensional patterns, giving seventeen in all—the seventeen **plane groups**. On a macroscopic scale the glide symmetry in a crystal would appear as simple mirror symmetry—the shift between the mirror-related parts of the motif would only by observable in an electron microscope which was able to resolve the individual mirror-related parts of the motif, i.e. distances of the order of 0.5–2 Å (50–200 pm).

The seventeen plane groups are shown in Fig. 2.6(a). They are labelled by 'shorthand' symbols which indicate the type of lattice (*p* for primitive, *c* for centred) and the

2.5   The seventeen plane groups   51

The Seventeen Plane Groups

p1 (1)   pm (3)   pg (4)   cm (5)

no axial symmetry

p2 (2)   p2mm (6)   p2mg (7)   c2mm (9)   p2gg (8)

180° symmetry

p4 (10)   p4mm (11)   p4gm (12)

90° symmetry

p3 (13)   p31m (14)   p3m1 (15)

120° symmetry

p6 (16)   p6mm (17)

60° symmetry

Notes:
Each group has a symbol and a number in ( ).
The symbol denotes the lattice type (primitive or centered), and the major symmetry elements
The numbers are arbitrary, they are those of the International Tables Vol.1, pp 58 - 72

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Fig. 2.6.   *(continued)*

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Fig. 2.6. (a) The seventeen plane groups (from *Point and Plane Groups* by K. M. Crennell). The numbering 1–17 is that which is arbitrarily assigned in the International Tables. Note that the 'shorthand' symbols do not necessarily indicate all the symmetry elements which are present in the patterns. (b) The symmetry elements outlined within (conventional) unit cells of the seventeen plane groups, heavy solid lines and dashed lines represent mirror and glide lines respectively (from *Manual of Mineralogy* 21st edn, by C. Klein and C. S. Hurlbut, Jr., John Wiley, 1999).

2.5   The seventeen plane groups   53
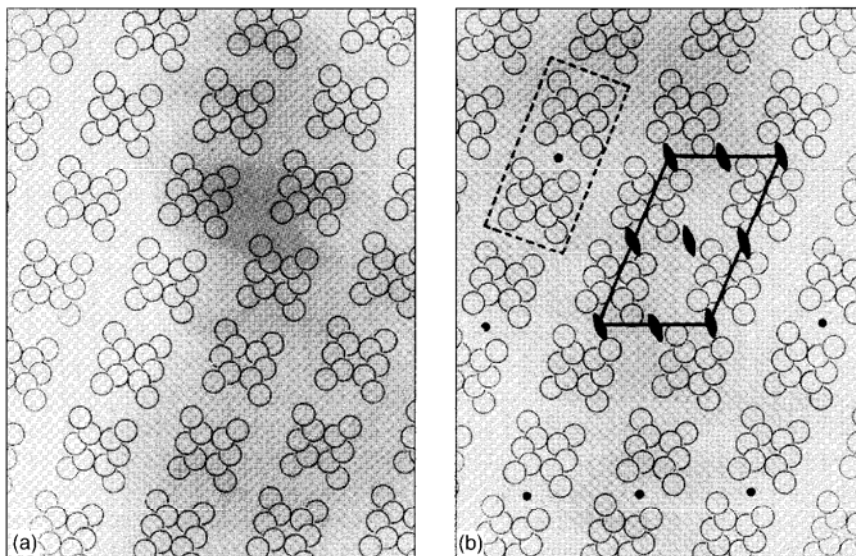
Fig. 2.7. Projection (a) of the structure of $C_6H_2(CH_3)_4$ (from *Contemporary Crystallography*, by M. J. Buerger, McGraw-Hill, 1970), with (b) the motif, lattice and symmetry elements indicated.

symmetry elements present, *m* for mirror lines, *g* for glide lines, 4 for tetrads and so on. The symmetry elements within a unit cell are shown in Fig. 2.6(b). It is a good exercise in recognizing the symmetry elements present in the 17 plane groups to lay a sheet of tracing paper over Fig. 2.6(a), to indicate the positions of the axes, mirror and glide lines of symmetry in an (arbitrary) unit cell and then to compare your 'answers' with those shown in Fig. 2.6(b) overleaf.

It is essential to practice recognizing the motifs, symmetry elements and lattice types in two-dimensional patterns and therefore to find to which of the seventeen plane groups they belong. Any regular patterned object will do—wallpapers, fabric designs, or the examples at the end of this chapter. Figure 2.7 indicates the procedure you should follow. Cover up Fig. 2.7(b) and examine only Fig. 2.7(a); it is a projection of molecules of $C_6H_2(CH_3)_4$. You should recognize that the molecules or groups of atoms are *not* identical in this two-dimensional projection. The motif is a *pair* of such molecules and this is the 'unit of pattern' that is repeated. Now look for symmetry elements and (using a piece of tracing paper) indicate the positions of all of these on the pattern. Compare your pattern of symmetry elements with those shown in Fig. 2.7(b). If you did not obtain the same result you have not been looking carefully enough! Finally, insert the lattice points—one for each motif. Anywhere will do, but it is convenient to have them coincide with a symmetry element, as has been done in Fig. 2.7(b). The lattice is clearly oblique and the plane group is *p2* (see Fig. 2.6).

The motifs of the seventeen patterns in Fig. 2.6 should be identified by circling them (lightly in pencil in case you make a mistake). You will find that, as a result of the presence of glide lines of symmetry, there are three plane groups (*pg*, *p2gg* and *p4gm*) in

