

Materials Research with Synchrotron Radiation
A short introduction to modern X-ray science

Preface

This booklet is meant to be a quick route to learning about modern X-ray science. It is based on the original idea of Prof. Jens Als-Nielsen and Prof. Friso van der Veen to establishing a training course at the Swiss Light Source for students, so that they can get hands-on experience about many of the basic features of X-ray science as it is carried out at a synchrotron X-ray facility. During a 6 week stay at Paul Scherrer Institute in the spring of 2009, Prof. Jens Als-Nielsen and the staff at the X05 beam line put most of the course together, resulting in a booklet, which we have revisited and updated to better suit the scope of the course on Materials Research with Synchrotron Radiation currently held by Prof. L. J. Heyderman.

All of the technical descriptions can be found on the Swiss Light Source homepage, whereas the present booklet gives the background for the exercises, including how the student should prepare herself/himself for the practical part of the course.

The data from the exercises are included, and from the Internet link henke.lbl.gov/optical_constants/ you can in fact simulate many of these data.

Introduction

The practical part of the course Materials Research with Synchrotron Radiation consists of two days that you will spend at the Optics Beamline (X05) at the Swiss Light Source at the Paul Scherrer Institute in Villigen.

You will perform the following experiment:

- Scattering from water and ice

In the following you will find general information on the interaction of X-ray with matter and specific information on how to perform the above experiment.

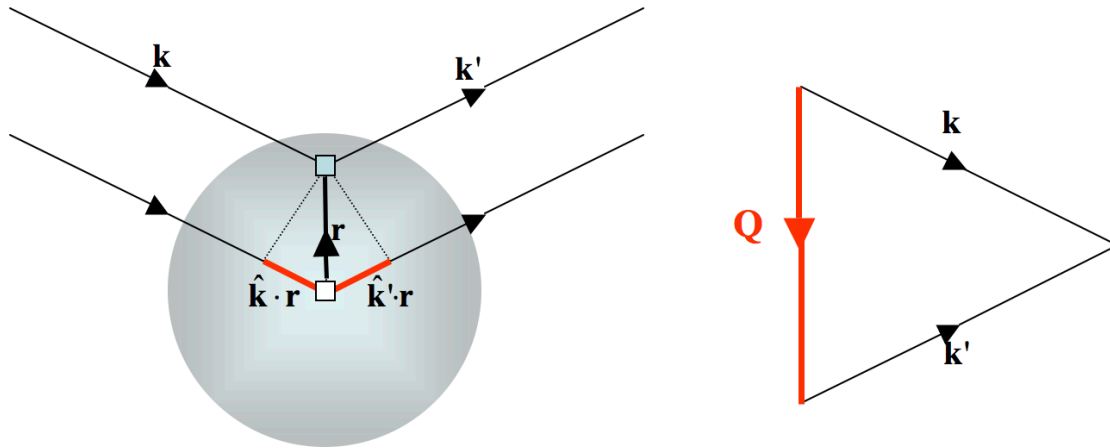
Experiment : Scattering from water and ice

Before looking in detail at the practical steps of the experiment, let us recall a few more concepts about X-ray interactions, and the differences between solid and liquid samples.

Atomic and molecular form factors

The scattering cross section from an atom with Z electrons is *not* just $Z r_0^2$, because the electrons in an atom do not scatter independently of each other as they do in an electron gas. Furthermore, it is *not* $(Z r_0)^2$ since all the electrons do not scatter in phase because the size of the atom is comparable to the X-ray wavelength.

The simplest model of the atom for the purpose here is just an electron cloud with the electron density $\rho(\mathbf{r})$, normalized so that $Z = \int \rho(\mathbf{r}) d^3\mathbf{r}$. We then have to add the amplitudes of scattered waves from different volume elements in the electron cloud.



