X-ray diffraction

Purpose

You will use diffraction techniques to determine the crystal structure of a variety of materials. In the first part of the lab, you will perform diffraction at visible optical wavelengths, using a white light source and a crystalline sample of small SiO_2 spheres, which self-assemble into a three-dimensional periodic array (a 'colloidal crystal') with a periodic length scale comparable to the wavelengths of visible light. You will use the optical diffraction to determine the crystalline structure and the lattice spacing for the structure. In the second part of the experiment, you will perform similar measurements, but using much shorter x-ray wavelengths. You will use x-ray diffraction to determine the crystal structure of several different materials, including an unusual 'mystery sample'.

Introduction

As children, we learn that gases are collections of atoms flying around with random positions and velocities, liquids are dense collections of atoms that are also moving around more or less randomly, and that solids are dense collections of atoms that have essentially fixed positions relative to their neighbors. What we are not often taught is that the experimental evidence for this atomic picture of matter is rather recent. The first direct evidence for the atomic structure of matter arguably came from x-ray diffraction experiments performed less than 100 years ago. X-ray diffraction is one of the most important techniques we know of for determining the atomic structure of materials. Max Von Laue won the Nobel Prize in 1914 "for his discovery of the diffraction of X-rays by crystals". This prize was immediately followed in 1915 with Nobel Prizes to the father and son team of Sir William Henry Bragg and William Lawrence Bragg, "for their services in the analysis of crystal structure by means of X-rays". X-ray techniques have been a source of much of our modern information on the structure of crystals and molecules. Additional Nobel Prizes for x-rays were earned by in 1924 by Karl Manne Georg Siegbahn "for his discoveries and research in the field of X-ray spectroscopy", in 1927 by Arthur Holly Compton "for his discovery of the effect named after him", and for various Nobel Prizes in other areas, such as Maurice Wilkins' prize for determining the structure of DNA or Max Perutz's for the structure of hemoglobin. Clearly, this technique is worthy of some study!

Many students in this course have already studied diffraction in the Fraunhofer experiment or the Fourier experiment in the optics section of the lab. X-ray diffraction techniques are based on the same physics as diffraction of a HeNe laser beam when it passes through a transmission grating or small slit: Electromagnetic radiation that passes through different parts of the object will constructively or destructively interfere along certain paths, leading, in the case of

constructive interference, to bright beams of diffracted radiation. However, in the case of x-ray diffraction from a crystalline solid, rather than having a simple 1-dimensional diffraction grating like the Roncchi grating, the crystal acts as a 3-dimensional diffraction grating, thus leading to rather more complicated diffraction patterns. By measuring and understanding the x-ray diffraction pattern, the crystalline structure AND the arrangement of atoms within the crystal can be determined.

Because of the complexity available in 3-dimensional periodic systems, and the associated range of diffraction patterns, the solid-state physics community has developed a language for crystal structure and the associated Fourier space. We need to be familiar with this language to make contact with the existing literature. With some practice, you can start to think in Fourier space!

The spatial structure of solids

The standard atomic view of crystalline solids is that they are composed of atoms, packed into a regular or crystalline array of positions. As you know, some solid materials fall into a structure that is very much like a 'frozen' snap-shot of a liquid, where the atomic positions do not have this regular periodicity. However, essentially all materials appear to take on crystalline structures in their equilibrium solid state.

This experimental fact that the equilibrium state of a solid material seems to require periodic spacing of the atoms, has never been adequately explained. We do not completely understand it; it remains largely a mystery. Never the less, x-ray diffraction experiments (and more recent experiments using scanning and transmission electron microscopes, field emission microscopes, tunneling microscopes, and atomic force microscopes) clearly tell us that a typical solid is actually built from periodically spaced groups of atoms.