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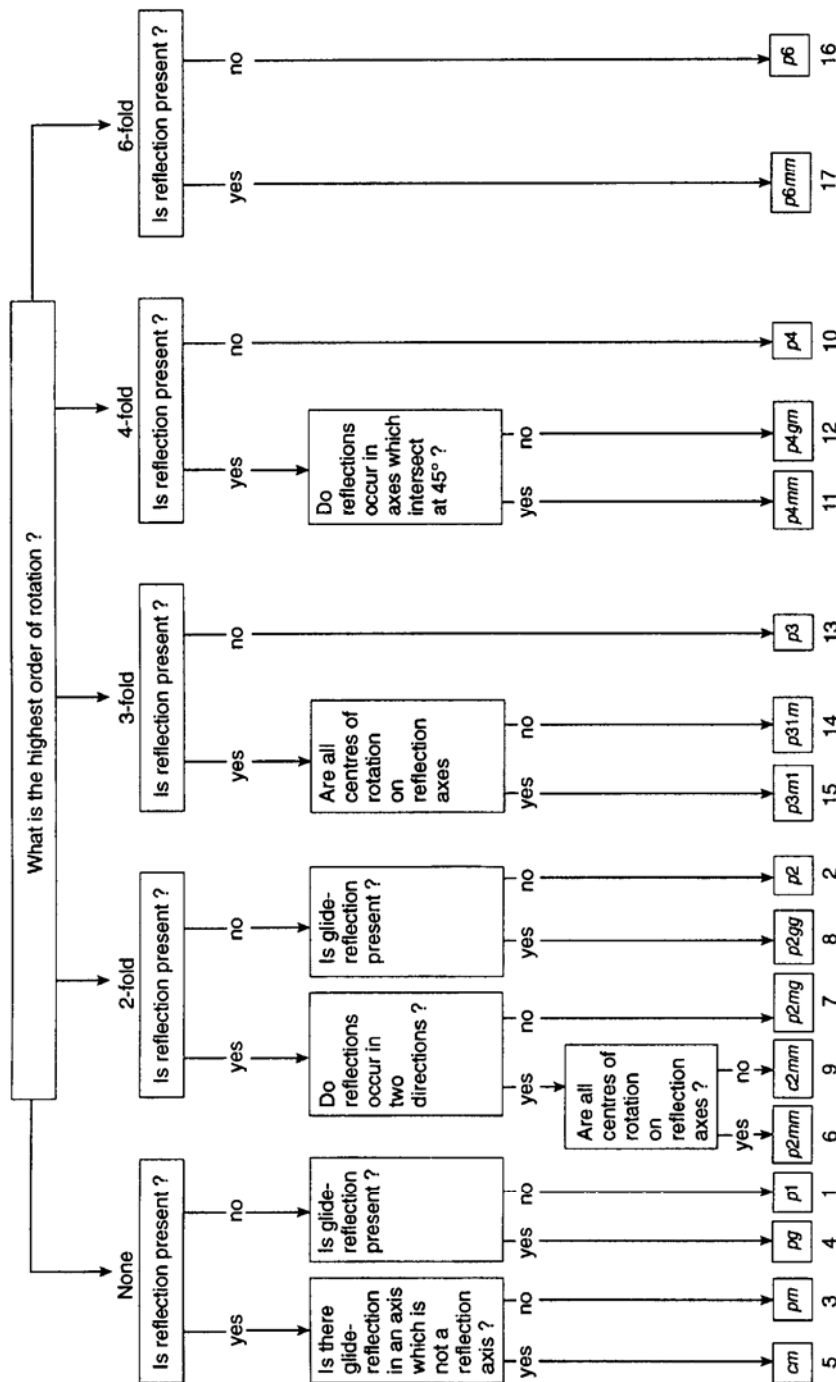**Fig. 2.8.** Flow diagram for identifying one of the seventeen plane patterns (redrawn from *The Geometry of Regular Repeating Patterns* by M. A. Hann and G. M. Thomson, the Textile Institute, Manchester, 1992). The numbering is that which is arbitrarily assigned in the International Tables (see Fig 2.6).

which the motif is asymmetric and one (*p2mg*) in which it has only one mirror-line of symmetry.

Another systematic way of identifying a plane pattern is to follow the 'flow diagram' shown in Fig. 2.8. The first step is to identify the highest order of rotation symmetry present, then to determine the presence or absence of reflection symmetry and so on through a series of 'yes' and 'no' answers, finally identifying one of the seventeen plane patterns whose plane group symbols are indicated 'in boxes', corresponding to those given in Fig. 2.6.

2.6   One-dimensional symmetry: border or frieze patterns

Identifying the number of one-dimensional patterns provides us with a good exercise in applying our more general knowledge of plane patterns. It is also a useful exercise in that it tells us about the different types of patterns that can be designed for the borders of wallpapers, edges of dress fabrics, friezes and cornices in buildings, and so on.

In plane patterns the symmetry operations and symmetry elements are (clearly) repeated in a plane; in one-dimensional patterns they can only be repeated in or along a line—i.e. the line or long direction of the border or frieze. This restriction immediately rules out all rotational symmetry elements with the exception of diads: two-fold symmetry alone can be repeated in a line: three-, four-, and six-fold symmetry elements require the repetition of a motif in directions other than the line of the border. For the same reason glide-reflection lines of symmetry, other than that along the line of the border, are ruled out. Mirror lines of symmetry are restricted to those along, and perpendicular to, the line of the border.

These restrictions result in seven one-dimensional groups, shown in Fig. 2.9. It is a good and satisfying exercise for you to derive these from first principles as outlined above. It is also useful to compare Fig. 2.9 with Fig. 2.6; the bracketed symbols in Fig. 2.9 indicate from which plane pattern the one-dimensional pattern may be derived. Notice that in one case two one-dimensional patterns—these with 'horizontal' and 'vertical' mirror planes—are derived from one plane pattern (*pm*). This is because the mirror lines in the plane group *pm* can be oriented either along, or perpendicular to, the line of the one-dimensional pattern.

Figure 2.19 (see Exercise 2.6) also shows examples of some of the border patterns. You can practice recognizing such patterns either by overlaying the pattern with a piece of tracing paper, and indicating the positions of the diads, mirror and glide lines as described above for plane patterns or by following the flow diagram (Fig. 2.10).

