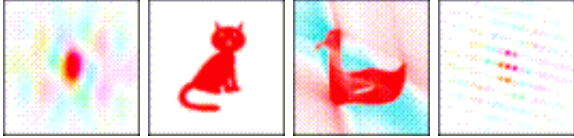Thank you to everyone who helped out with my survey. The results have been posted here.

Kevin Cowtan's Book of Fourier

This is a book of pictorial 2-d Fourier Transforms. These are particularly relevant to my own field of *X-ray crystallography*, but should be of interest to anyone involved in signal processing or frequency domain calculations.

Contents:

- Introduction
- Book of Crystallography
- Duck Tales and missing data.
- A little Animal Magic and cross phasing.
- A Tail of Two Cats and image restoration.
- Animal Liberation and free-sets.

- The Gallery. Other interesting pictures.

Other topics:

The Interactive Structure Factor Tutorial: Learn about structure factors and maps.

An introduction to crystallographic Fourier transforms. The mathematical link between Scattering theory and Fourier theory. An explanation of the convolution theorem.

Teaching materials elsewhere

- Randy Read's crystallography course at MRC Cambridge.
- Bernhard Rupp's crystallography course at LLNL.
- X-ray and neutron diffraction by R. B. Neder & T. H. Proffen at W?rzburg, Germany.

Back to my homepage.

Kevin Cowtan: cowtan@ysbl.york.ac.uk

The Fourier Duck

Behold the duck.
It does not cluck.
A cluck it lacks.
It quacks.
It is specially fond of a puddle or pond.
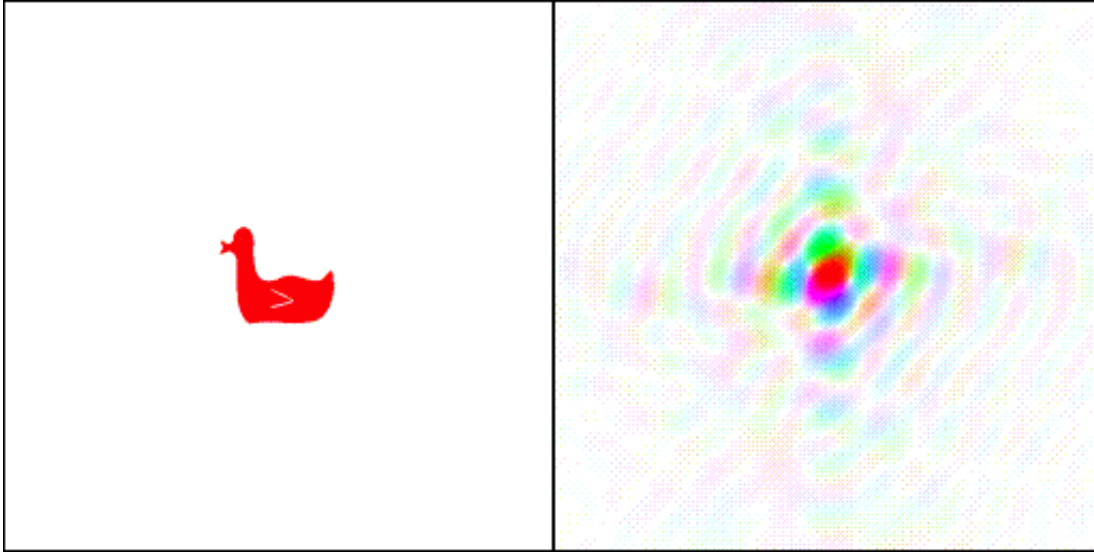When it dines or sups, it bottoms ups.

The Fourier Duck originated in a book of optical transforms (*Taylor, C. A. & Lipson, H., Optical Transforms, Bell, London 1964*). An optical transform is a Fourier transform performed using a simple optical apperatus.
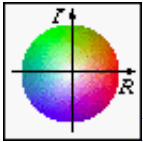
Back to the Fourier Duck.

The Fourier Duck

A duck, and its Fourier Transform:


Crystallographic Interpretation:

Note the *real* image gives rise to a *Hermitian* diffraction pattern.

More Fourier transforms. Back to the index.

Introduction

Since we are dealing with *amplitudes and phases*, it is necessary two represent two values for each point in the pictures that follow. I have adopted a colourful scheme for representing complex numbers on the two-dimensional images. Amplitude is represented by colour **saturation** and **brightness**, while phase is given by **hue**. This is illustrated in the following figure:
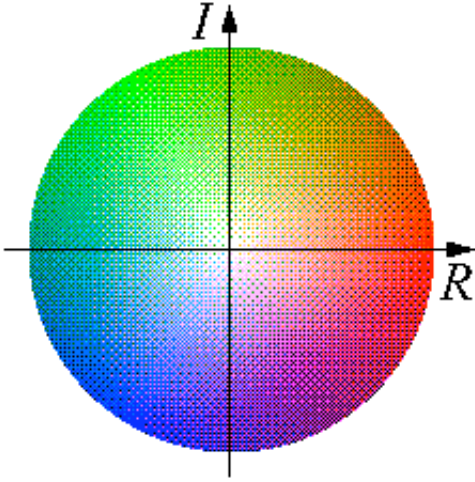
The positive real (horizontal) axis to the right represents a phase of 0. Phase increases anti-clockwise, thus **0 degrees** is *red*, **120 degrees** is *green*, and **240 degrees** is *blue*.
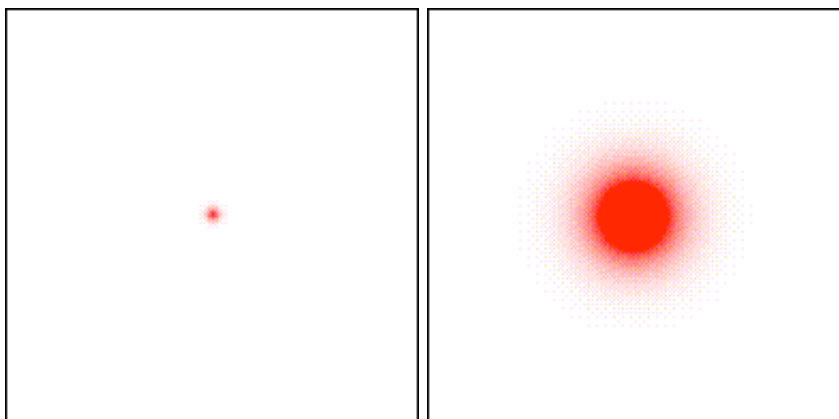
Note that positive real numbers are *red*, and negative real numbers are *cyan*. *White* represents zero magnitude.

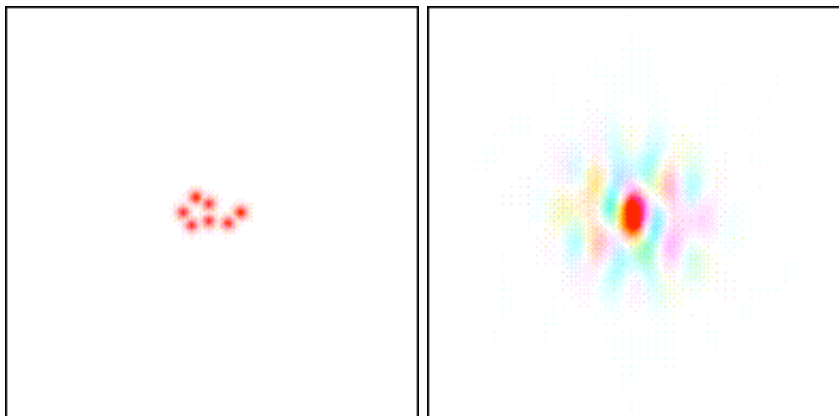 [Some](#) Fourier transforms. [Back](#) to the index.

The Book of Crystallography

An atom, and its Fourier Transform:

Note the both functions have circular symmetry. The atom is a sharp feature, whereas its transform is a broad smooth function. This illustrates the reciprocal relationship between a function and its Fourier transform.

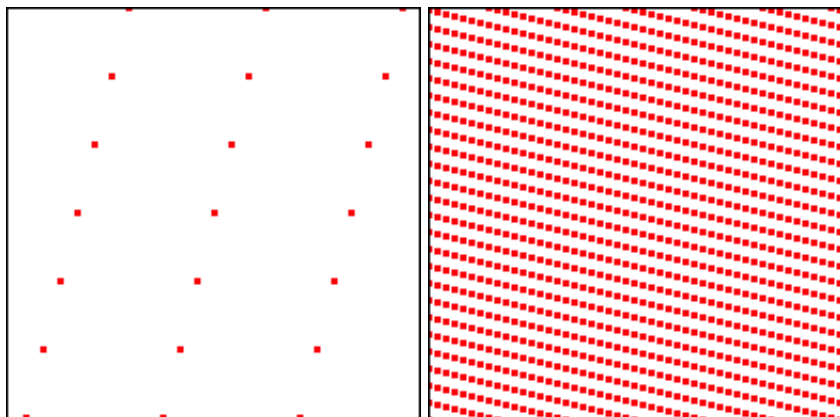A molecule, and its Fourier Transform:

The molecule consists of seven atoms. Its transform shows some detail, but the overall shape is still that of the atomic transform. We can consider the molecule as the convolution of the *point atom structure* and the *atomic shape*. Thus its transform is the product of the *point atom transform* and the *atomic transform*.

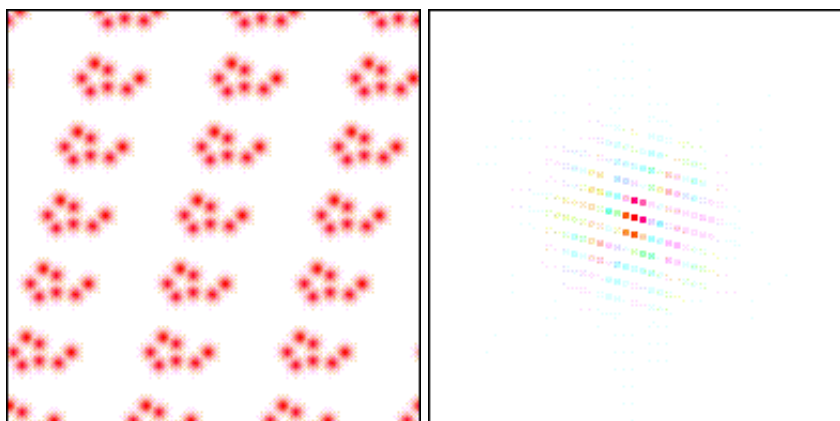More Fourier transforms. Back to the index.

The Book of Crystallography
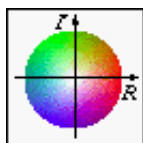
An lattice, and its Fourier Transform:

The grid points (delta functions) are exaggerated for clarity. Note that the Fourier transform of a grid is a grid with reciprocal *directions* and *spacings*. This is the origin of the reciprocal lattice.
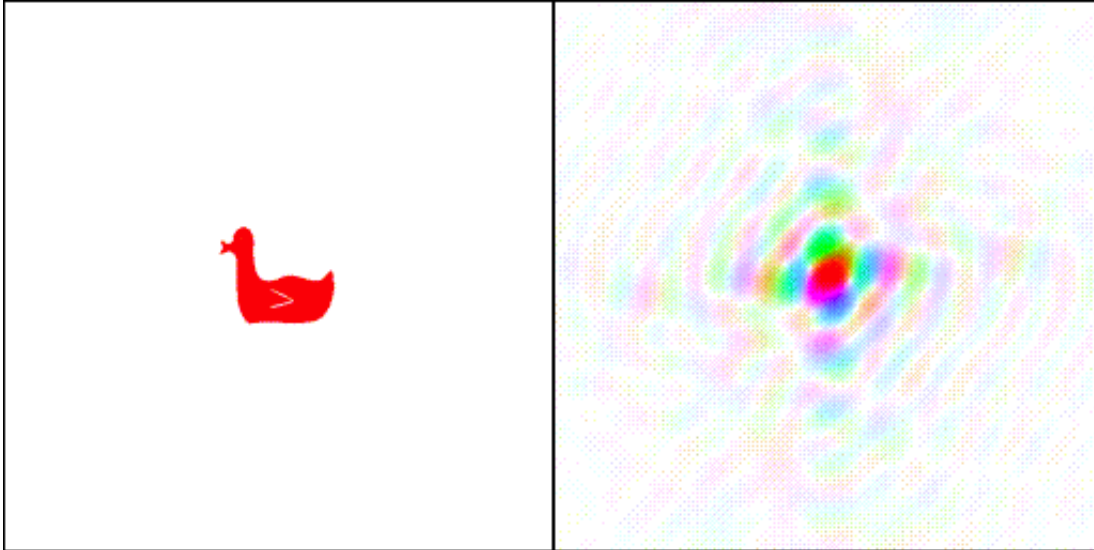
A crystal, and its Fourier Transform:

Finally, we build up a crystal by convoluting the *molecule* with the *grid*. The result is a crystal structure. The Fourier transform of the crystal is thus the product of the *molecular transform* and the *reciprocal lattice*. This is the *diffraction pattern*.