Figure 1 shows simple 1-dimensional and 2-dimensional examples: In this figure, atoms are represented by green dots. If you sit at any particular atomic position and look out into the crystal, you see a particular periodic array of atoms extending outwards towards infinite distances. In an ideal crystal, you can sit at any atomic position and see an identical surrounding environment. In real crystals, which have some finite size, some atoms reside at or near surfaces, so that they see a very different surrounding environment, but for most of the atoms, the ideal crystalline environment is a very good approximation to reality. In Figure 1, we also show vectors that allow you to step from any one atom to any other atom in the crystal by some combination of an integer number of vector translations. These vectors and their integer combinations are referred to as Direct Lattice Vectors. The shortest direct lattice vectors, from which the various integer combinations are constructed, are referred to as Primitive Lattice Vectors.

One-dimensional lattice with parameter a

$r = u\mathbf{a}$

Two-dimensional lattice with parameters a and b
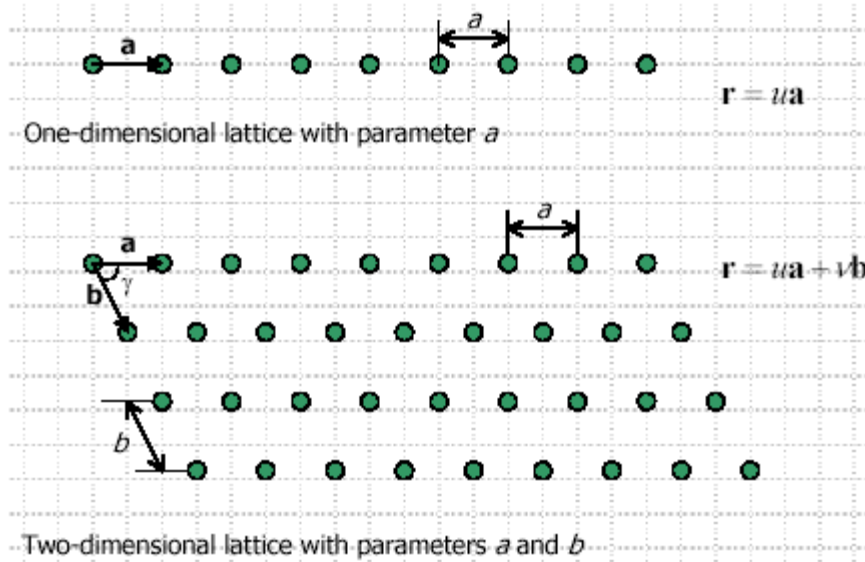
$r = u\mathbf{a} + v\mathbf{b}$

Figure 1.

In Figure 2, we show a simple cubic 3-dimensional crystal. Clearly, the number of primitive lattice vectors is equal to the number of spatial dimensions. In Figure 3, we indicate that there are many variations on the cubic lattice theme, where the three primitive vectors may be of different lengths, and may not be at right angles to each other. The infinite set of points that can be reached by all possible direct lattice vectors is called a Lattice. For example, in Figure 2, the lattice is an infinite set of points located at the corners of cubes.
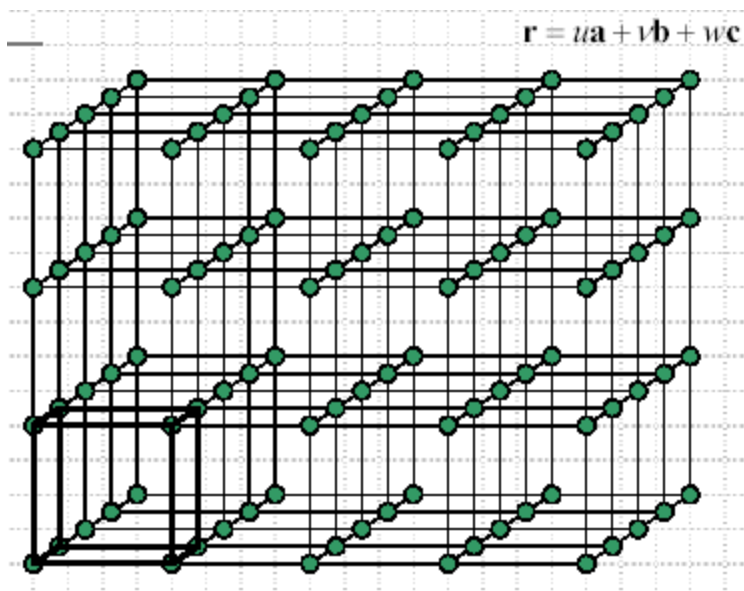

$r = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$

Figure 2.