2.7   Symmetry in art and design: counterchange patterns

We have a rich inheritance of plane and border patterns in printed and woven textiles, wallpapers, bricks and tiles which have been designed and made by countless craftsmen and artisans in the past 'without benefit of crystallography'. The question we may now ask is: 'Have all the seventeen plane groups and seven one-dimensional groups been

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utilized in pattern design or are some patterns and some symmetries more evident than others? If so, is there any relationship between the preponderance or absence of certain types of symmetry elements in patterns and the civilization or culture which produced them?'
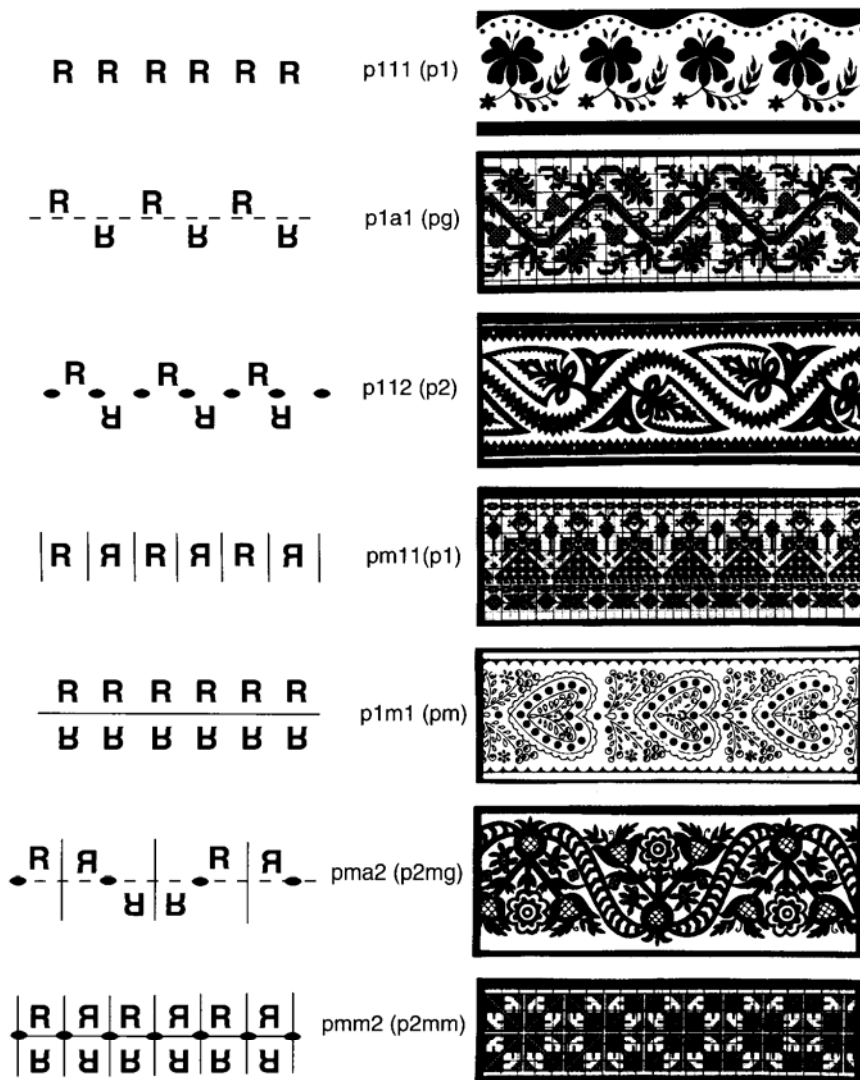
Fig. 2.9. (*left*) the seven one-dimensional groups or classes of border or frieze patterns (drawn by K. M. Crennell, 1999); (solid lines indicate mirror lines, dashed lines indicate glide lines and ◖ symbols indicate diads); (*centre*) their symmetry symbols and (*bracketed*) the plane point groups from which they are derived; and (*right*) examples of Hungarian needlework border patterns (from *Symmetry Through the Eyes of a Chemist* by I. and M. Hargittai, Plenum Press, New York and London 1995).

2.7 Symmetry in art and design: counterchange patterns   57
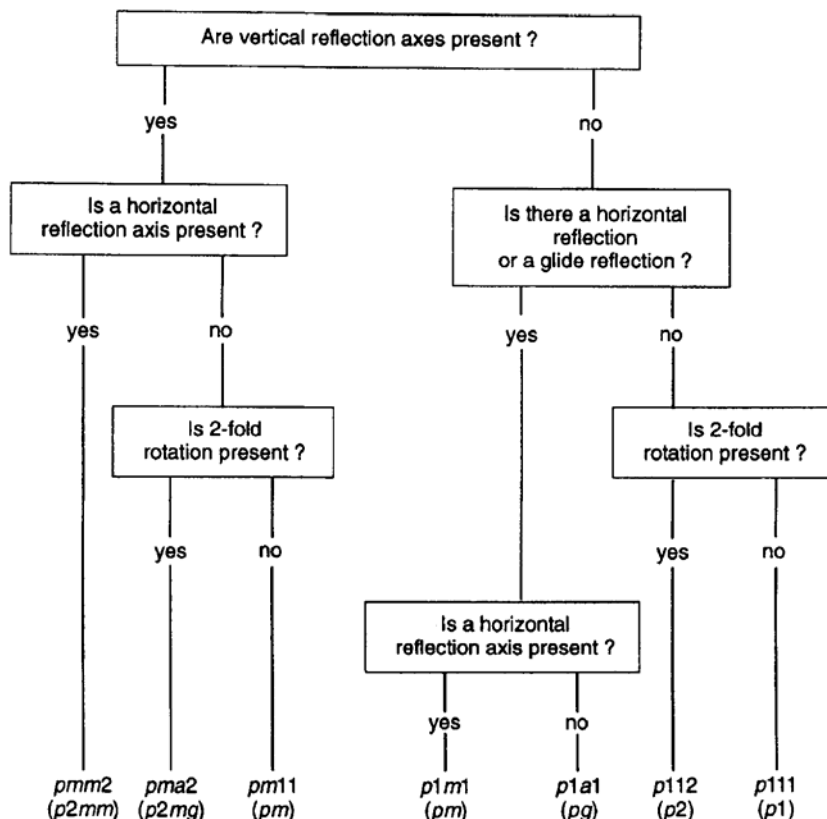
Fig. 2.10. Flow diagram for identifying one of the seven border patterns (from *The Geometry of Regular Repeating Patterns*, loc. cit.).

Questions such as these have exercised the minds of archaeologists, anthropologists and historians of art and design. They are, to be sure, questions more of cultural than crystallographic significance, but patterns play such a large part in our everyday experience that a crystallographer can hardly fail to be absorbed by them, just as he or she is absorbed by the three-dimensional patterns of crystals.