[More](#) Fourier transforms. [Back](#) to the index.
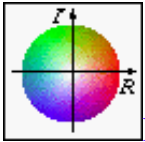
The Fourier Duck

A [duck](), and its Fourier Transform:

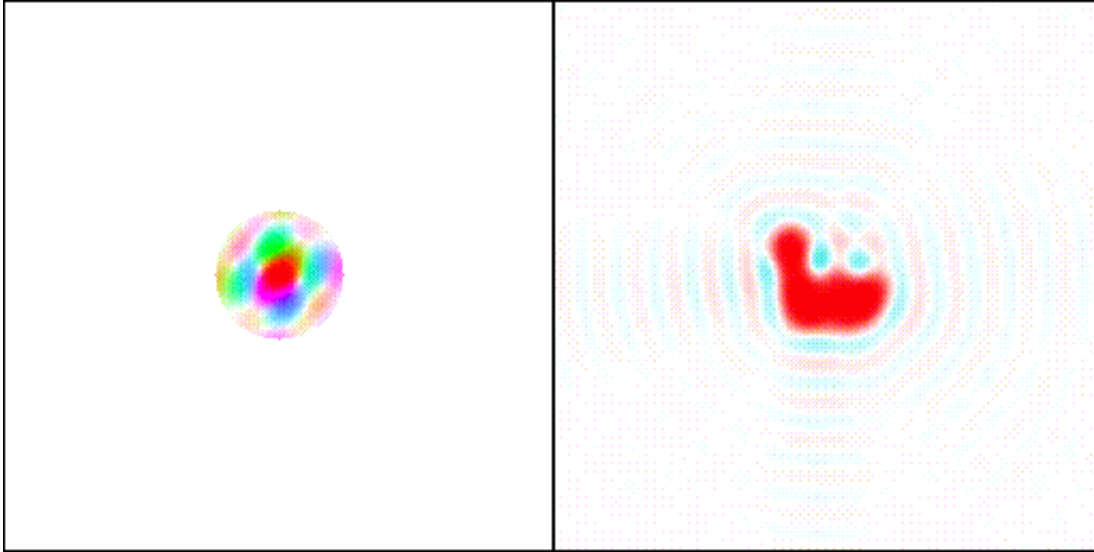## Crystallographic Interpretation:

Note the *real* image gives rise to a *Hermitian* diffraction pattern.

[More]() Fourier transforms. [Back]() to the index.

The Fourier Duck

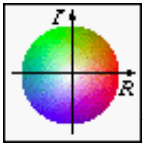If we only have the low resolution terms of the diffraction pattern, we only get a low resolution duck:

Crystallographic Interpretation:

There is considerable loss of detail. At low resolution, your atomic model may reflect more what you expect to see than what is actually there.

Note the ripples around the duck. These could be mistaken for solvation shells.

 More Fourier transforms. Back to the index.

The Fourier Duck

If we only have the high resolution terms of the diffraction pattern, we see only the edges of the duck:
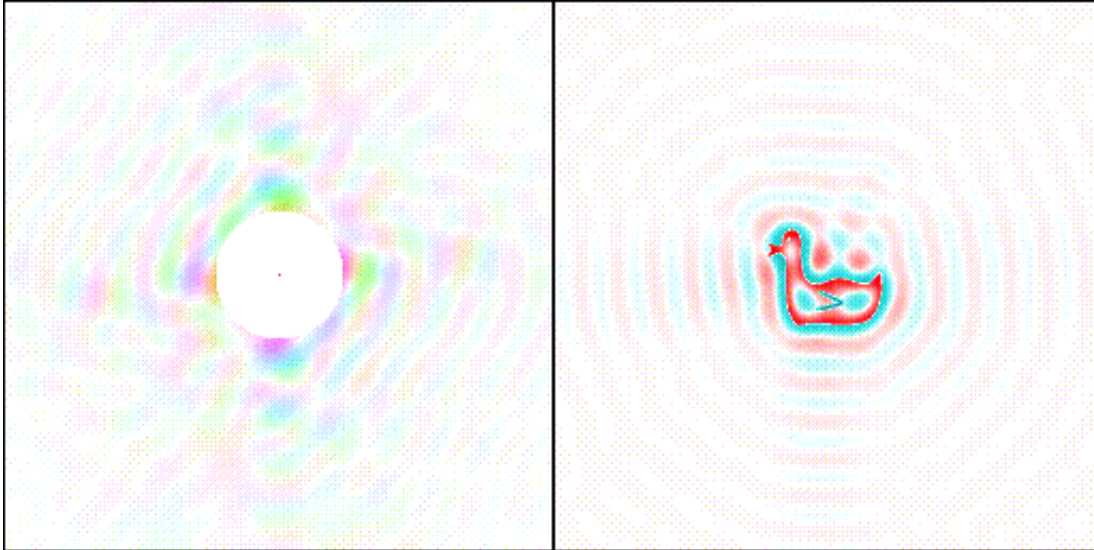
Crystallographic Interpretation:

It may be difficult to distinguish the solvent and protein regions. This will handicap both building and density modification. You may need to contour at a lower level inside the protein. There are prominent artifact peaks in the solvent.

Do not omit your low resolution data. Collect it and use it.

[More](#) Fourier transforms. [Back](#) to the index.

The Fourier Duck

If a segment of data is missing, features perpendicular to that segment will be blurred.
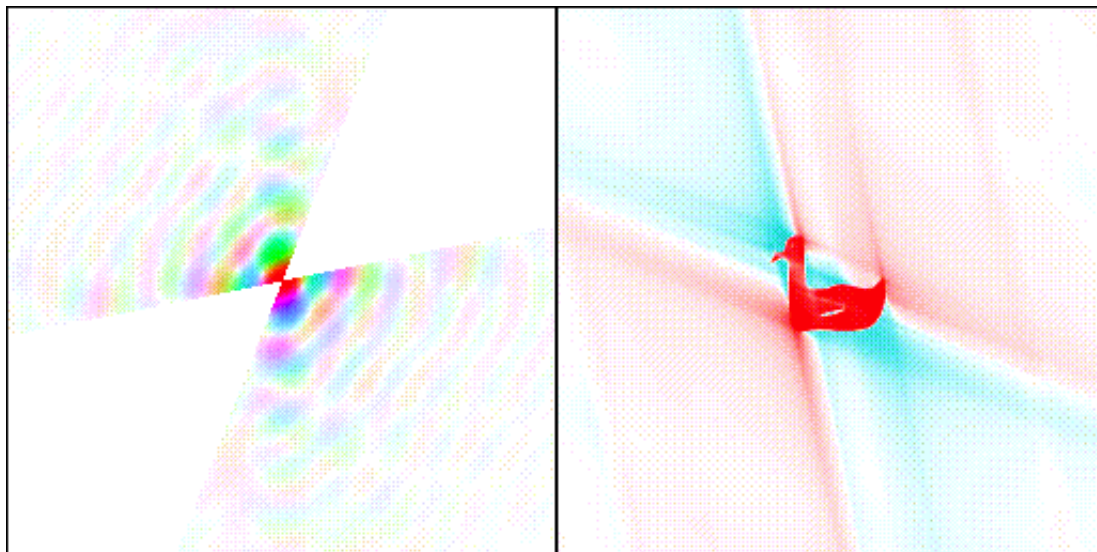
Crystallographic Interpretation:

Helices parallel to the missing data axis will become cylinders. Beta sheets parallel may merge into a flat blob. Beta sheets perpendicular to the missing data may be very weak. You could get into a lot of trouble with anisotropic temperature factors in this case.

Try not to omit *any* data. Collect it and use it.
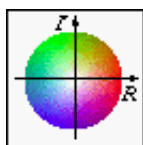
More Fourier transforms. Back to the index.

The Free-Fourier Duck

For the purposes of cross validation we may chose to omit some of our data.

If 10% of the reciprocal space data are omitted at random, then the following images are obtained:
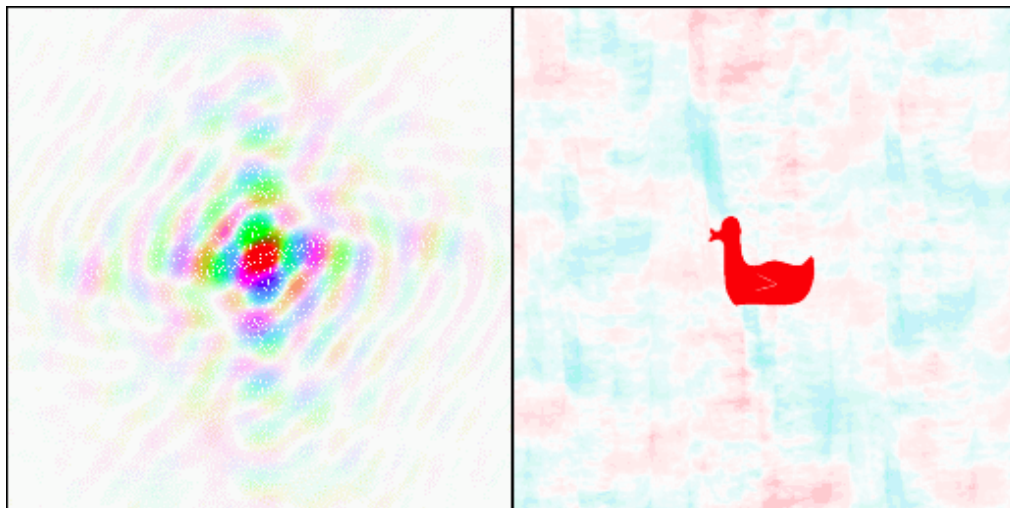
If 10% of the reciprocal space data are omitted in thin spherical shells, then the following images are obtained:
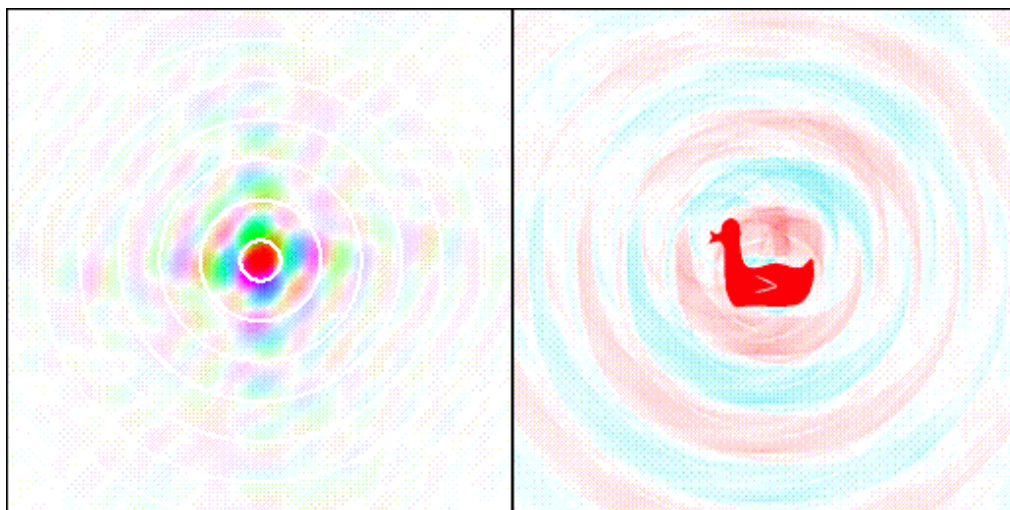
Crystallographic Interpretation:

Using *Free-Reflections* is a good validation of coordinate refinement, but is unwise when calculating maps. Particular care must be taken when using free-sets in density modification calculations, as the absence of the free-set can systematically bias the rest of the data.
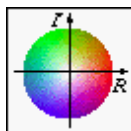
 More Fourier transforms. Back to the index.