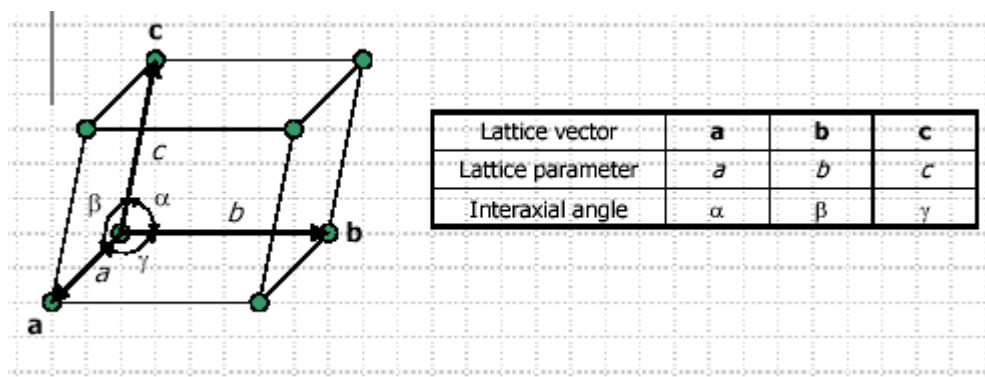| Lattice vector	a	b	c
Lattice parameter	*a*	*b*	*c*
Interaxial angle	α	β	γ

Figure 3.

In a more general crystal, rather than having a single atom at each lattice point, you could have a more complicated collection of atoms, say an entire molecule, at each lattice point. For example, many protein molecules will form crystalline solids, with one or more molecules at each lattice site. When each molecule assumes the same orientation, this arrangement is still a periodic system. The particular arrangement of atoms that sits at each lattice site is called the Basis. Any real crystal then consists of a lattice of points, with a basis of atoms at each point.

Just to add to the terminology, the basis of atoms around each lattice point can be surrounded by a small volume, shaped so that each small volume is also reproduced around each lattice point, with the sum of all these volumes filling all space. For example, you could have a small cubic volume surrounding the atoms of a simple cubic lattice. If the small cubic volume has each side of the cube have a length equal to the lattice spacing, then these cubes just fit together to fill all space. This type of volume is referred to as a Unit Cell.

Obviously, there are an infinite number of possible crystalline structures if you are prepared to call each combination of particular basis, primitive vector lengths and angles a unique object. However, if you disregard the particular physical lengths and angles, then it's also clear that lattices can fall into families. For example, any crystal where the basis sits at the corners of cubes could be classified as an example of a Simple Cubic Lattice (the first example in Figure 4.). Your might think that there are an infinite number of families. However, one of the great mathematical achievements of the 19th century, by the mathematician Bravis (pronounced 'bra-vey'), was to prove that there are actually only 14 distinct lattice families in 3-dimensional space. Figure 4 shows the 14 Bravis Lattices.
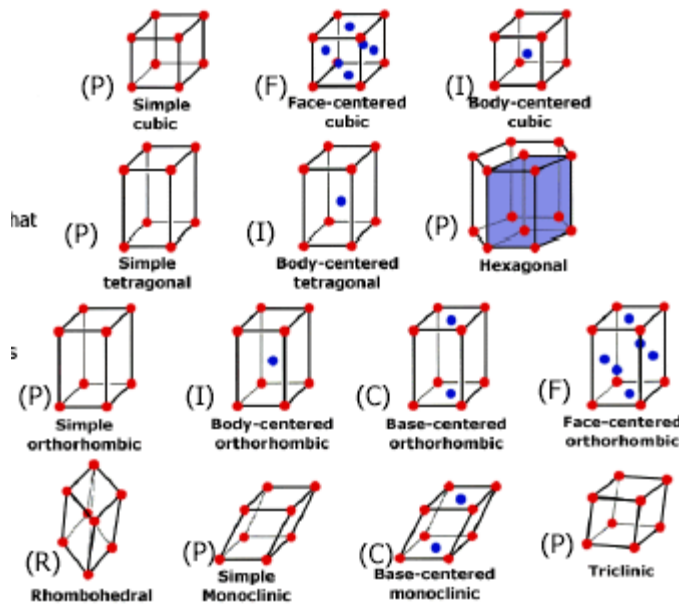
Figure 4.