The study of plane and one-dimensional patterns (and indeed three-dimensional (space) patterns) is complicated by the question of colour—'real' colours in the case of plane and one-dimensional patterns, or colours representing some property, such as electron spin direction or magnetic moment, in space patterns (Chapter 4). Colour changes may also be analysed in terms of symmetry elements in which colours are alternated in a systematic way. Clearly, the greater the number of colours, the greater the complexity. The simplest cases to consider are two-colour (e.g. black and white) patterns. Figure 2.11 shows the generation of plane motifs through the operation of what are called counter-change or colour symmetry elements, which are distinguished from ordinary (rotation) axes and mirror lines of symmetry by a prime superscript. For

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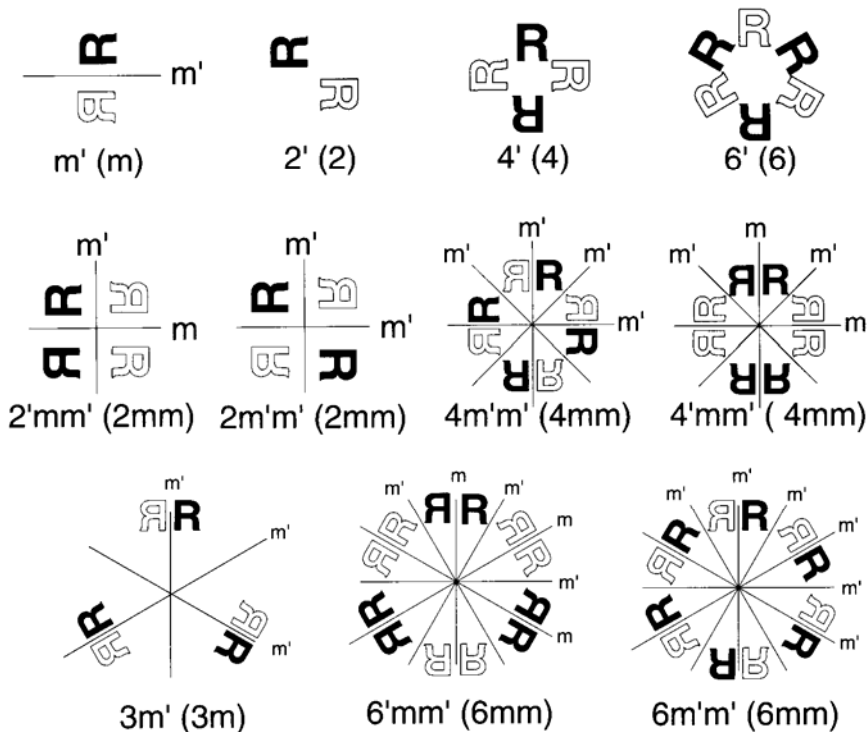Fig. 2.11. The eleven counterchange (black/white) point groups and (bracketed) the point group symbols for the plane point groups to which they correspond (see Fig. 2.3). The counterchange symmetry elements are denoted by prime superscripts. (Drawn by K. M. Crennell, 1999.)

example, the operation of a 2′ axis is a twice repeated rotation of an asymmetric object by 180° plus a colour change at each rotation; the operation of an $m′$ mirror line is a reflection plus colour change. Altogether there are eleven counterchange point groups (Fig. 2.11) compared with the ten plane point groups (Fig. 2.3). Note that there are **no** counterchange point groups corresponding to the plane point groups with only odd-numbered axes of symmetry (the monad and the triad), but that there are in each case two possible counterchange point groups corresponding to the plane point groups with symmetry 2*mm*, 4*mm* and 6*mm*.

The derivation of the counterchange one- and two-dimensional patterns also involves the operation of a $g′$ glide line which involves a reflection plus a translation of half a lattice spacing **plus** a colour change and gives (to extend our footprint analogy) a sequence of black/white (i.e. right/left footprints).

Accounting for two-colour symmetry gives rise to a total of forty-six (rather than seventeen) plane patterns and seventeen (rather than seven) one-dimensional patterns. Figure 2.12 shows an example of plane group pattern *p2gg* (No. 8—see Fig. 2.6(a), (b)) and the two possible counterchange patterns (symbols *p2′gg′* and *p2g′g′*) which are based upon it.

2.8   Non-periodic patterns and tilings   59

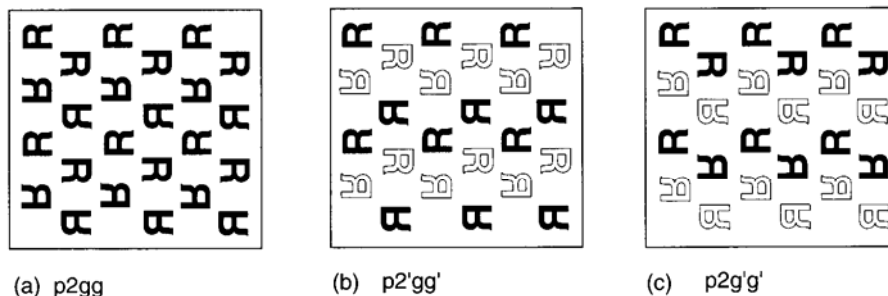(a) p2gg   (b) p2'gg'   (c)   p2g'g'

Fig. 2.12.   (a) Plane group *p2gg* and (b) and (c) the two counterchange plane groups *p2'gg'* and *p2g'g'* respectively which are based upon it. (Drawn by K. M. Crennell, 1999.)

Probably the most influential and pioneering study of patterns was *The Grammar of Ornament* by Owen Jones, first published in 1856[1]. Owen Jones attempted to categorize both plane and border patterns in terms of the different cultures that produced them, and although the symmetry aspects of patterns are touched on in the most fragmentary way, there is no doubt that the superb illustrations and encyclopaedic character of the book provided later writers with material which could be classified and analysed in crystal-lographic terms. Perhaps the best known of these was M. C. Escher (1898–1971) who drew inspiration for his drawings of tessellated figures from visits to the Alhambra in the 1930s, and also presumably from Owen Jones' chapter on 'Moresque Ornament' in which he describes the Alhambra as 'the very summit of Moorish art, as the Parthenon is of Greek art'. Escher's patterns encompass all the seventeen plane groups, eleven of which are represented in the Alhambra.