The wavevectors of the incident and the scattered beam are \mathbf{k} and \mathbf{k}' , respectively. The difference is the scattering vector $\mathbf{Q} = \mathbf{k} - \mathbf{k}'$. The two volume elements, represented by white and blue coloured squares separated by the vector \mathbf{r} , do not scatter in phase. The incident ray hits the white volume element later than it hits blue volume element. The path length difference is \mathbf{r} projected onto \mathbf{k} , i.e. $\hat{\mathbf{k}} \cdot \mathbf{r}$, where the superscript “hat” indicates a unit vector. The phase difference is 2π times the ratio of the path length difference to the wavelength, i.e. it is simply $\mathbf{k} \cdot \mathbf{r}$. Similarly for the scattered wave: the scattered wavelet from the blue element is ahead of that from the white element, the phase difference being $\mathbf{k}' \cdot \mathbf{r}$. Note that in the drawing $\mathbf{k} \cdot \mathbf{r}$ is negative, but $\mathbf{k}' \cdot \mathbf{r}$ is positive, so the total phase difference is $(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r} = \mathbf{Q} \cdot \mathbf{r}$. The net result is that the

scattering length from the entire electron cloud is $A(\mathbf{Q}) = \int r_0(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}} d^3\mathbf{r}$. In units of (r_0) , the scattered amplitude is just the Fourier transform of the electron density, which is also called the *atomic form factor*.

$$f^0(\mathbf{Q}) = \int r_0(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}} d^3\mathbf{r}$$

In the small angle limit, $\mathbf{Q} \rightarrow 0$, the atomic form factor approaches Z , the atomic number. For reference values, see International Tables of Crystallography and Table 4.1 in “*Elements of Modern X-Ray Physics*”.

However, when the X-ray photon energy is close to an absorption edge in the atom, the cloud density model of the atom turns out to be too simple. In that case the phase shift is no longer exactly 180° and also the modulus of the atomic form factor is changed. This is written as the following:

$$f(\mathbf{Q}, E) = f^0(\mathbf{Q}) + f'(E) + if''(E)$$

where f' and f'' are known as the dispersion corrections to f^0 . A convenient link for getting the energy dependence of atomic scattering factors at $\mathbf{Q}=0$ is http://henke.lbl.gov/optical_constants. In some cases they show a simple but dramatic effect of the dispersion corrections.

2. Molecules

The scattering length of a molecule composed of atoms with atomic form factors f_j and situated at positions \mathbf{r}_j is

$$f_{mol}(\mathbf{Q}) = \sum_j f_j(Q) e^{i\mathbf{Q}\cdot\mathbf{r}_j}$$

However, in trying to measure the *molecular* scattering length from a gas there is a complication compared to the monoatomic gas. The molecule, in contrast to an atom, is not isotropic. Therefore the angle between the scattering vector \mathbf{Q} and an axis in the molecule varies from molecule to the molecule in the gas, and one has to carry out an orientational average procedure. Let's consider the simplest case, a linear molecule of two atoms. The scattering amplitude from the two atoms separated by \mathbf{r} is $A^{(2)}(\mathbf{Q}) = f_1 + f_2 e^{i\mathbf{Q}\cdot\mathbf{r}}$, and the intensity for a particular orientation of the molecule is

$I^{(2)} = |f_1|^2 + |f_2|^2 + 2f_1f_2e^{i\mathbf{Q}\cdot\mathbf{r}}$. Therefore, the scattering length of the molecule, averaged over all possible orientations, is given by $\langle e^{i\mathbf{Q}\cdot\mathbf{r}} \rangle_{\text{orient.av.}}$:

$$\langle e^{i\mathbf{Q}\cdot\mathbf{r}} \rangle = \frac{\iint e^{i\mathbf{Q}\cdot\mathbf{r}} \sin \theta d\theta d\varphi}{\iint \sin \theta d\theta d\varphi} = \text{sinc}(Qr)$$

One can then generalize to the case of N atoms in the molecule, with the distance between atom i and j being denoted r_{ij} . Letting $x_{ij} = Q r_{ij}$, we have the result:

$$\begin{aligned} I_{\text{orient.av.}}^{(N)} = & |f_1|^2 + |f_2|^2 + \dots + |f_N|^2 \\ & + 2f_1f_2\text{sinc}(x_{12}) + 2f_1f_3\text{sinc}(x_{13}) + \dots + 2f_1f_N\text{sinc}(x_{1N}) \\ & + 2f_2f_3\text{sinc}(x_{23}) + \dots + 2f_2f_N\text{sinc}(x_{2N}) \\ & + \dots + 2f_{N-1}f_N\text{sinc}(x_{N-1,N}) \end{aligned}$$