The first row of Figure 4 shows the three possible cubic lattices, the simple cubic (sc), face centered cubic (fcc), and the body centered cubic (bcc). The simple cubic structure is very rare in nature, but the bcc and fcc structures are very common. Together, bcc and fcc crystalline structures account for the majority of structures taken on by the elements. If you include the diamond structure, and the hexagonal, you have covered essentially all of the crystal structures taken on by the elements. Notice that 'diamond' is not one of the structures listed. The crystal structure of diamond (carbon) is actually an fcc lattice, but with a pair of carbon atoms as the basis.

The job of x-ray and other diffraction techniques is to take some material and determine the specific atomic structure. Given that crystals have such a nice periodic structure, you can imagine that the diffraction pattern might tell you a great deal about the lattice spacing. In the next sections, we discuss the details.

The reciprocal lattice

All the physical properties of a crystal, say the charge density, must be periodic functions, which repeat at each lattice site. This requirement of periodicity of any function on a Bravis Lattice is important and leads us to consider an additional set of vectors referred to as the Reciprocal Lattice Vectors. Consider for example, the charge density at some location in the crystal. The charge density arises from the electronic and nuclear charges of the atoms. Because of the periodicity of the crystal, the charge density at any particular location must be equal to the charge density at any other location that is different by a direct lattice vector. Therefore:

$$\rho(\vec{r}) = \rho\left(\vec{r} + \vec{R}\right)$$

where R is a direct lattice vector. Since the charge density (or any other local physical property) is a periodic function, we can profitably consider its Fourier transform:

$$\rho(\vec{r}) = \sum_{\vec{q}} \rho_{\vec{q}} \exp\left(i\vec{q} \cdot \vec{r}\right)$$

or

$$\rho(\vec{r} + \vec{R}) = \sum_{\vec{q}} \rho_{\vec{q}} \exp\left(i\vec{q} \cdot \vec{r}\right)\exp\left(i\vec{q} \cdot \vec{R}\right)$$

Since these equations must be equal for periodic charge density, we must require that:

$$\exp\left(i\vec{q} \cdot \vec{R}\right) = 1$$

In other words, only certain special wave vectors are required to build the periodic function. You're not surprised by this result: You already know for 1-dimensional functions that are periodic over some finite wavelength you only need the sine and cosine functions with regular multiples of the given wavelength. Now you can see that the same type of restriction on the 3-dimensional sines and cosines will also hold.

In detail, recall that the direct lattice vector is a combination of integer numbers of primitive lattice vectors. Therefore, we can rewrite the restriction on the Fourier components in a new way:

$$\exp\left(i\vec{q} \cdot \vec{R}\right) = 1$$
becomes
$$\exp\left(i\vec{q} \bullet \left(n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3\right)\right)$$
OR
$$\vec{q} \bullet \left(n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3\right) = 2\pi m$$

where m is an integer.

We define three new vectors of the form:

$$\vec{b}_i = 2\pi \frac{\vec{a}_j \times \vec{a}_k}{\vec{a}_i \cdot \left(\vec{a}_j \times \vec{a}_k\right)}$$

so that

$$\vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$$

Then, we can expand the q in terms of these basis vectors and immediately see that we get the desired result.

$$\vec{q} \cdot \vec{R} = 2\pi m$$

The set of vectors b are referred to as the Reciprocal Lattice Vectors. Notice that each reciprocal lattice vector has the dimensions of inverse length, so that the dot product of a reciprocal lattice vector with a direct lattice vector is dimensionless. The reciprocal lattice vectors also form a Bravis Lattice (now a lattice in the space of wave vectors)! These reciprocal lattice vectors are the full set of wave-vectors that you need to build the Fourier representation of the periodic crystal charge density. X-ray diffraction directly measures these reciprocal lattice vectors. Once you know all the Fourier components, you can add them up to get back the spatial structure of the crystal. THAT'S how x-ray diffraction works.