More recent work has identified clear preponderances of certain plane symmetry groups, and the absences of others[2]. For example, nearly 50% of traditional Javanese batik (wax-resist textile) patterns belong to plane group *p4mm* (Fig. 2.6), others, such as *p3*, *p3m1*, *p31m* and *p6* are wholly absent. In Jacquard-woven French silks of the last decade of the nineteenth century, nearly 80% of the patterns belong to plane group *pg*. In Japanese textile designs of the Edo period *all* plane groups are represented, with a marked preponderance for groups *p2mm* and *c2mm*. What these differences mean, or tell us about the cultures which gave rise to them, is, as the saying goes, 'another question'.

2.8   Non-periodic patterns and tilings

Johannes Kepler was the first to show that pentagonal symmetry would give rise to a pattern which was non-repeating. Figure 2.13 is an illustration from perhaps his greatest work *Harmonices mundi* (1619) which shows in the figures captioned 'Aa' and 'z' a pattern or tiling of pentagons, pentagonal stars and 10 and 16-sided figures which radiate

[1] Owen Jones. *The Grammar of Ornament*, Day & Sons Ltd., London, reprinted by Studio Editions, London (1986).
[2] M. A. Hann. *Symmetry of Regular Repeating Patterns: Case studies from various cultural settings*. Journal of the Textile Institute (1992), Vol. 83, pp. 579–580.

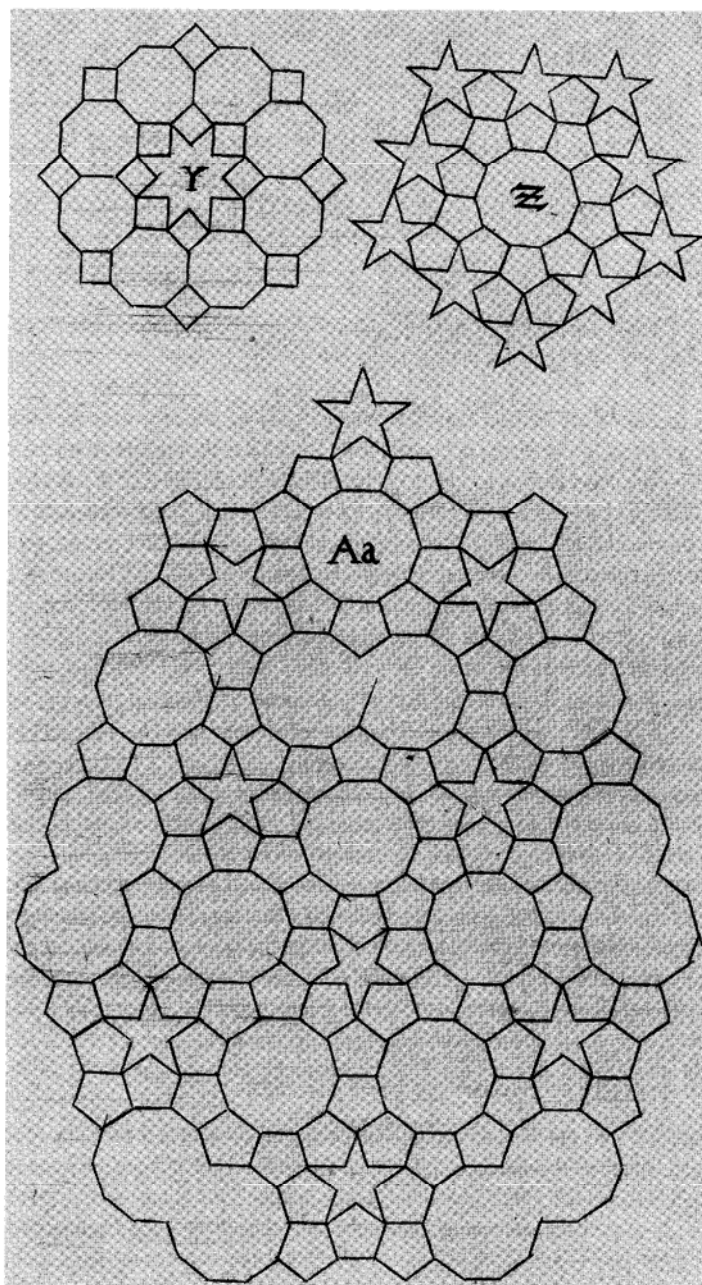60   Two-dimensional patterns, lattices and symmetry

Fig. 2.13. Non-periodic tiling patterns 'z' and 'Aa' (from *Harmonices Mundi* by Johannes Kepler, 1619, reproduced from the copy in the Brotherton Library, University of Leeds, by courtesy of the Librarian).

out in pentagonal symmetry from a central point. Grünbaum and Shephard[3] have shown how the tiling 'Aa' can be extended indefinitely giving long-range orientational order but the pattern does not repeat and cannot be identified with any of the seventeen plane groups (Fig. 2.6). A. L. Mackay[4] has shown how a regular, but non-periodic pattern, can be built up from regular pentagons in a plane with the triangular gaps covered by pieces cut from pentagons, which he describes with the title (echoing Kepler) *De nive quinquangula*—on the pentagonal snowflake.

These are but two examples of non-periodic or 'incommensurate' tilings, the mathematical basis of which was largely developed by Roger Penrose and are generally named after him. Figure 2.14 shows how a Penrose Tiling may be constructed by linking together edge-to-edge 'wide' and 'narrow' rhombs or diamond-shaped tiles of equal edge lengths. The angles between the edges of the tiles (as shown in Fig. 2.14(a)) are not arbitrary but arise from pentagonal symmetry as shown in Fig. 2.14(b) (where the tiles are shown shaded in relation to a pentagon); nor are they linked together in an arbitrary fashion but according to local 'matching rules', shown in Fig. 2.14(a) by little triangular 'pegs' and 'sockets' along the tile edges. These are omitted in the resultant tiling (Fig. 2.14(c)), partly for clarity and partly because their work in constructing the pattern is done. (An alternative of showing how the tiles must be fitted together is to colour or shade them in three ways and then to match the colours, like the pegs and sockets, along the tile edges.) The tiling can be viewed as a linkage of little cubes where we see three cube faces; the 'front' and 'top' faces (represented by the 'wide' diamonds) and 'side' face (represented by the 'narrow' diamond)).