Animal Magic

Here is our old friend; the Fourier Duck, and his Fourier transform:
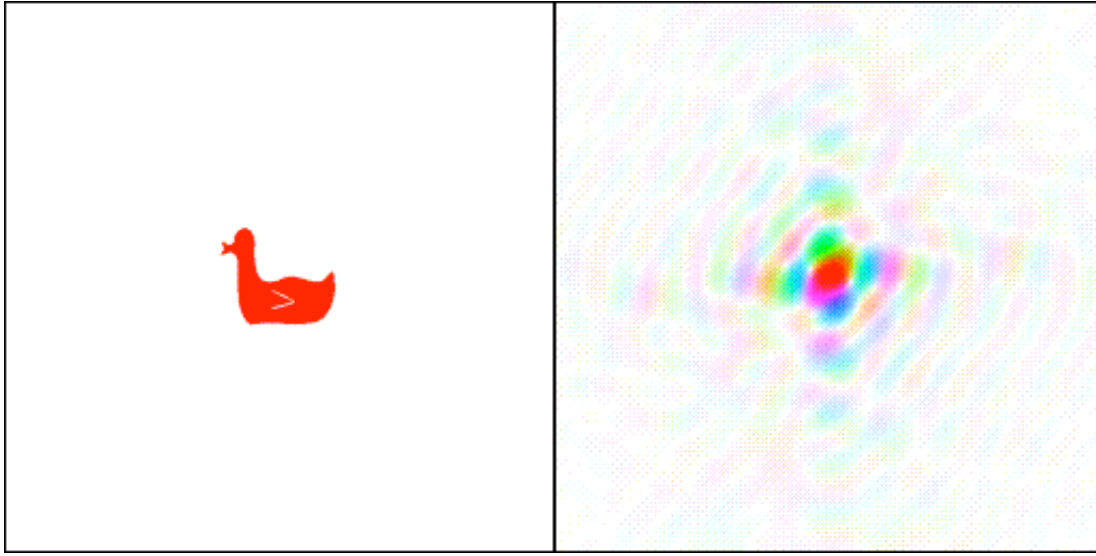
And here is a new friend; the Fourier Cat and *his* Fourier transform:
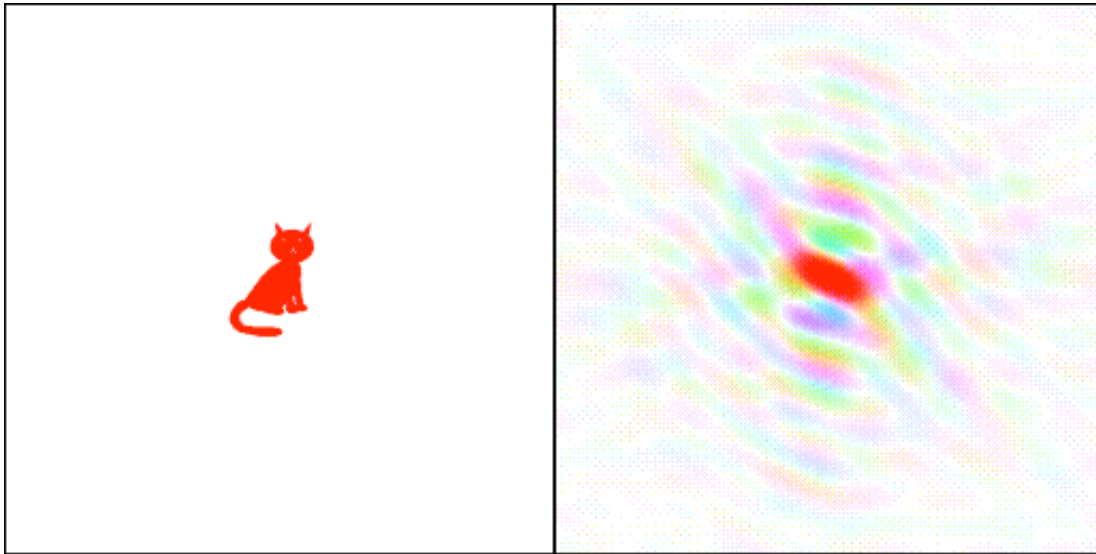
Now we will mix them up. Let us combine the the magnitudes from the Duck transform with the phases from the Cat transform. (You can see the brightness from the duck and the colours from the cat). If we then transform the mixture, we get the following:
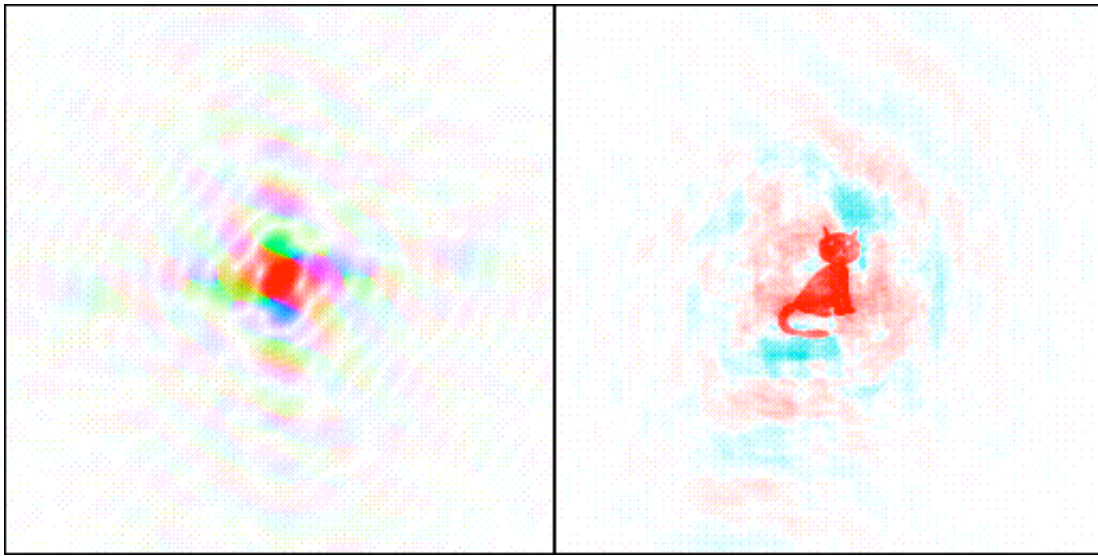
We can do the same thing the other way round. Using the magnitudes from the Cat transform and the phases from the Duck transform, we get:
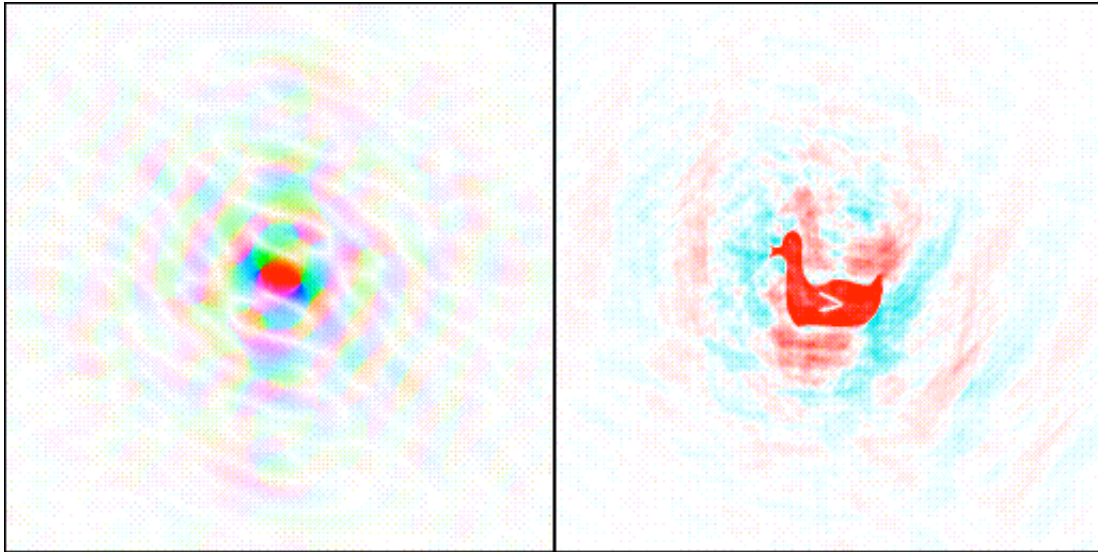
In each case, the image which contributed the phases is still visible, whereas the image which contributed the magnitudes has gone!

Crystallographic Interpretation:

In X-ray diffraction experiments, we collect only the diffraction magnitudes, and not the phases. Unfortunately the phases contain the bulk of the structural information. That is why crystallography is difficult.

[More](#) Fourier transforms. [Back](#) to the index.

A Tail of Two Cats

It is possible to reconstruct an image from the Fourier magnitudes alone if we have a similar image to provide phase information. For example, suppose we are trying to reconstruct the image of a cat, and have the fourier magnitudes for it.
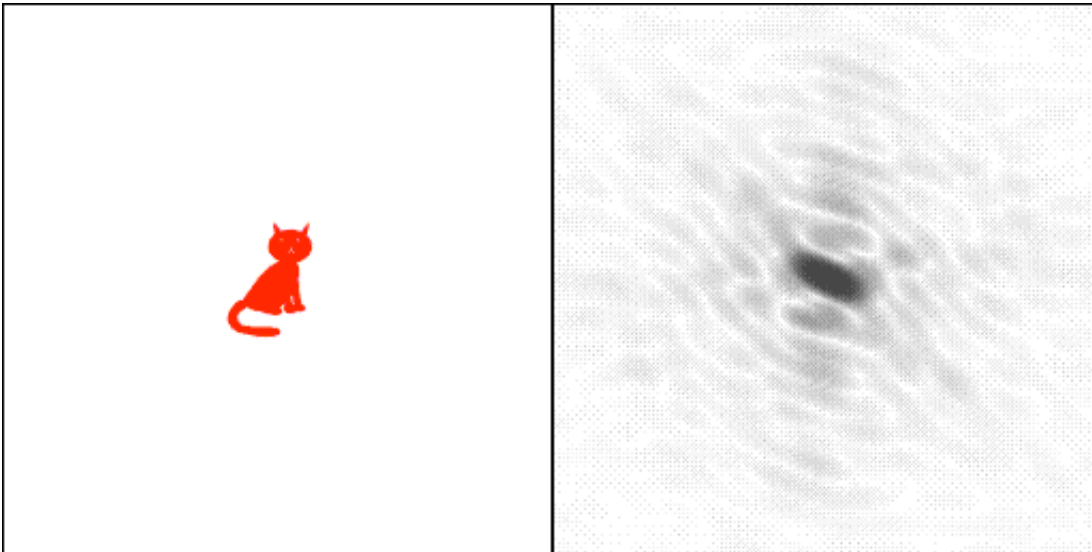
Since for this experiment we only have the magnitudes of the transform it is represented in monochrome, and we cannot reconstruct the image.

In addition to these magnitudes, we have an image which we know is similar to the missing cat. This image is of a Manx (tailless) cat. Since we have the image, we can calculate both the Fourier magnitudes and phases for the manx cat.
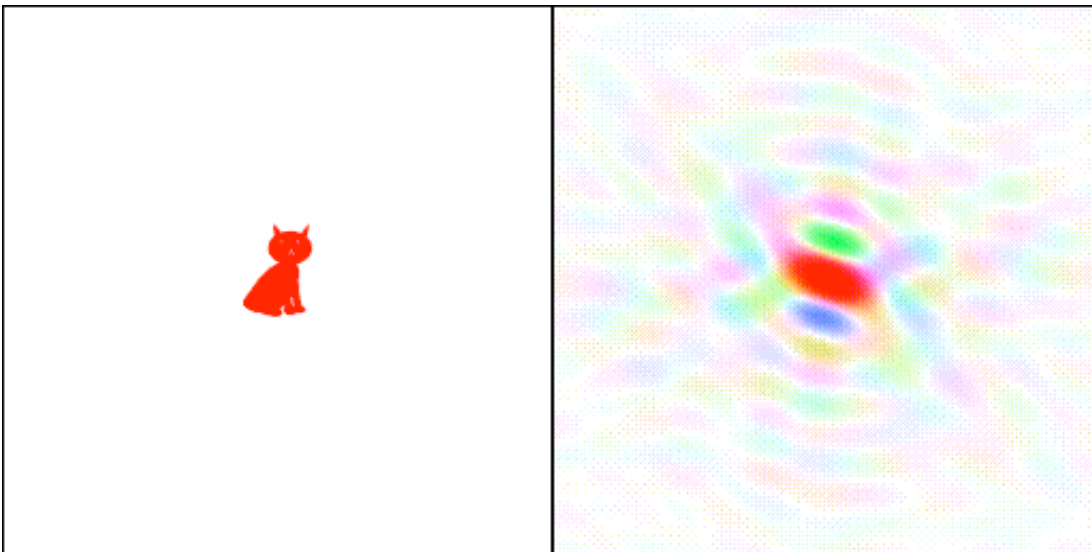
One simple method to try and restore the image of the cat is to simply calculate an image using the known Fourier magnitudes from the cat transform with the phases from the manx cat:
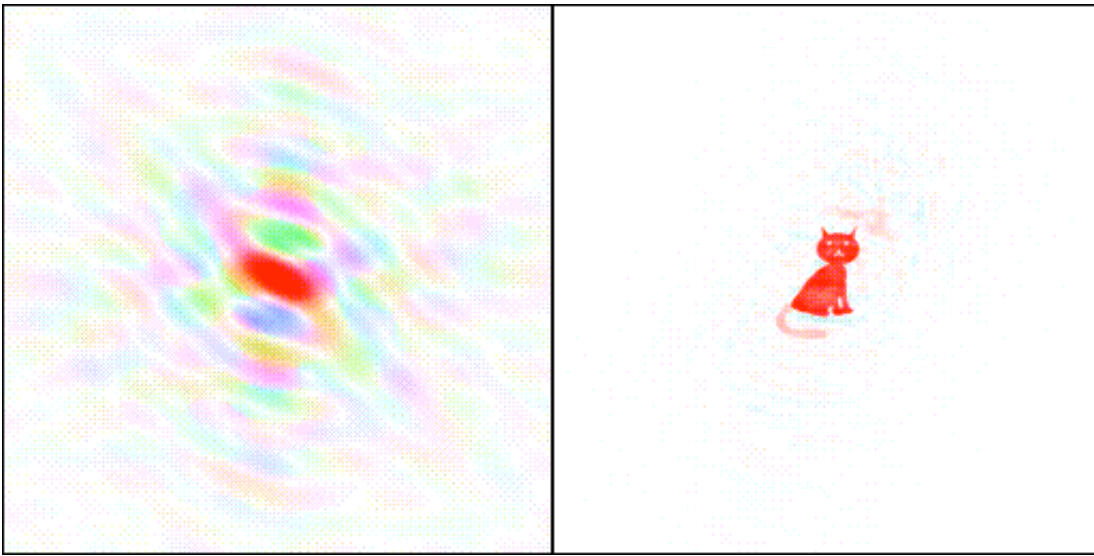
Despite the fact that the phases contain more structural information about the image than the magnitudes, the missing tail is restored at about half of its original weight. This occurs only when the phases are almost correct. The factor of one half arises because we are making the right correction parallel to the estimated phase, but no correction perpendicular to the phase (and $<\cos^2>=1/2$). There is also some noise in the image.