Diffraction techniques: The Bragg approach

Now let's see directly how x-ray diffraction actually measures the reciprocal lattice vectors. We imagine applying a monochromatic incident field and looking for scattered radiation as in Figure 5:
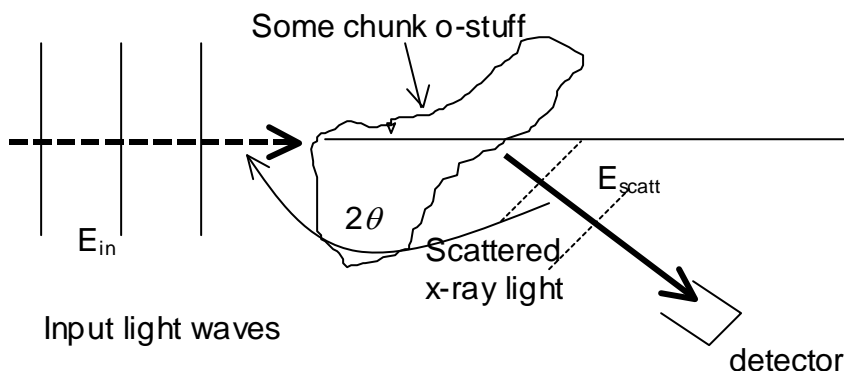

Figure 5. X-ray diffraction geometry.

Bragg Law

A typical textbook explanation of x-ray diffraction (see Kittel) begins by considering the sheets of atoms in the solid as reflective planes and gives the traditional Bragg interpretation of constructive interference requirements for the reflected wave. This argument yields the Bragg law:

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

Go look it up if you like. The Bragg Law is great in its own way, but the physical picture of the system is rather poor. Further, it completely misses the systematic importance of the reciprocal lattice, so you miss the chance to see how to fully reconstruct the crystalline structure. Bummer, so let's do a more general treatment.

Diffraction techniques: Von Laue approach

The scattered field depends on the input x-rays and the interaction of these waves with the solid. Since the input field varies rapidly with time, we expect it interacts most strongly with the electrons. After all, it's the electrons that are light enough to be able to respond quickly to the electric field of the x-rays. Recall from electrodynamics that matter responds to electromagnetic fields by setting up a dipole moment per unit volume, or polarization. Without worrying too much about the details, we expect that the polarization will be related to the strength of the incident electric field and to the local charge density. Thus, we expect an induced polarization of the form:

$$\vec{P} = A\vec{E}_{in}\rho(\vec{r},t)$$

The strength of the scattered wave is directly related to the polarization since it is the motion of the electrons which radiates the scattered field. The radiated piece is basically proportional to the polarization so that:

$$\vec{E}_{out} \propto \vec{P}$$

Break the output wave into its Fourier components. With the reasoning above, we expect the components of the scattered wave to be:

$$\vec{E}_{out}\left(\vec{k},\omega\right) = B\int d\vec{r}\int dt e^{(ik\cdot r - i\omega t)}\vec{E}_{in}\rho\left(\vec{r},t\right)$$
$$= B\vec{E}_0\int d\vec{r}\int dt e^{(i(k-k_0)\cdot r - i(\omega-\omega_0)t)}\rho\left(\vec{r},t\right)$$

In the second line, we have assumed that the incident wave has a single frequency (monochromatic radiation) and a single wavelength. We define two quantities:

$(k - k_0) = K \rightarrow$ Momentum transfer

$(\omega - \omega_0) = \Omega \rightarrow$ Energy transfer

Let's consider the result so far. If the charge dist. is static in time, then the time integral is a delta function i.e., if the charge density does not move, then the frequency of the scattered wave must be equal to the frequency of the incident wave. Another way to say it is that the energy of the scattered photons is the same as the energy of the incident photons. In this case, we refer to the scattering as elastic. We've just learned another important thing: If the charge density DOES move, it's possible for the incident beam to transfer energy to the material and the scattered beam can then leave with less energy (or more energy if the material gives energy back to the photon) per photon. In other words, energy transfer occurs due to internal motions. Cool!