This general result, obtained by Debye in 1915, can be illustrated for the CF_4 molecule (The C-F bond length is 1.38 Å). There are 5 atoms, but the four Fluorine atoms are identical and have the same mutual distance r_{FF} , whereas the distance from the central Carbon atom to any of the F atoms is r_{FC} .

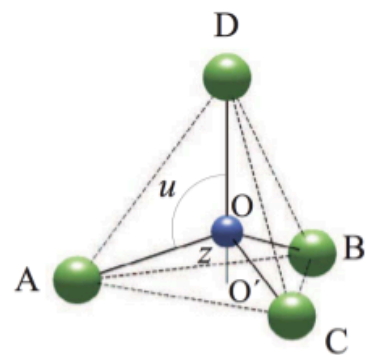
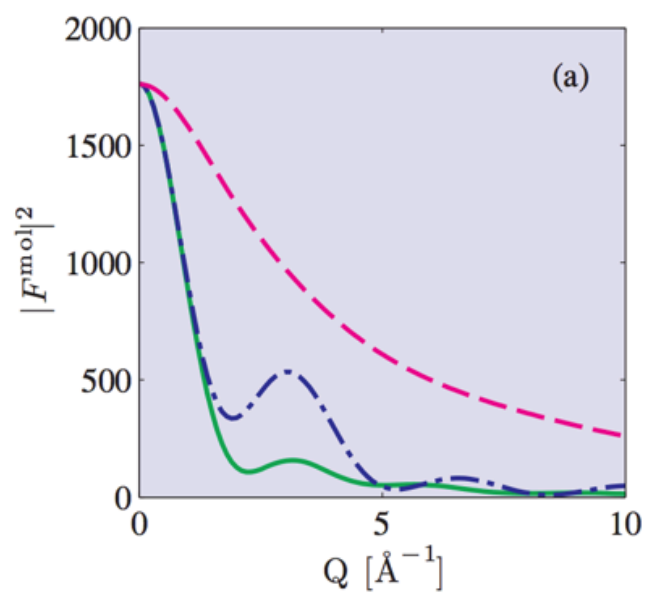
Problem 3. Show that the tetragonal structure implies $r_{FF} = \sqrt{8/3} r_{CF}$

One therefore gets

$$\begin{aligned} I_{\text{orient.av.}}^{(N)} = & |f_C|^2 + 4|f_F|^2 \\ & + 12f_Ff_F\text{sinc}(\sqrt{8/3} x) + 8f_Ff_C\text{sinc}(x) \end{aligned}$$

where $x = Q r_{CF}$.

In the figure below we illustrate the difference between the molecular form factor for a fixed orientation of the CF_4 relative to the scattering vector \mathbf{Q} (dashed-dotted blue line), and the orientational averaged form factor (solid green line). Although the oscillations are to some extent washed out by the orientational averaging it is still possible to determine the CF bond length from the gas scattering experiment.



3. Crystals

To complete the discussion of adding the scattering from different entities, we shall also here consider the diffraction from crystals, i.e. samples that contain a macroscopic number of molecules. The key feature of a crystal is that a basic, microscopic structure called the *unit cell* is repeated a macroscopic number of times on a lattice. The lattice points are represented by lattice vectors $\mathbf{R}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, where \mathbf{a}_i are the primitive lattice vectors and n_j are integer numbers. Any lattice point can be defined by n_j , i.e. an integer sum of these lattice vectors. A crystal is made up of many “unit cells”, which are the basic building block of the crystal, and are repeated at each lattice point. The unit cell consists of ν atoms at positions \mathbf{r}_j with scattering amplitude $f_j(\mathbf{Q})$ and its scattering

amplitude is $f_{u.c.}(\mathbf{Q}) = \sum_{j=1} f_j(\mathbf{Q}) e^{i\mathbf{Q}\cdot\mathbf{r}_j}$. The total scattering amplitude of the crystal is therefore found by summing up over the lattice points:

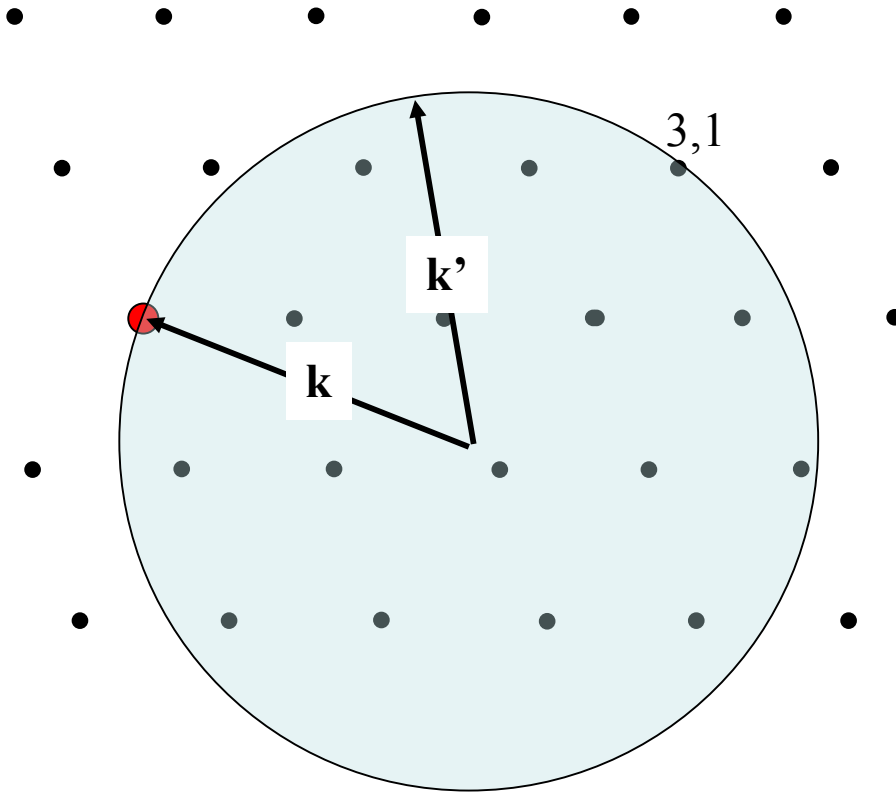
$$A_{crystal}(\mathbf{Q}) = f_{u.c.}(\mathbf{Q}) \sum_{\mathbf{n}}^N e^{i\mathbf{Q}\cdot\mathbf{R}_n}$$

The sum in this equation, a lattice sum, encompasses a macroscopic number of terms, which are all complex numbers distributed on the unit circle in the complex plane. In general they will tend to cancel each other, *unless* $\mathbf{Q}\cdot\mathbf{R}_n$ magically happens to be a multiple of 2π for all \mathbf{R}_n . In that case the lattice sum is simply N . The “magic” condition is that $\mathbf{Q}=\mathbf{G}_h$, a lattice vector in reciprocal space that is defined by reciprocal lattice vectors \mathbf{a}_j^* analogous to the lattice vectors for the crystal in real space. The reciprocal lattice vectors are defined by $\mathbf{a}_1^* = 2\pi(\mathbf{a}_2 \times \mathbf{a}_3)/V$, and the two other corresponding cyclic relations, where $V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$ is the unit cell volume. Therefore we have the reciprocal lattice vectors $\mathbf{G}_h = h_1\mathbf{a}_1^* + h_2\mathbf{a}_2^* + h_3\mathbf{a}_3^*$.

A crystal acts as an *amplifier* of the unit cell scattering amplitude. The amplifier gain is enormous, N , but works only when the scattering vector coincides with a reciprocal lattice vector. This is known as Bragg reflection.