This suggests a simple way to restore the tail at full weight: apply double the correction to the magnitudes. An image is therefore calculated with twice the magnitude from the desired image minus the magnitude from the known image:
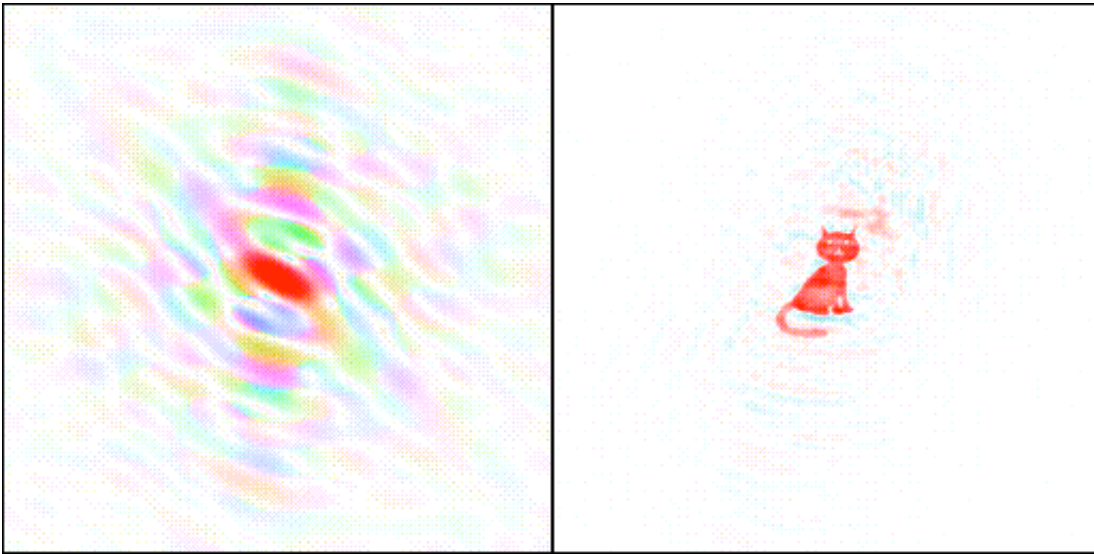
The resulting image shows the tail at full weight. However the noise level in the image has also doubled.

Crystallographic Interpretation:

Often in crystallography we have an *incomplete model*. Thus we have observed structure factor magnitudes for a complete molecule, but a model (from which we can calculate both magnitudes and phases) for only part of it. In this case the missing potrion of the model may be reconstructed by use of the appropriate Fourier coefficients.

The first attempt to reconstruct the cat's tail above corresponds to an $|F_o|$ map, the second to a $2|F_o|-|F_c|$

map.

In modern crystallography $2|F_o|-|F_c|$ maps have been superceded by more advances map coefficients, such as $2m|F_o|-D|F_c|$ (sigmaa-a) and maximum-likelihood map coefficients, but the principles are similar.

Thanks to [Eric Galburt](#) for suggesting this page.

[More](#) Fourier transforms. [Back](#) to the index.

Gallery

Some other examples of Fourier tranforms:
[Click here](#) to open a second window onto this page.

The Fourier transform of two points is a grating. This is a common optical transform which can be performed with a laser and two pinholes.
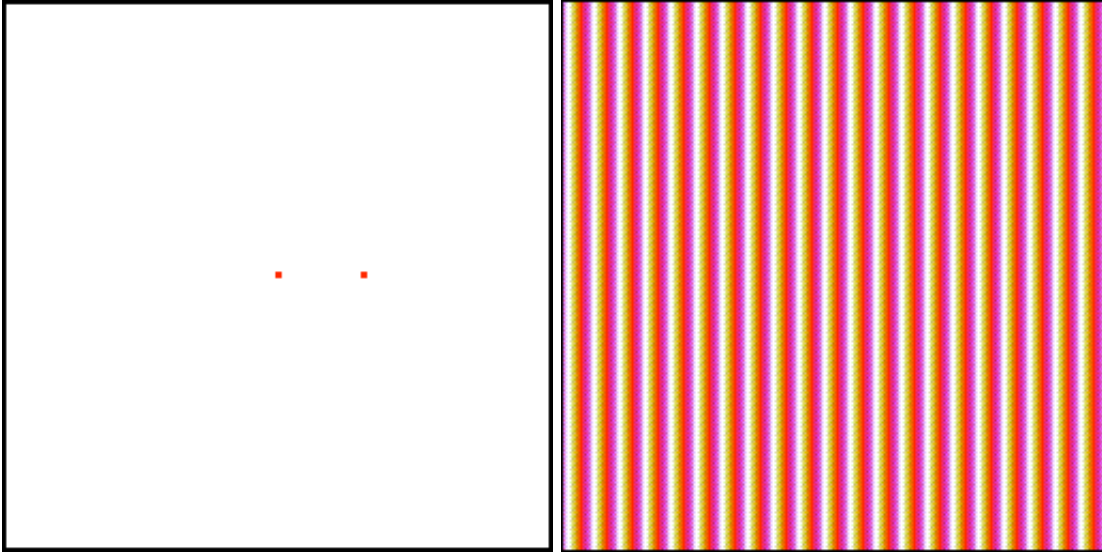
Eight points in an array make a very small crystal lattice. Since the lattice is very small, the diffraction spots are very large.
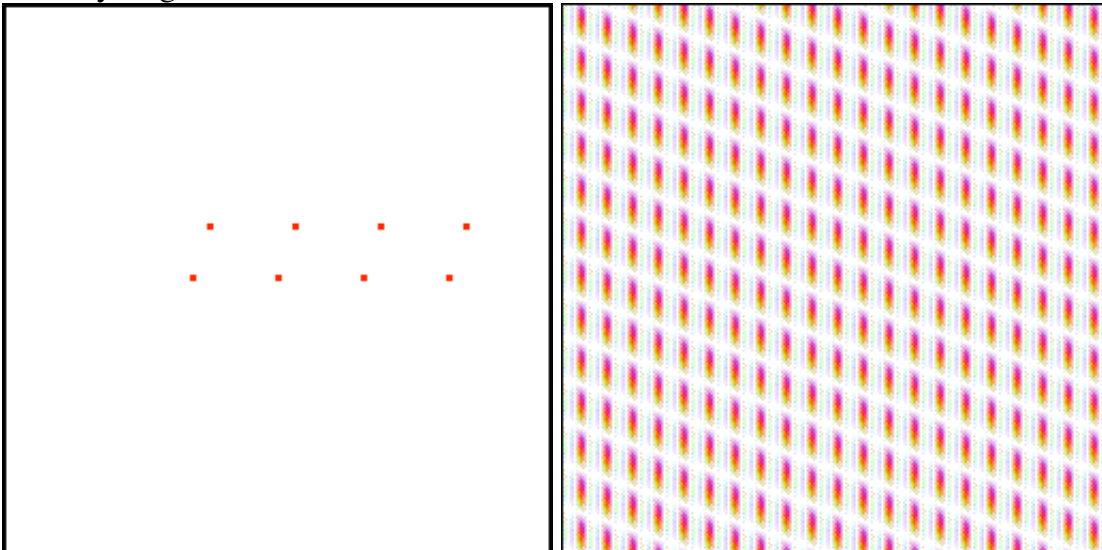
Fifteen points in an array make a more realistic crystal lattice. The reciprocal lattice is clearer now.
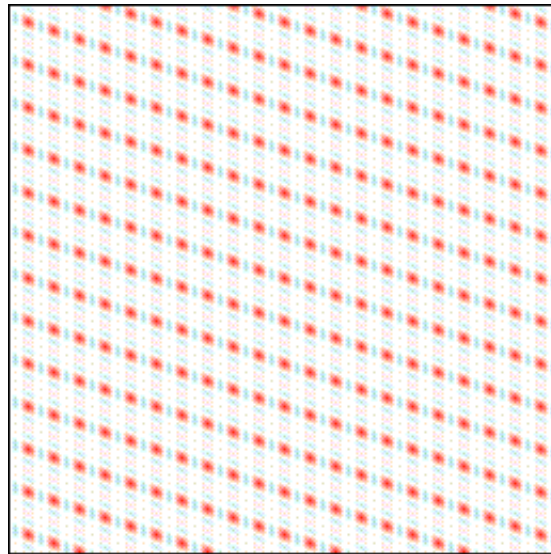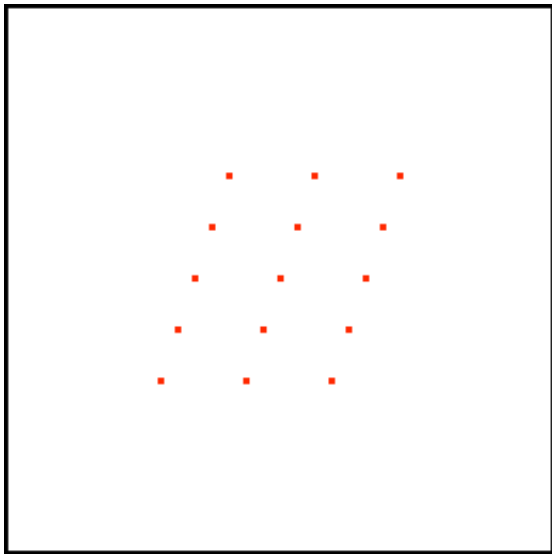
A molecule.
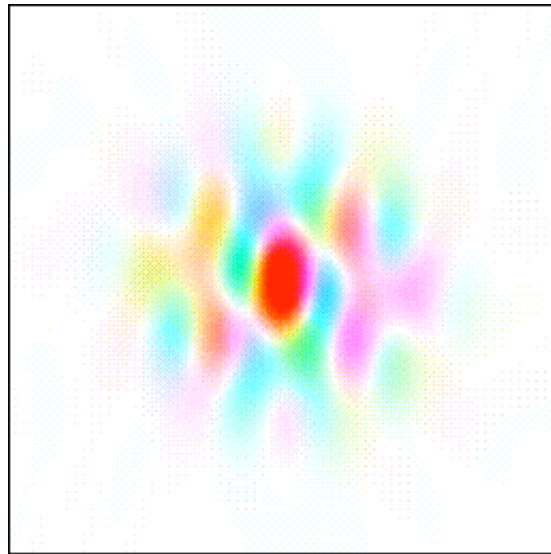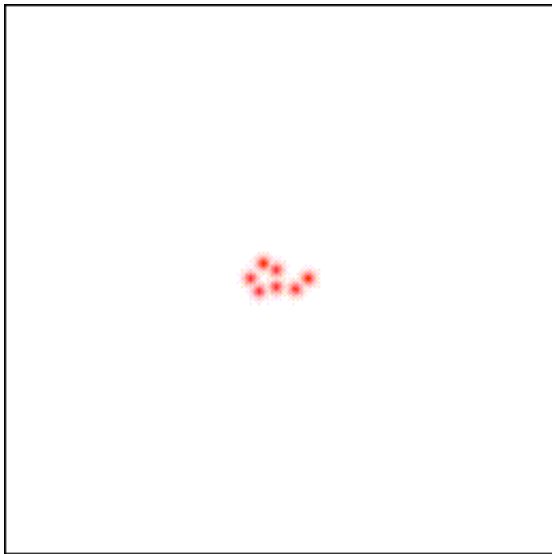
Two molecules.
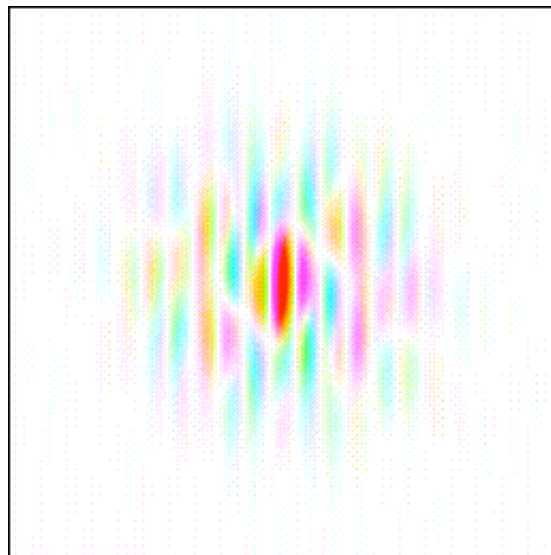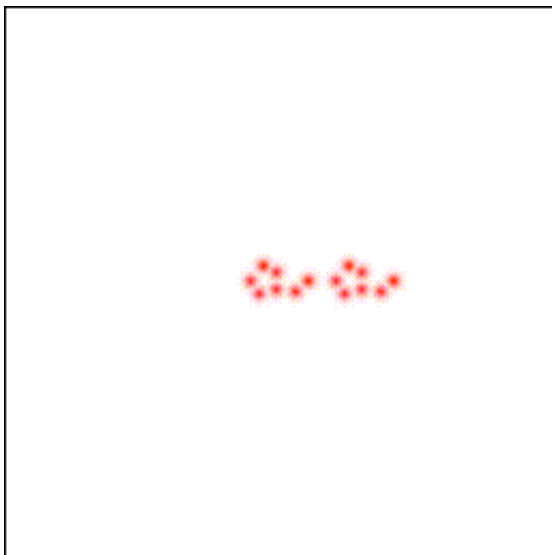
Eight molecules.
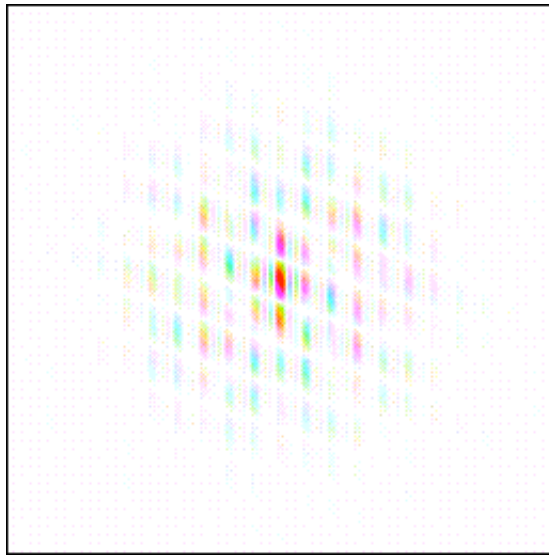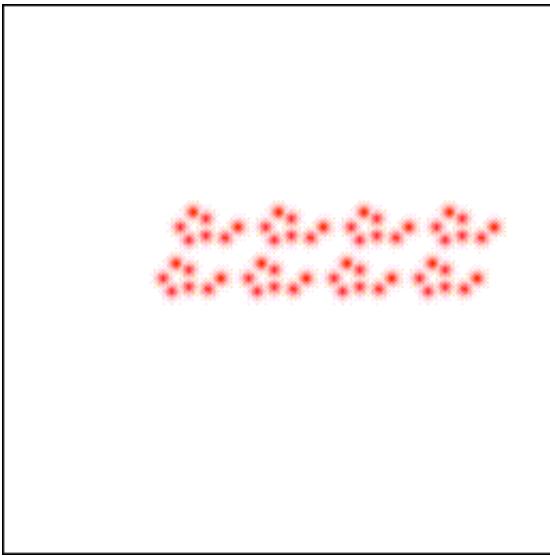
Fifteen molecules.
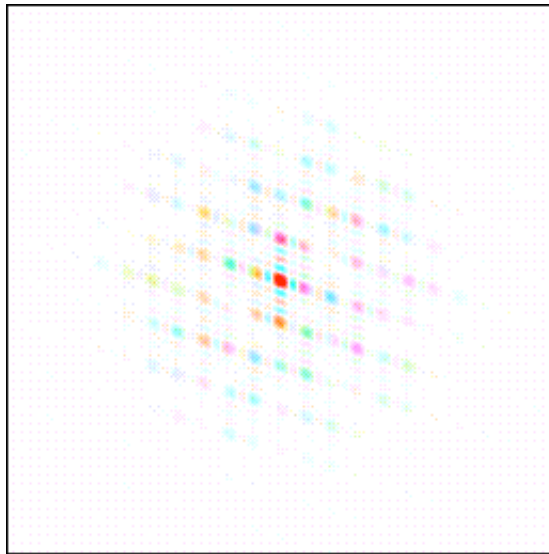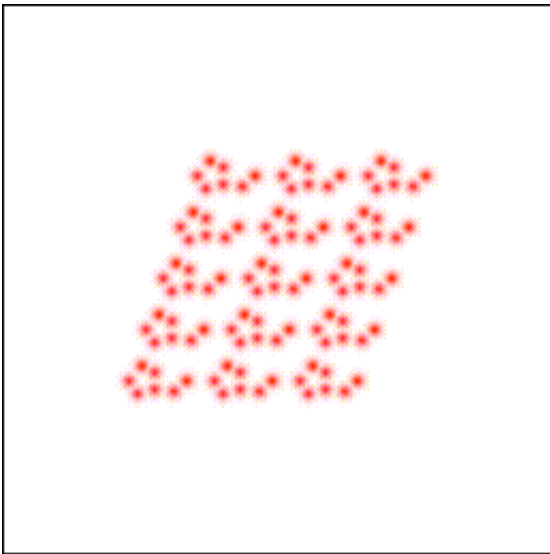
A duck with a missing shell of data:
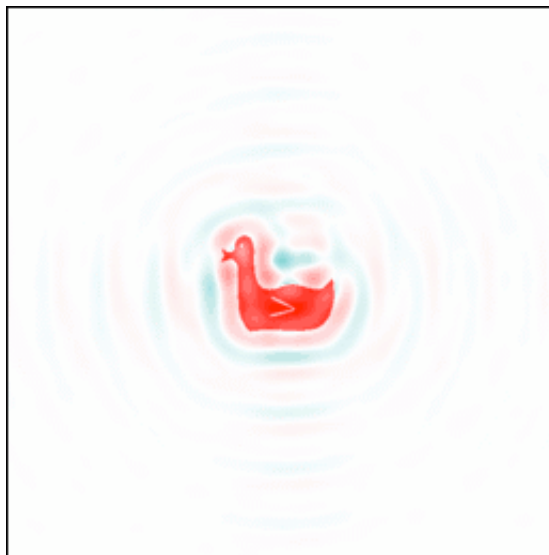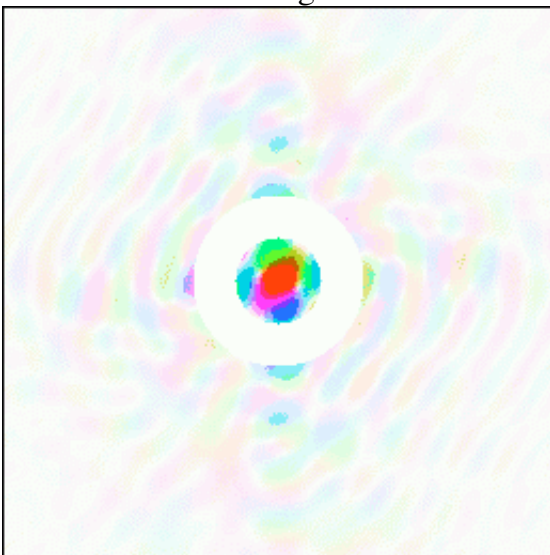
The edges are sharp, but there is smearing around them from the missing intermediate resolution terms. The core of the duck is at the correct level, but the edges are weak.