For now, we proceed by considering static charge dist. so that scattering is elastic. Under this condition, we also require the magnitude of k be the same as the incident wave due to the fact that ω does not change and

$$k = \frac{\omega}{c}$$

Then,

$$\vec{E}_{scatt} \propto \delta\left(\Omega\right)\int d\vec{r} e^{(i\vec{K}\cdot\vec{r})}\rho\left(\vec{r}\right)$$

This is an important intermediate result. It says that the scattered wave at some momentum transfer, K, is proportional to the Fourier component of the charge density at that particular K.

OK, now if you are dealing with a crystal, the charge density is known to be a periodic function. In other words, IT ONLY HAS FOURIER COMPONENTS AT THE RECIPROCAL LATTICE VECTORS. In other words, you're not going to see any scattered radiation unless you choose a combination of input and scattered k-vectors so that K happens to be a vector of the reciprocal lattice. This result is referred to as the Laue condition for scattering:

$$\vec{K} \equiv \left(\vec{k} - \vec{k}_0 \right) = \vec{q}$$

Where q must be one of the reciprocal lattice vectors, or you don't get any scattering.

To see it mathematically, since we are dealing with a periodic structure, think about breaking up the integral over all space in the scattered wave. You can convert the integral over all space into an integral over the unit cell, and then add all the unit cells (which are identical) over all the direct lattice vectors. Then the integral is a sum of integrals only over the unit cell i.e. if we decompose position into u+R, then

$$\vec{E}_{scatt} = AE_0 \delta(\Omega) \sum_R \left[\int_{uc} d\vec{u}\, \rho(\vec{u}) e^{iK \cdot u} \right] e^{iK \cdot R}$$
$$= AE_0 \delta(\Omega) \sum_R \hat{\rho}(K) e^{iK \cdot R}$$

In the second line, we have defined the Fourier integral of the charge density over a single unit cell. This quantity is referred to as the Structure Factor. OK, ok,… lots of language. But here's the point: The result above says that the scattered wave is determined by adding up all the terms in the sum over the direct lattice vectors. If K is some arbitrary k-vector, then some of the terms will be positive and some will be negative as the various sine and cosine contributions oscillate around. However, if K is special, say equal to a reciprocal lattice vector, then all the sine and cosine terms are of the same size BECAUSE THEN,

$$\underline{\exp\left(i\vec{K} \cdot \vec{R} \right) = 1}$$

Again, we see that the scattered wave is going to be large only if you choose input and output wave vectors so that their difference is a reciprocal lattice vector.

This result yields the Bragg condition. To see how, we insist that the momentum transfer is equal to a reciprocal lattice vector:

$$\left(\vec{k} - \vec{k}_0 \right) = \vec{q}$$

Take the dot product of each side with itself:

$$\left(k^2 - 2k \bullet k_0 + k_0^2 \right) = q^2$$

Recall the relationship between the k-vector of an electromagnetic wave and its wavelength AND that the incident and scattered wave must have the same wavelength for elastic scattering and you find:

$$\left(\frac{2\pi}{\lambda}\right)^2 (1 - 2\cos 2\theta + 1) = q^2$$

Next, recall that the reciprocal lattice vectors are integer multiples of the b-vectors, which are inversely related to the primitive lattice spacing. Then, you can write the result as:

$$2\left(\frac{2\pi}{\lambda}\right)^2 (1 - \cos 2\theta) = \left(\frac{2\pi m}{d}\right)^2$$

Now take the square root and do some minor trigonometry to find the Bragg condition:

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

Excellent! However, the most important point to take away is that the scattered radiation will only be strong when the combination of incident and scattered wave vectors is just a reciprocal lattice vector. If you measure all the directions of strong scattering (all the diffraction peaks) then you are measuring all the Fourier components of the charge density. Add them up and you get the spatial structure of the atomic system!