The mathematical analysis of non-repeating patterns is rather difficult (especially in three-dimensions—see Section 4.8), but we can perhaps understand their essential 'incommensurate' properties by way of a one-dimensional analogy or example. Consider a pattern made up of a row of arrows and a row of stars extending right and left from an origin O. If the spacings of the arrows and stars are in a ratio of whole numbers then, depending on the values of these numbers, the pattern will repeat. Figure 2.15(a) shows a simple case where the ratio of spacings is 3/2 and the pattern repeats (i.e. the arrows and stars coincide) every third arrow or second star. If, however, the spacings of the arrows and stars cannot be expressed as a ratio of whole numbers, in other words if the ratio is an *irrational* number, then the pattern will never repeat—the arrows and stars will never come into coincidence. Figure 2.15(b) shows an example where the ratio of spacings is $\sqrt{2}/1 = 1.414213\ldots$ an irrational number, like π, where there is 'no end' to the number of decimal places and no cyclic repetition of the decimal numbers.[5]

[3] B. Grunbaum and G. C. Shephard. *Tilings and Patterns: An Introduction.* W. H. Freeman, New York, 1989.
[4] A. L. Mackay. *De nive quinquangula. Physics Bulletin* 1976, p. 495.
[5] The discovery that some numbers are irrational is one of the triumphs of Greek mathematics. The proof that $\sqrt{2}$ is irrational, which is generally attributed to Pythagoras, may be expressed as follows. Suppose that $\sqrt{2}$ *can* be expressed as a/b where a and b are whole numbers which have no common factor (if they had, we could simply remove it). Hence $\sqrt{2}b = a$ and squaring $2b^2 = a^2$. Now $2b^2$ is an *even* number, hence a^2 is also an even number and, since the square of an even number is even, a is an even number. Now an even number can be expressed as $2 \times$ (any number), i.e. $a = 2c$. Squaring again $a^2 = 4c^2 = 2b^2$, hence $2c^2 = b^2$ and, for the same reason as before, since $2c^2$ is an even number then b is an even number. So, both a and b are even and have a common factor 2 which contradicts our initial hypothesis which therefore must be false.
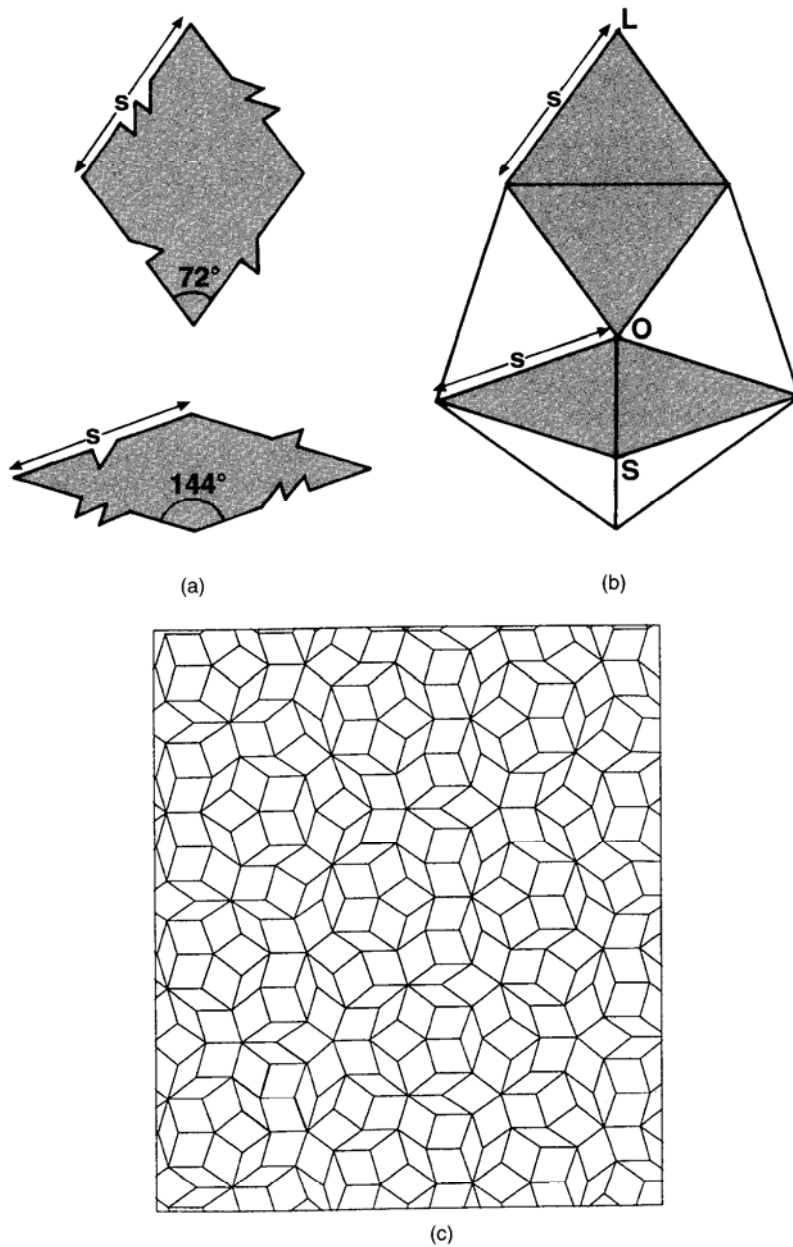
Fig. 2.14. (a) The two types ('wide' and 'narrow') tiles for the construction of a Penrose tiling. The triangular 'pegs' and 'sockets' along the tile edges indicate how they should be linked together edge-to-edge. (b) The geometry of the tiles in relation to a pentagon. The ratio OL/s (wide tile) $= s/OS$ (narrow tile) $= (\sqrt{5} - 1)/2 = 1.618\ldots$ (c) shows the resultant tiling (pegs and sockets omitted for clarity) (reproduced by courtesy of Prof. Sir Roger Penrose).
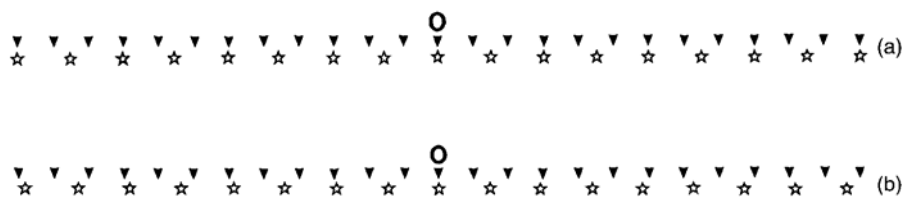
Exercises 63