The Convolution Theorem

The convolution theorem is one of the most important relationships in Fourier theory, and in its application to x-ray crystallography. It can be stated as follows:

Consider functions *a* and *b*. Let *A* be the Fourier transform of *a*, and *B* be the Fourier transform of *b*. Then the Fourier transform of the product *ab* is the convolution of *A* and *B*. Call the result of this convolution *C*, then:

$$C(x) = \sum_y A(y)\, B(x-y)$$

The product of two functions is simple - the values of the two functions are simply multiplied at every point.

The convolution of two functions is more complex. To convolute two functions, the first function must be superimposed on the second at every possible position, and multiplied by the value of the second function at that point. The convolution is the sum of all of these superpositions.

For example, here is a line, and its Fourier transform:
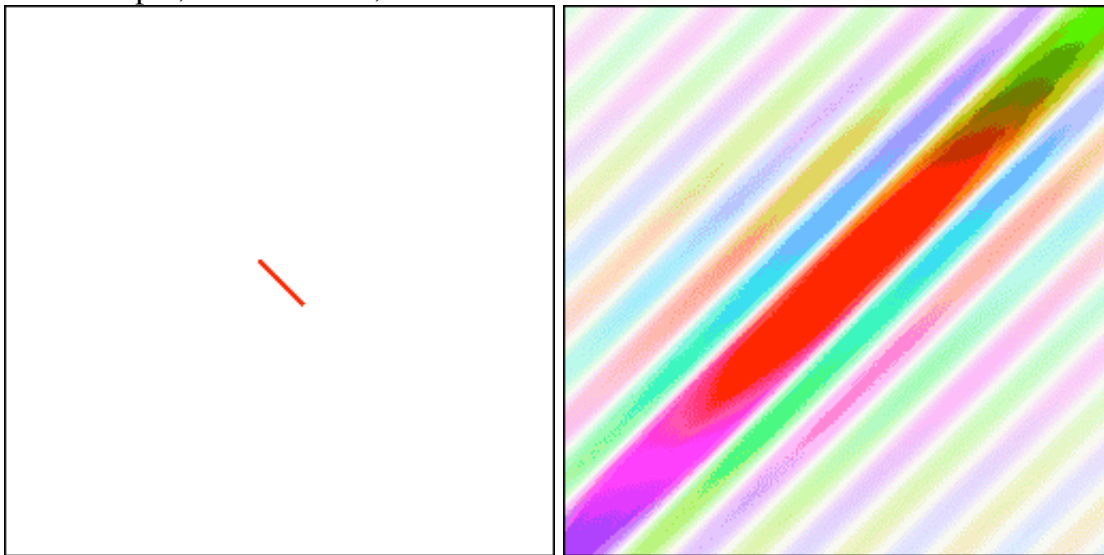
The line can be convoluted with a circle:
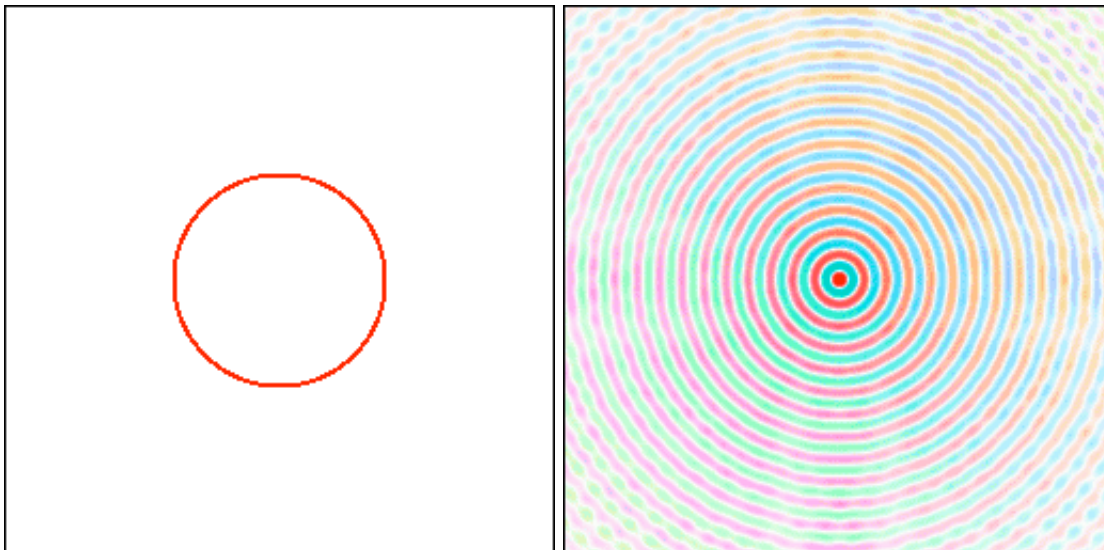
The result is a circle spread by moving it along the line, or alternatively a line spread by moving it around the circle. It is clear that the Fourier transform of the convolution is equal to the product of the transforms of the functions themselves.
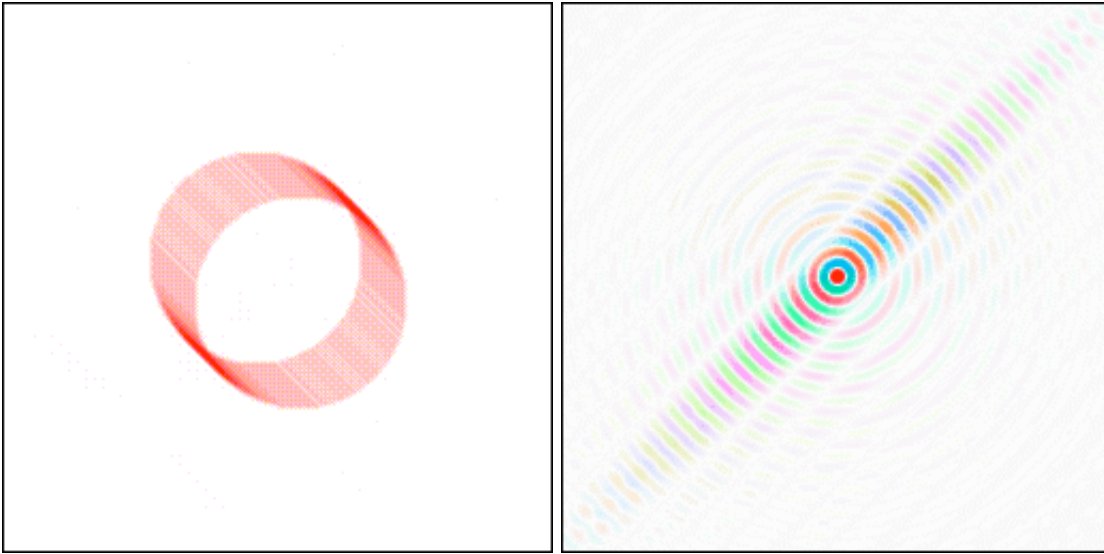
Most of the time we simply convolute one function with one or more delta-functions. If we convolute the duck with a delta function at the origin, we get back the duck at the origin.
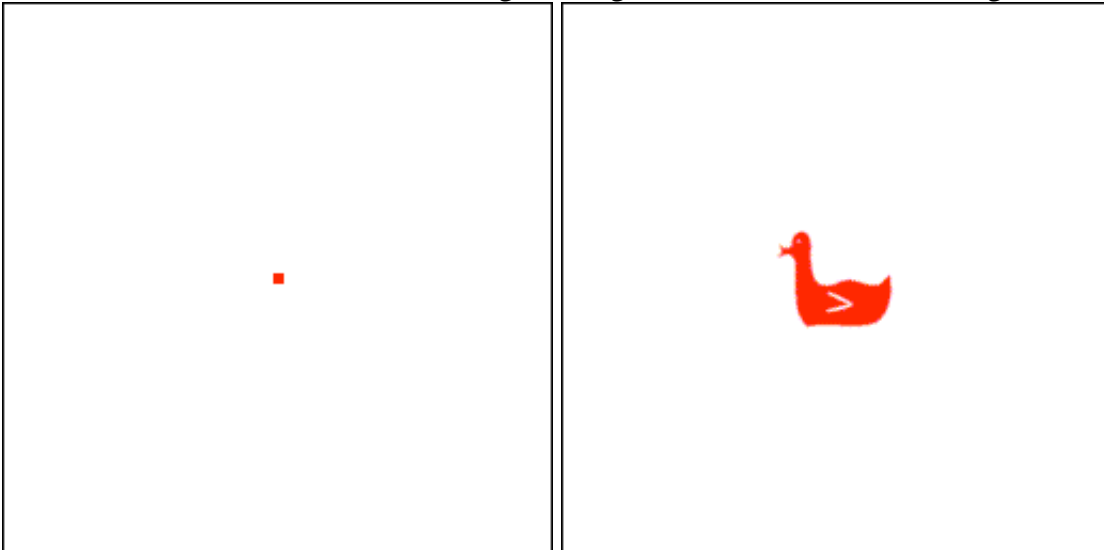
If we convolute it with a delta-function somewhere else, then the duck is moved to that point.
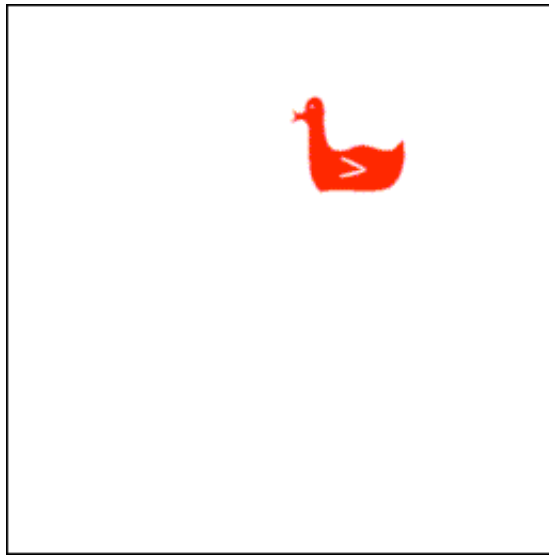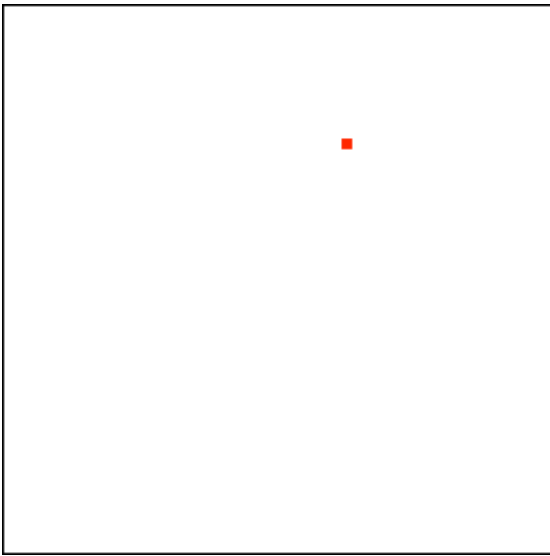
If we convolute the duck with several delta-functions, we get a copy of the duck at each delta-function.
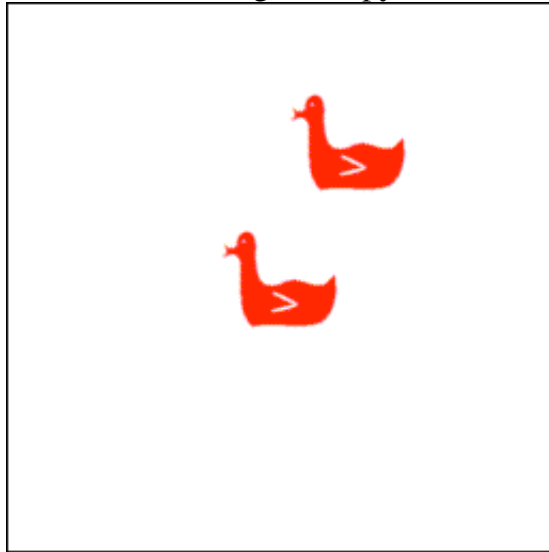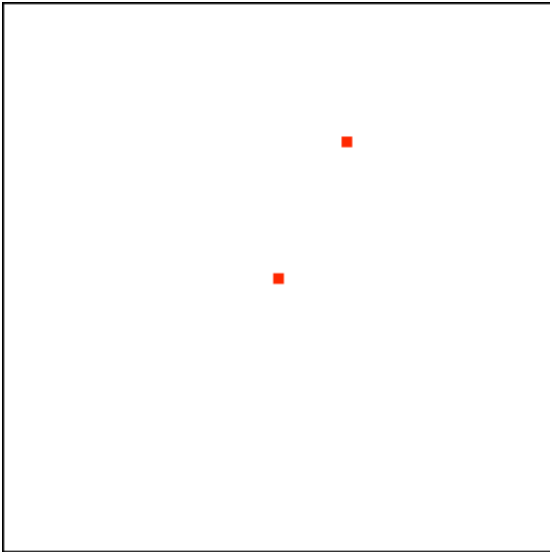
Some Basic Definitions