Outline of the Experiment

1. Safety Training
   - Go to the EH&S website at http://www.colorado.edu/EHandS/hpl/ and take the Radiation Safety Test. You need to have passed this test before you can use the x-ray diffraction lab.

2. Colloidal Crystal diffraction and structure determination
   - Find the various samples of colloidal crystal
   - Setup an optical monochrometer using a white light source (a light bulb) and one of the laboratory grating monochrometers.
   - Verify that the output of the monochrometer provides tunable colors of light.
   - Align the light to shine on the colloidal crystal sample. Choose an incident angle and a scattered angle for observation. Determine the wavelengths of the strongly scattered colors. Use them along with the known diffraction angles that you selected, to determine the crystal structure and lattice constants of the colloidal crystals.

3. X-ray powder patterns.
   - Learn how to use the x-ray diffraction system to do variable angle, single x-ray wavelength studies.
   - Determine the crystal structure of silicon, germanium, and the mystery sample by analyzing the diffraction from power samples.

References

1. X-Ray Diffraction: A practical approach, by C Suryanarayana and M. Grant Norton, Plenum (1998).

2. Solid State Physics, by N. W Ashcroft and N. David Mermin, Holt Rinehart Winston (1976).

3. Introduction to Solid State Physics (7th Ed.), by Charles Kittel, Wiley (1996).

4. Stanford University X-ray diffraction course

Problems

1. <u>Determine the reciprocal lattice for simple cubic (sc), body centered cubic (bcc), and face centered cubic (fcc) crystals</u>. Referring to Figure 4, of the 14 Bravis lattices, three are cubic structures (shown in the first row). In this problem, your goal is to define a set of direct lattice vectors, use them to calculate the primitive reciprocal lattice vectors, and then visualize what the reciprocal lattice looks like.

    - Draw a portion of a simple cubic lattice. Draw your choice of three primitive direct lattice vectors that will allow you to reach all lattice points. Calculate the associated *b*-vectors, which are the primitive vectors of the reciprocal lattice. Show that the reciprocal lattice is a simple cubic lattice in k-space.

    - Draw a portion of a bcc lattice. Draw your choice of three primitive direct lattice vectors. Calculate the primitive reciprocal lattice vectors. Show that the reciprocal lattice is a face centered cubic lattice in k-space!

    - Repeat the process for the fcc direct lattice. Show your primitive direct lattice vectors, Calculate the reciprocal lattice vectors. Show that the reciprocal lattice is a body centered cubic in k-space.

    In the first part, you are showing that the Fourier transform of a cubic set of points is another cubic set of points in k-space. In the last two parts, you basically show that the fcc and bcc lattices are Fourier transforms of each other. This result is important and useful.

2. <u>Scattering from colloidal crystals</u>. Assume that the colloidal crystal is a simple cubic lattice of 1 micron spheres, packed together so that the spheres are just touching.

    - The shortest reciprocal lattice vectors take you from a point on the reciprocal lattice to one of the neighboring points in the kx-, ky-, or kz-directions on the lattice. There are six nearest neighbor points, corresponding to +/-1 integer translation by one of the *b*-vectors. Thus, there are six of these shortest reciprocal lattice vectors. List the magnitude of these vectors for the assumed colloidal crystal. Then, list the magnitude of the next longest family of reciprocal lattice vectors AND the length of the third longest family.

    - Assume that you use a scattering geometry as in Figure 5, with $2\theta = 2\pi$ i.e., direct backscattering. Use the Laue condition to determine the wavelength of light that would be scattered for the three families of reciprocal lattice vectors you just determined.

3. <u>Angular measurements</u>. Suppose that you only have a single wavelength of light to work with. Assume a wavelength of 250 nm. Calculate the angles where you would expect to see strong scattered light for the assumed simple cubic colloidal crystal.

Technical Details of the Experiment

1.   Colloidal Crystals

2.   Optical monochrometer

3.   X-ray diffraction system

4.   Analysis of powder patterns