Fig. 2.15. One-dimensional examples of (a) a periodic pattern and (b) a non-periodic pattern. In (a) the pattern repeats every third arrow and second star, in (b) the ratio of the spacings is $\sqrt{2}$ and the pattern never repeats.

In Penrose five-fold or pentagonal tiling it turns out (Fig. 2.14(b)) that the ratio of the diagonal OL to the edge length s (for the wide tile) and the ratio of the edge length s to the diagonal OS (for the narrow tile) are also both equal to an irrational number $(\sqrt{5}+1)/2 = 1.618034\ldots$ called the *Golden Mean* or *Golden Ratio*. The Golden Ratio also applies to a rectangle whose sides are in the ratio $(\sqrt{5}+1)/2:1$; if a square is cut off such a rectangle, then the rectangle which remains also has sides which are in this ratio, i.e. $(\sqrt{5}+1)/2 - 1:1 = 1:(\sqrt{5}+1)/2$. The Golden Ratio also occurs as the convergence of the ratio of successive terms in the so-called *Fibonacci series* of numbers where each term is the sum of the preceding two. *Any* number can be used to 'start off' a Fibonacci series, e.g. 1, 1, 2, 3, 5, 8, 13, 21, 34 ... or 3, 3, 6, 9, 15, 24, 39, 63.... Not only is the Golden Ratio a subject of mathematical interest, but it is also of relevance in architectural proportion and spiral growth in animals and plants (e.g. the spirals traced out in the head of a sunflower). However, this is a subject which we must regretfully now leave.

Exercises

2.1 Lay tracing paper over the plane patterns in Fig. 2.6. Outline a unit cell in each case and indicate the positions of all the symmetry elements within the unit cell. Notice in particular the differences in the distribution of the triad axes and mirror lines in the plane groups $p31m$ and $p3m1$.

2.2 Figure 2.16 is a design by M. C. Escher. Using a tracing paper overlay, indicate the positions of all the symmetry elements. With the help of the flow diagram (Fig. 2.8), determine the plane lattice type.

2.3 Figure 2.17 is a projection of the structure of FeS_2 (shaded atoms Fe, unshaded atoms S). Using a tracing paper overlay, indicate the positions of the symmetry elements, outline a unit cell and, with the help of the flow diagram in Fig. 2.8, determine the plane pattern type.

2.4 Figure 2.18 is a design by M. C. Escher. Can you see that the two sets of men are related by glide lines of symmetry? Draw in the positions of these glide lines, and determine the plane lattice type.

2.5 Determine (with reference to Fig. 2.11) the counterchange (black–white) point group symmetry of a chessboard.

2.6 Figure 2.19 shows examples of border or frieze patterns from *The Grammar of Ornament* by Owen Jones. Using a tracing paper overlay, indicate the positions of the symmetry elements and, with the help of the flow diagram (Fig. 2.10), determine the one-dimensional lattice types.

Experiments in Diffraction Using Optical Crystals and Computer Simulation
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2.7   Figure 2.20(a) is a 'wood block floor' or 'herringbone' pattern with plane group symmetry
       p2gg. Using a tracing-paper overlay (and with the help of Fig. 2.6(b) and the flow chart, Fig.
       2.8), locate the positions of the diad axes and glide lines. Now place your tracing paper over
       the counterchange patterns (Fig. 2.20(b)) and determine which of the symmetry elements
       become counterchange (2' or *g'*) symmetry elements. To which of the counterchange
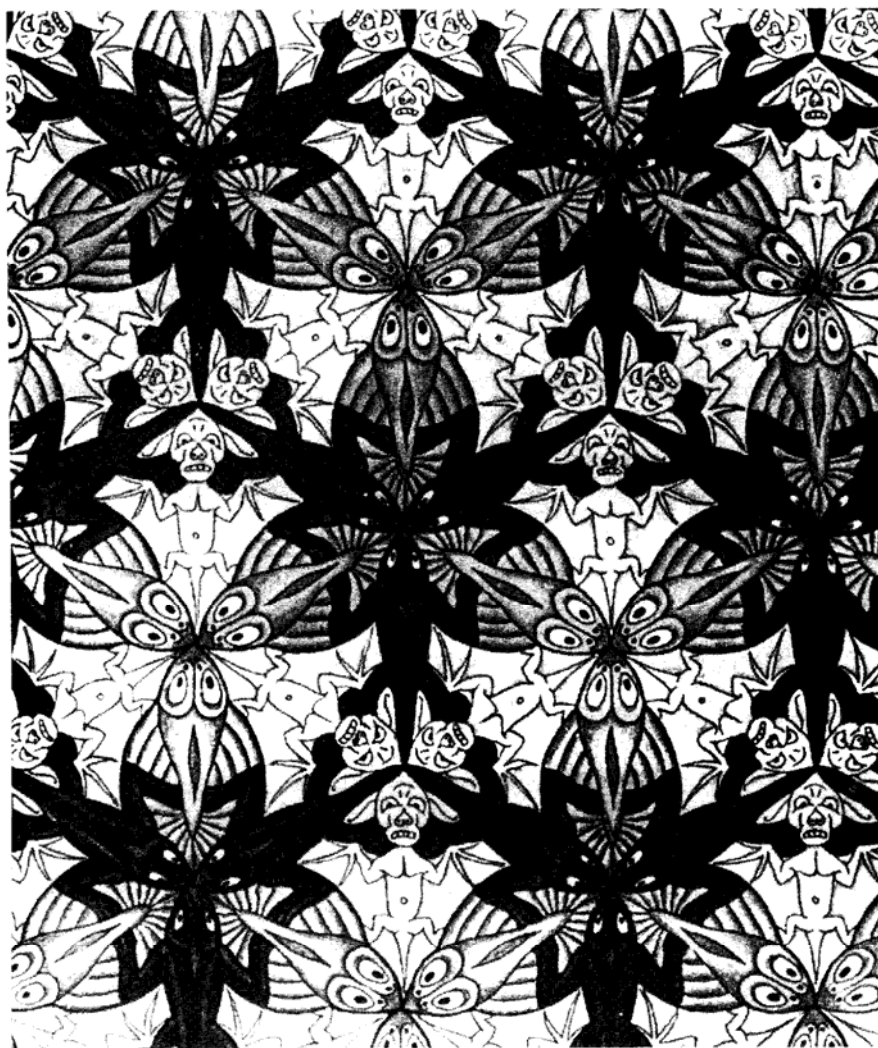   patterns shown in Fig. 2.12 does this pattern belong?