LATTICE = An infinite array of points in space, in which each point has identical surroundings to all others.

CRYSTAL STRUCTURE = The periodic arrangement of atoms in the crystal.

It can be described by associating with each lattice point a group of atoms called the **MOTIF** (**BASIS**)
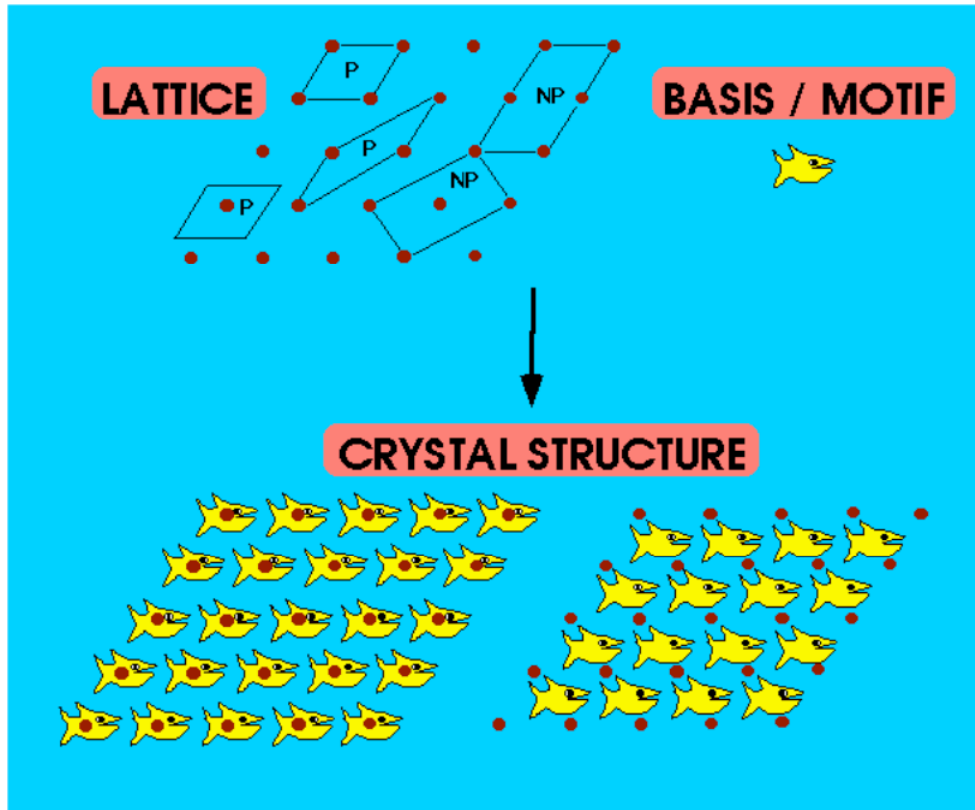
- Don't mix up atoms with lattice points
- Lattice points are infinitesimal points in space
- Atoms are physical objects
- Lattice Points do not necessarily lie at the centre of atoms

UNIT CELL = The smallest component of the crystal, which when stacked together with pure translational repetition reproduces the whole crystal

- **Primitive** (**P**)unit cells contain only a *single lattice point*

Semiconductor Crystals

The Lattice and the Basis

A crystal is a regular, ordered arrangement of atoms over a large scale. The atoms may be of a single type or the repetition of a complex arrangement of many different types of atoms. The crystal can be thought of as consisting of two separate parts: the lattice and the basis. The lattice is an ordered arrangement of points in space, while the basis consists of the simplest arrangement of atoms which is repeated at every point in the lattice to build up the crystal structure. A good analogy, is patterned wallpaper. The basis is like a motif on the wallpaper and the lattice would be periodic pattern of points on which of the motif is repeated. In Figure 1, the lattice points correspond with the centre of the basis, but this does not have to be the case.
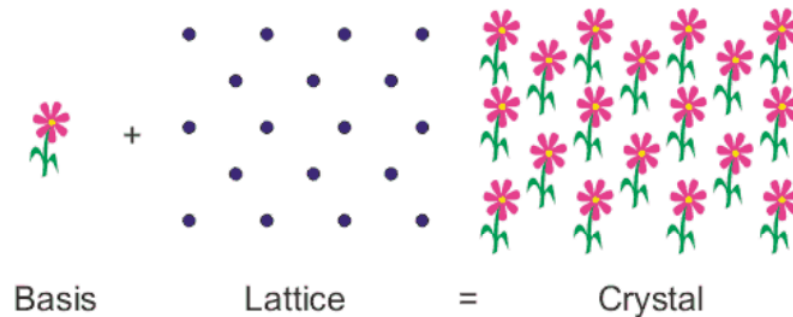
Figure 1. A crystal can be thought of as being like wallpaper. The motif is analogous to the basis and the arrangement of the motif over the surface is like the lattice.

The points on the lattice are specified using vectors. *Lattice vectors* are the shortest distances to the nearest neighbouring points on the lattice and are conventionally denoted by **a** , **b** and **c** . The angles between these vectors are given the symbols , α, β and γ. A simple two-dimensional example is shown in Figure. 2. Any two lattice points can be reached using a combination of the lattice vectors **a** and **b** . Obviously, in three dimensions, any point on the lattice can be reached using a combination of the three lattice vectors **a** , **b** and **c**. In 2-dimensions this is,

$$\mathbf{R} = n_1\,\mathbf{a} + n_2\,\mathbf{b}$$

The *basis vector* , **R** is a vector from one lattice point to another in terms of the lattice vectors. Since the lattice looks the same (invarient) in going from one lattice point to another, the lattice has translational symetry.

Primitive Cell

The *primitive cell* is the smallest part of the lattice that which repeated would reconstruct the entire crystal structure.

The *unit cell* - is a volume repeated throughout the entire lattice. The unit cell does not have to be the primative cell.

●→● R=a+3b
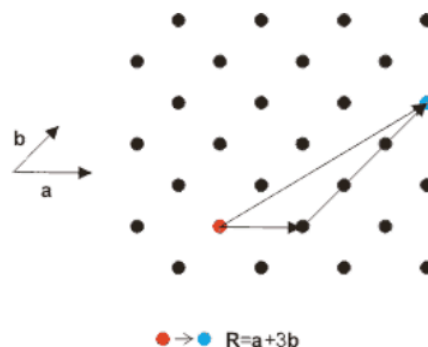
Figure 2. Lattice vectors are a linear combination of the basis vectors.

The Graphite Honeycomb Lattice
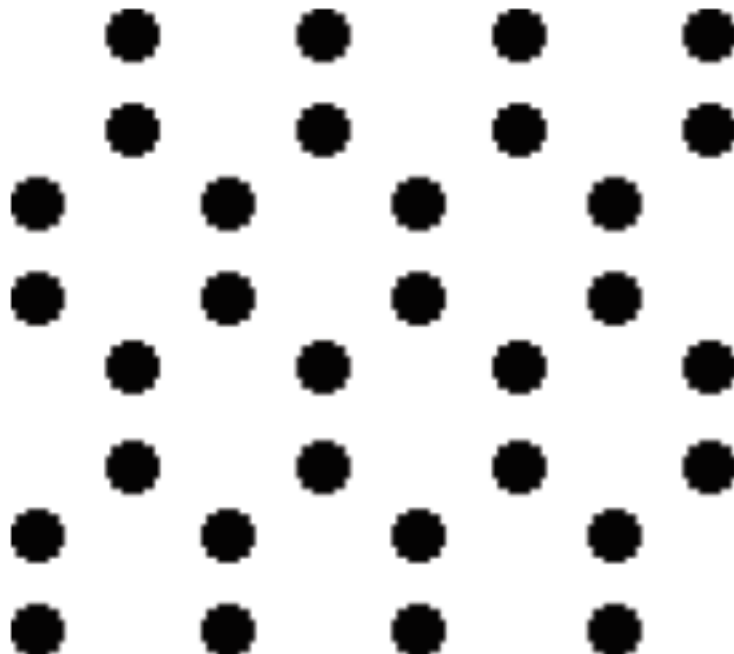
The Associated Bravais Lattice
and the 2 Atom Basis

Bravais
Lattice: ×

Basis:
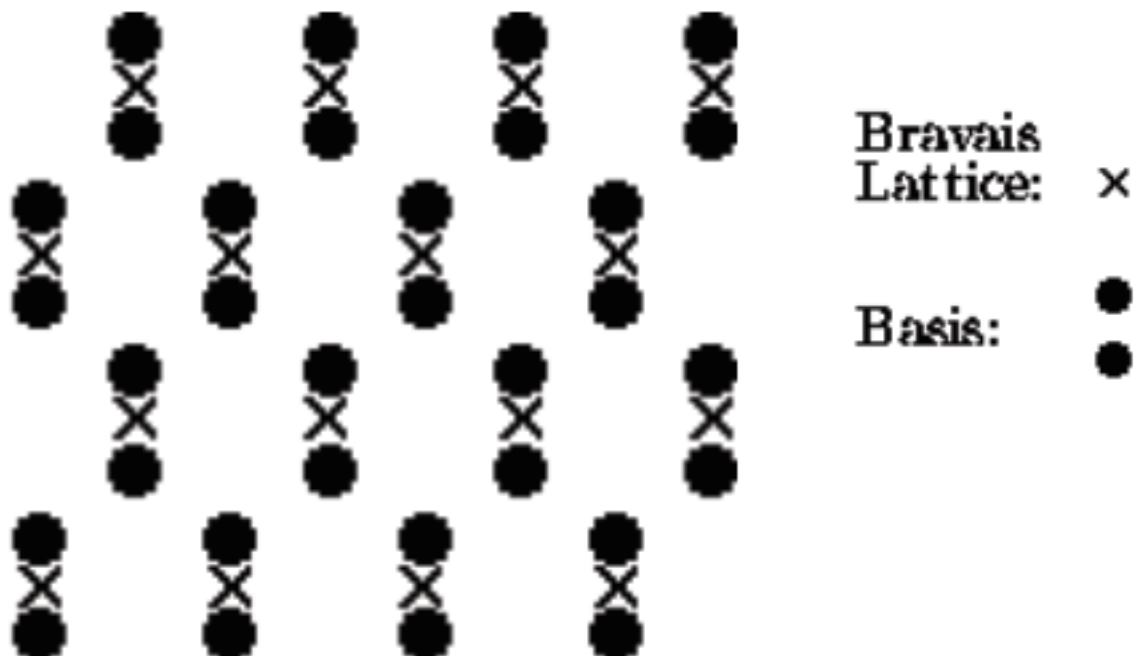
Crystal Structures

A *crystal* is a periodic array of atoms. Many elements and quite a few compounds are crystalline at low enough temperatures, and many of the solid materials in our everyday life (like wood, plastics and glasses) are not crystalline. Nevertheless, typical solids state physics texts start with the discussion of crystals for a good reason: The treatment of a large number of atoms is immensely simplified if they are arranged into a periodic order.
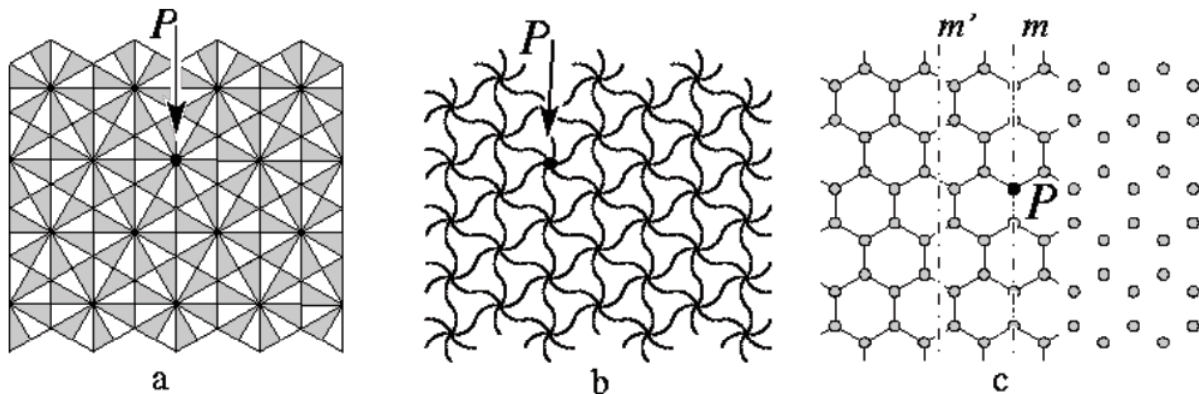
Figure 1.1: Examples of crystals in two dimension. Dots, curved lines or shaded areas represent various molecules or atomic arrangements.

Figure 1.1 shows a few two-dimensional ``crystals''. All crystals have *discrete translational symmetry*: If displaced by a properly selected *lattice vector* $\vec{R}$, every atom moves to the position of an identical atom in the crystal. Due to this translational symmetry, a crystal can be constructed by repeating the *basis* at every *Bravais lattice* point. The basis is the ``building block'' of the crystal. It may be simple, a spherical atom, or as complex as a DNA molecule. Sometimes we have to use a basis made up of two (or more) atoms, even if there is only one type of atom in the crystal (see the example in Figure 1.2).

The *Bravais lattice*, or *space lattice*, is an infinite array of points, determined by the lattice vectors $\vec{R}$, where $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$ such that every n_i is an integer. The $\vec{a}$'s are the three *primitive vectors* of the Bravais lattice; in three dimensions they must have a nonzero $\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$ product. There are an infinite number of different choices for the primitive vectors of a given lattice. For example, $\vec{a}_1' = \vec{a}_1 + \vec{a}_2$; $\vec{a}_2' = \vec{a}_1 - \vec{a}_2$; and $\vec{a}_3' = \vec{a}_3$ will describe the same lattice. The *lattice spacings* are the lengths of the shortest possible set of primitive vectors.

All three crystals in Figure 1.1 have the same Bravais lattice. Note that not all symmetric arrays of points are Bravais lattices! For example, Figure 1.2 shows a *honeycomb lattice* and a choice for its Bravais lattice and basis.
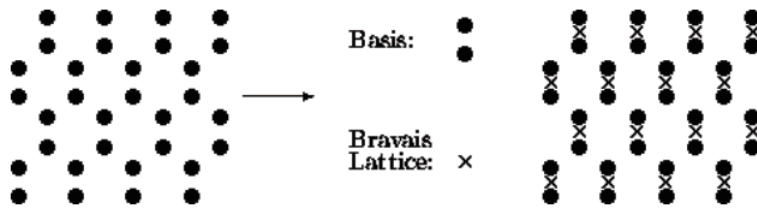
Figure 1.2: Example of a regular array of points that is not a Bravais lattice (honeycomb lattice).

In addition to the translational symmetry, most crystals also have other symmetries, including reflection, rotation, or inversion symmetry, or more complicated symmetry operations, like the combination of rotation and translation by a fraction of the lattice vector. In Figure 1.1 the three-fold rotational symmetry around the point P is common to all three crystals. The honeycomb lattice (Figure 1.1c) also has a ``mirror line'' m, while the other two crystals do not have this symmetry. A less trivial symmetry operation is mirroring the honeycomb lattice with respect of the line m', and then shifting it parallel to the line, until it overlaps with itself.

The collection of symmetry operations forms a *symmetry group*. The important property that defines a symmetry group is the relationship between the symmetry elements - i.e., what happens if two symmetry operations are applied subsequently. In the language of group theory, this relationship is described by the multiplication (direct product) table. The symmetry group can be represented in many ways (collections of matrices, symmetry operations of a simple geometric object, and so on). As long as the multiplication table is the same, we are dealing with the same group. The crystals in Figures 1.1a and 1.1b have equivalent symmetry groups, while some of the symmetries of the honeycomb lattice are different.

When all possible symmetry operations are taken into account we talk about *crystallographic space groups*. Any given three-dimensional crystal belongs to one of the 230 possible crystallographic space groups. (Two-dimensional crystals are much simpler; there are only 17 inequivalent ``crystallographic plane groups''.) The symmetries are often identified by the name of a representative material, like ``sodium chloride structure'', ``diamond structure'', ``wurzite (or zincblende, zinc sulfide) structure'', and so on. More sophisticated group theoretical notations are used by crystallographers. For a complex structure the identification of the symmetry group may be a rather nontrivial task.

A subset of symmetry operations that leaves at least one point invariant makes up the *crystallographic point group*. There are 32 different crystallographic point groups in three dimensions, and 10 in two dimensions. Considering the examples in Figure 1.1, the rotations around P and the mirror line m are point group symmetries, but the combination of mirroring around m' and the subsequent shift is *not* a point group operation.

Sorting out the symmetries of the Bravais lattices is much simpler. There are 14 different space groups for three-dimensional Bravais lattices, including the simple cubic (*sc*), face centered cubic (*fcc*), body centered cubic (*bcc*), simple tetragonal, body centered tetragonal, and others. Figure 1.3 shows all possible Bravais lattices in two dimensions. It is important to emphasize that the symmetries of the Bravais lattice are intimately related to the symmetries of the original lattice. For example, the three-fold rotational symmetry of the honeycomb lattice results in the requirement that its Bravais lattice must have three-fold rotational invariance (which leaves the hexagonal lattice as the only choice, see Figure 1.2).

Figure 1.3: Two-dimensional Bravais lattices.

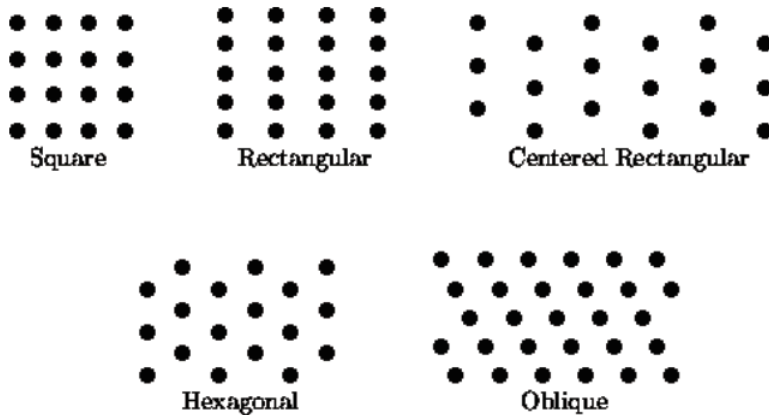Finally, when the point group symmetries of the Bravais lattices are considered, the choices are further limited, and in three dimensions only seven distinct groups are left. These define the seven *crystal systems*: Cubic, tetragonal, orthorhombic, monoclinic, triclinic, trigonal, and hexagonal. (In two dimensions there are four crystal systems. The rectangular and centered rectangular Bravais lattices shown in Figure 1.3 make up the ``rectangular'' system.)

The *primitive unit cell* or *primitive cell* is a volume which will fill space completely, without overlap, if shifted by each of the lattice vectors. The primitive unit cell contains exactly one Bravais lattice point and the atoms in it can be used as the basis to construct the crystal. The volume made up by the primitive vectors is a possible primitive unit cell, but there are many other possibilities. More often than not, the primitive unit cell is less symmetric than the Bravais lattice.

The *unit cell* is a volume that fills up space with an integer multiplicity, if shifted by each of the lattice vectors. It contains an integer number of lattice points. Sometimes it is more convenient than the primitive unit cell (as shown in Figure 1.4).
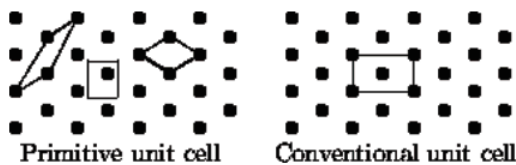
Figure 1.4: Some choices of primitive unit cells and the conventional unit cell for a centered rectangular lattice.

The *Wigner-Seitz cell* (WS cell) is a volume made up of space which is closer to a given lattice point than to any other point. There is a practical recipe for the construction of this cell: Select a lattice point, draw the lines connecting it to its neighbors (nearest and next-nearest is usually sufficient), and draw the perpendicular bisecting planes to these lines. The smallest volume enclosed within these planes is the WS cell. The WS cell is a primitive unit cell that preserves the symmetries of the Bravais lattice.

Imagine that a crystal is made of spheres with their diameters being equal to the nearest-neighbor distance. The *filling factor* is the volume fraction of the spheres relative to the total volume. The *coordination number* is the number of nearest-neighbors to any sphere.

When waves are scattered from a periodic array the constructive interference is often described by the *Bragg condition*: $n\lambda = 2d\sin\theta$, where λ is the wavelength, d is the spacing between subsequent lattice planes (that is, planes containing a high density of lattice points) and θ is the angle between the incident beam and the lattice planes. The scattered beam will have the same angle with respect to the planes as the incident beam, so the total scattering angle is 2θ.

Instead of wavelength, the concept of the *wavevector* is often used to characterize the a plane wave. The wavevector $\vec{k}$ points in the direction of the propagation of the wave, and the magnitude of the vector is $|\vec{k}| = 2\pi/\lambda$. The condition for

constructive interference can be expressed in terms of wave vectors as $(\vec{k} - \vec{k'}) \cdot \vec{d} = 2\pi n$, where n is an integer, $\vec{k}$ and $\vec{k'}$ are the incident and scattered wavevectors, and $\vec{d}$ is the vector pointing from one scattering center to another.