Fig. 2.16.   A plane pattern (from *Symmetry Aspects of M. C. Escher's Periodic Drawings*, 2nd edn, by
C. H. MacGillavry. Published for the International Union of Crystallography by Bohn, Scheltema and
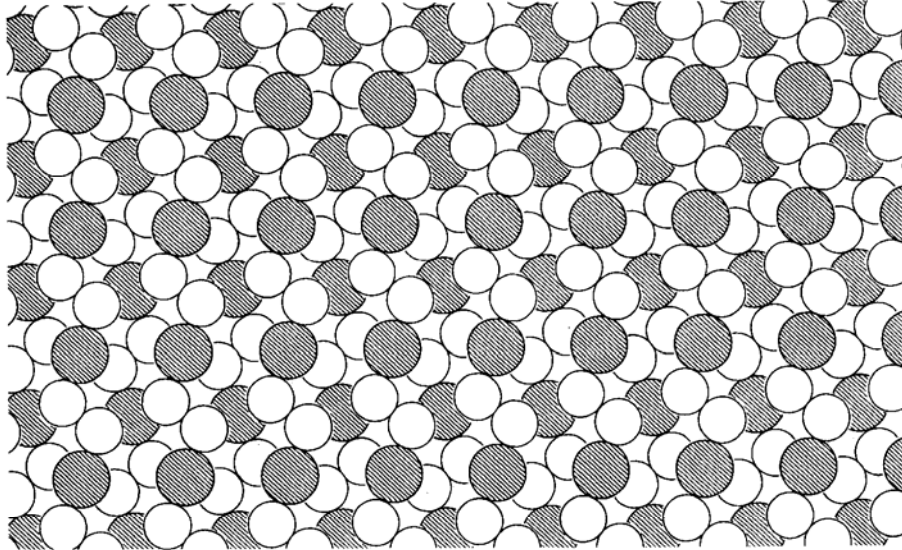Holkema, Utrecht, 1976).

Fig. 2.17. A projection of the structure of marcasite, FeS$_2$ (from *Contemporary Crystallography* by M. J. Buerger, McGraw-Hill, New York, 1970).

Fig. 2.18. A plane pattern (from C. H. MacGillavry, loc. cit.).

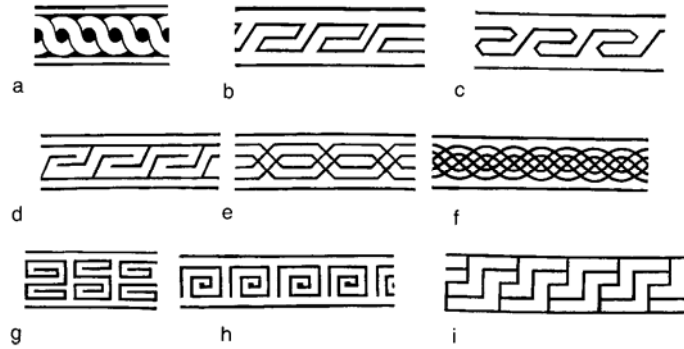66   Two-dimensional patterns, lattices and symmetry

Fig. 2.19. Examples of border or frieze patterns (from *The Grammar of Ornament* by Owen Jones, Day & Son, London 1856, reprinted by Studio Editions, London, 1986). a, b, Greek; c, d, Arabian; e, Moresque; f, Celtic; g, h, Chinese; i, Mexican.
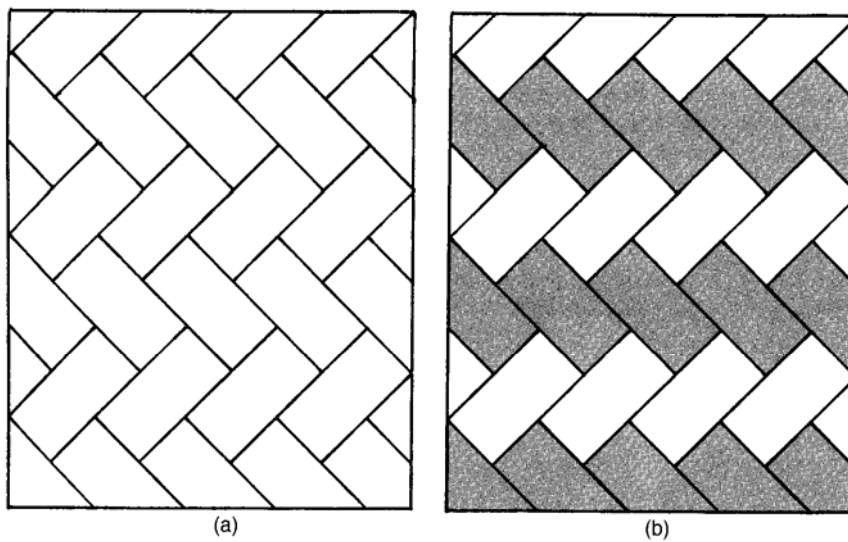

Fig. 2.20. 'wood block floor' or 'herringbone brickwork' patterns (a) with all blocks the same colour, and (b) with alternating black and white blocks.