The *reciprocal lattice* is a very useful tool to handle the diffraction of waves; it is generally used to describe all things of ``wavy nature" (like electrons and lattice vibrations). Definitions of the reciprocal lattice are as follows:

- The collection of all wave vectors that yield plane waves with a period of the Bravais lattice (*note:* any $\vec{R}$ vector is a possible period of the Bravais lattice).
- A collection of vectors $\vec{G}$ satisfying $\vec{G} \cdot \vec{R} = 2\pi n$, or $e^{i\vec{G} \cdot \vec{R}} = 1$.
- There is also a practical definition in three dimensions:

$$\vec{g}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{V} , \qquad (1.1)$$

and cyclic permutations of 1 2 3, where $V = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$ is the volume of the unit cell.

The volume of the primitive unit cell in the reciprocal lattice is $(2\pi)^3/V$. The crystal system of the reciprocal lattice is the same as the direct lattice (for example, cubic remains cubic), but the Bravais lattice may be different (*e.g.*, *fcc* becomes *bcc*). The *Brillouin zone* is the WS cell in the reciprocal lattice.

Using the reciprocal lattice, the condition for constructive interference becomes quite simple: If the difference between the incident ($\vec{k}$) and scattered ($\vec{k'}$) wave vectors is equal to a reciprocal lattice vector, the diffracted intensity may be nonzero. This is the *Laue condition*. With $\vec{K} = \vec{k'} - \vec{k}$, this leads to the simple equation $\vec{K} = \vec{G}$, or $\vec{K} \cdot \vec{G} = 1/2|\vec{G}|^2$. The *Ewald construction* is a geometric representation of these equations.

The *Miller indices*, h, k, and l, are obtained from the ``coordinates" of a reciprocal lattice vector $\vec{G} = h\vec{g}_1 + k\vec{g}_2 + l\vec{g}_3$.

By definition, the Miller indices are integers. For a simple cubic lattice these numbers are real coordinates in a Cartesian coordinate system.

There is an interesting relationship between Miller indices and lattice planes. For any plane there is an infinite number of other, parallel lattice planes, separated by a distance d. It is easy to see that the ratio $x: y: z$ is the same for all parallel planes, where x, y, and z are the intercepts of a given plane with the coordinate axis defined by the primitive vectors $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$.

Sometimes the need arises to classify these planes. There is a convenient mapping between a given class of lattice planes and a lattice vector in reciprocal space: For any family of lattice planes separated by a distance d, there is a reciprocal vector with length $|\vec{G}| = 2\pi/d$, and this vector is perpendicular to the lattice planes. One can show (nontrivially) that

$h: k: l = (1/x): (1/y): (1/z)$.

The Laue condition is based solely on the Bravais lattice, so the positions of the diffraction peaks are independent of the atomic basis. However, the intensities of the peaks are strongly influenced by the basis. The *structure factor*, $S(\vec{G})$, and the *form factor*, f_α , tell us how the intensities of the peaks depend on the atoms making up the crystals. These quantities are calculated as a sum (or integral) within the unit cell; therefore they may be totally different for two different crystals, even if the crystals have the same Bravais lattice. In the simplest approximation the scattering depends on the atomic charge distribution $\rho_\alpha(\vec{r})$, and the intensity is proportional to the absolute value squared of

$$S(\vec{G}) = \sum_\alpha f_\alpha e^{-i\vec{G} \cdot \vec{r}_\alpha} \qquad (1.2)$$

and

$$f_\alpha(\vec{G}) = \frac{1}{e} \int \rho_\alpha(\vec{r}) e^{-i\vec{G}\cdot\vec{r}} d^3\vec{r} , \qquad (1.3)$$

where e is the electron charge, the sum is over the atoms in the unit cell, and the integration is over the volume of an atom. Similar formulae work for electron and neutron scattering, except the form factor integral is different depending on the microscopic interaction at play. Even for X-rays, the calculation of the form factor as an integral over the charge density works only for the simplest cases. For a realistic calculation of scattered radiation intensities one has to include factors representing the directional dependence of the scattering by a single point charge, the absorption of the radiation, and other effects. For powder samples this process is called *Rietveld analysis*. The expression becomes much more complicated for example, if there is a match between the energy of atomic transitions and the X-ray quanta.

When the atomic positions are time-dependent (for example, if lattice waves are excited in the crystal), the crystal scatters radiation at a frequency different from the incident frequency. In this case energy is either absorbed or emitted by the crystal. The process can be described by the *dynamic structure factor*, which depends also on the frequency difference ω between the incident and scattered radiation: $S = S(\vec{k}, \omega)$. The general expression

$$S(\vec{k}, \omega) = \frac{1}{N} \int \frac{dt}{8\pi} e^{i\omega t} \langle \rho(\vec{k}, 0) \rho(-\vec{k}, t) \rangle , \qquad (1.4)$$

relates the structure factor to $\langle \rho(\vec{k}, 0) \rho(-\vec{k}, t) \rangle$, the density-density correlation function. (Here N is the number of primitive unit cells and $\rho(\vec{k}, t)$ is the charge density at time t.) This formula is equally useful when dynamics of the system are described by quantum mechanics (and the $\langle \ \rangle$ expectation value is that of the density operators) or at finite temperature [when the (classical) atoms have thermal motion]. For a static array of classical atoms the quantity $\int d\omega S(\vec{G}, \omega) = S(\vec{G})$ is identical to the structure factor defined in Eq. 1.2.

III. Crystals and Symmetry

A. Convolution Theorem:

1. <u>Convolution</u>: take one function, f($\mathbf{r}$), and put it down at every point of a second function, g($\mathbf{r}$); f($\mathbf{r}$)*g($\mathbf{r}$). Here * is the <u>convolution operator</u>.

2. <u>Convolution Theorem</u> states: **FT** [f($\mathbf{r}$) * g($\mathbf{r}$)] = F($\mathbf{S}$) • G($\mathbf{S}$); that is, the Fourier transform of one function **convoluted** with another is the same as the Fourier transform of the first **multiplied** by the Fourier transform of the second (here we will set a convention; real space functions and their coordinant symbols are expressed in lower case, *e.g.* f, g, and $\mathbf{r}$, and their Fourier transforms and frequency space coordinants are expressed in upper case, *e.g.* F, G, and $\mathbf{S}$). The converse is also true: F($\mathbf{S}$) * G($\mathbf{S}$) = **FT** [f($\mathbf{r}$)•g($\mathbf{r}$)]. <u>So what</u>!!!

B. A crystal is a convolution of one function (a motif) with another (a lattice)

1. <u>Motif</u> is any object; *e.g.* a protein molecule, skunk etc.

2. <u>Lattice</u> -- an array of regularly spaced mathematical points

3. Lattice * Motif = Crystal

Figure 4 is an example of a 2-dimensional crystal formed by convoluting a motif with a 2-dimensional lattice. This is a small crystal owing to space limitations; normally crystals are very large in terms of numbers of unit cells and are considered to be infinite in extent. A 3-dimensional crystal would result from convolution of a motif with a 3-dimensional lattice. The <u>Unit Cell</u> of a crystal is the smallest unit from which the entire crystal can be generated by translations alone. In Fig. 4 the unit cell is a single skunk, but Figure 6 shows a more complicated unit cell.

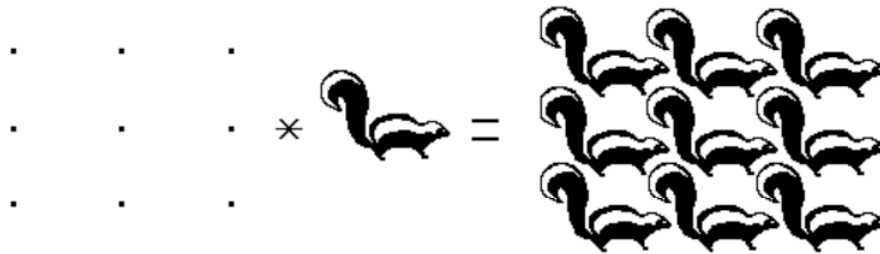Fig. 4

C. Fourier Transform of a Crystal (Diffraction Pattern)

1. FT (motif) -- a continuous function -- no sharp discontinuities

2. FT (lattice) -- another lattice with spacings which are reciprocal of those of the original lattice

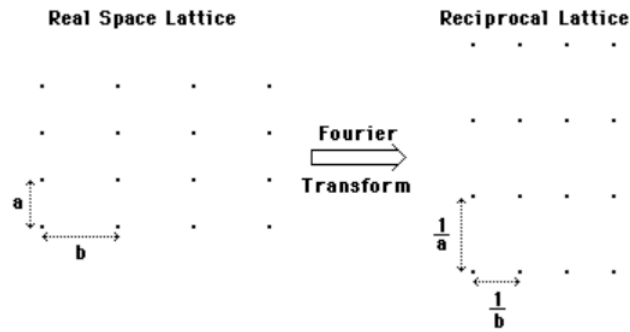**Real Space Lattice**   **Reciprocal Lattice**

Fig. 5

Note again that the coordinants of Reciprocal space are inverse distance; for example, if **a** and **b** are measured in Å, the dimensions of the reciprocal lattice, $\frac{1}{a} = \mathbf{a^*}$ and $\frac{1}{b} = \mathbf{b^*}$ will be Å-1.

3. FT(crystal) = **FT**[(motif) * (lattice)] = **FT**(motif) . **FT**(lattice) = **FT**(motif) . (Reciprocal Lattice). Thus, the continuous Fourier transform of the motif is <u>sampled</u> at the points of the Reciprocal lattice; the Fourier transform of the crystal is only non-zero at the points of the Reciprocal lattice. Examples: Fig. 17-4 from Eisenberg and Crothers.

D. Symmetry: The motif of a crystal may be symmetric and exhibit one or more types of <u>Point Group Symmetry</u> such as 2-, 3-, 4-, 5-, 6-fold rotation axes, screw rotation axes (rotation followed by translation), mirror planes, or inversion centers; biological macromolecules are inherently chiral (they contain asymmetric carbon atoms) however and cannot contain mirror planes or inversion centers.

The Crystal in Fig. 6 shows two types of symmetry in each unit cell (outlined in dashed lines). Filled ellipses show positions of 2-fold rotation axes relating upside down skunks to rightside up skunks. The second type of symmetry is shown by single-headed arrows; these indicate positions of 2-fold screw axes which relate one set of skunk dimers at the corners of the unit cell to another set of skunk dimers at the centers of the unit cell. The symmetry operation in this case is 2-fold rotation about the axis followed by translation along the axis by 1/2 of a unit cell. Different types of point groups symmetry are given symbols: 2 for a 2-fold axis and 21for a 2-fold screw axis in this example. The <u>Space Group</u> of a crystal is a set of symbols which describe the type of lattice followed by the point group symmetry of the unit cell. In Fig. 6 the Space Group is **P2₁2₁2** in which P means the lattice is primitive (as opposed to, for example, face-centered or body-centered).
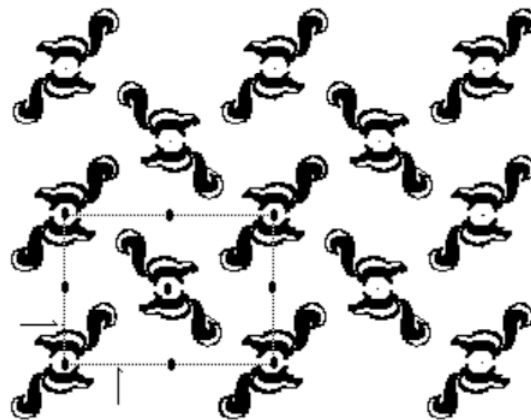
E. A Real Example: Optical Diffraction Pattern of an Electron Micrograph of a Cytochrome Oxidase Crystal

This is an electron micrograph of a flat crystal of cytochrome oxidase dimers negatively stained with uranyl acetate.
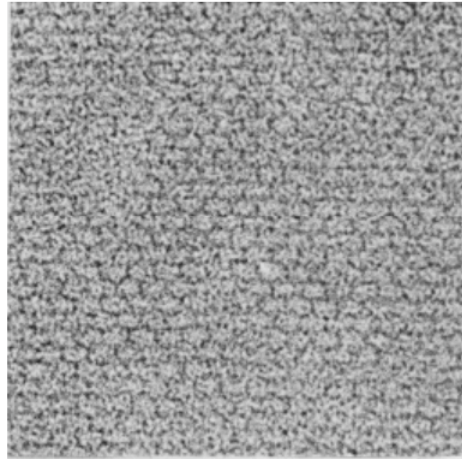
This is an Fourier Transform (actually an optical diffraction parttern) of the cytochrome oxidase crystal image shown above. Note that, except for background noise, the diffraction pattern has spots only at the points of a lattice. These spots are commonly called "Reflections, and each can be specified or indexed on the Reciprocal Lattice by specifying their inteter coordinants. Compare this "Reciprocal Lattice" with the original crystal lattice outlined in the filtered image of the crystal shown at the bottom. Note that the spacings of the real crystal latice are the reciprocal of the "Reciprocal Lattice"; i.e. in the real lattice the longest spacing is along the vertical axis (y-axis) while in the Reciprocal lattice the longest spacing is in the horizontal axis (the h-axis which corresponds to the x-axis in the crystal). Each