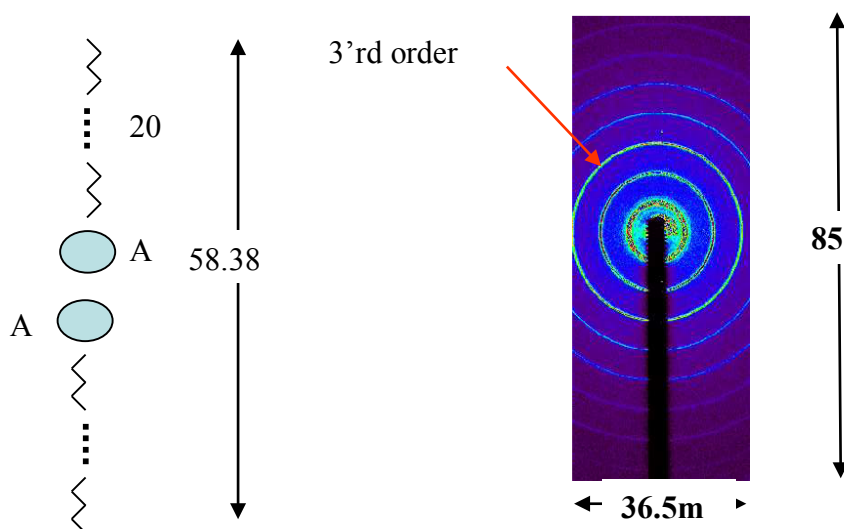
Ewald sphere

The mathematical formulation of a Bragg reflection, where $\mathbf{Q} = \mathbf{G}_h$, may be better understood by a picture, the Ewald sphere. The idea is that the spectrometer is set at a particular incident monochromatic energy, or wavevector \mathbf{k} , and the detector can be set at any scattering angle 2θ . The scattering is elastic, so the scattered wavevector \mathbf{k}' will be on a sphere with radius $|\mathbf{k}|$ which is called the Ewald sphere. The reciprocal lattice is associated with the sample, so by mechanically rotating the sample around several axes one can rotate the reciprocal lattice around so that a given reciprocal lattice vector \mathbf{G}_h lands on the Ewald sphere. This is illustrated in the figure below, for the sake of simplicity in only two dimensions. The reciprocal lattice points are indicated by black spots, except for the origin, which is red. In the figure, the (3,1) reflection appears to be on the Ewald sphere. Note that the Ewald sphere has a certain shell thickness, which is the energy bandwidth of the monochromator. A typical bandwidth is of order 10^{-4} for a Si monochromator crystal, but 10^{-2} for a multilayer monochromator.



Powder diffraction.

Whilst for a single crystal sample, the orientation has to be chosen carefully in order to scatter off a Bragg reflection, a powder sample has a large number, maybe of order millions, of small single crystals with random orientations. This means that for any sample orientation some, maybe thousands, of these crystals will be oriented for (h,k,l) Bragg reflection, i.e. the glancing angle from the incident beam to the lattice planes happens to be the Bragg angle fulfilling $\sin 2\theta = 2d_{hkl} \sin \theta$. These Bragg reflected beams will be incident on a flat detector at distance L in a circle (the Debye-Scherrer circle) with a radius R given by $\tan 2\theta = R/L$. Another set of Miller indices (h,k,l) yields a different d-spacing, i.e. a different scattering angle, and thus yields a different circle on the detector. An example is shown below for the organic salt AgBehenate. The crystal unit cell of AgBehenate has one very long dimension (about 6 nm) due the length of the hydrocarbon chain of behenic acid, whereas the hydrocarbon chains pack laterally with a spacing of around 0.5 nm. The innermost Bragg reflections will therefore be concentric circles of equidistant radii. The figure below show an experimental diffraction pattern recorded with an area detector. One can immediately identify, for example, the 3rd order ring.



Problem 1: Find the Bragg angle and the Debye-Scherrer radius for the (0,0,) reflections for $n=1,2,3,4$ using the following data:

AgBehenate , $d=58.38 \text{ Ang}$ @ $10 \text{ keV}=1.24 \text{ \AA}$.

Sample-detector distance = 250 mm

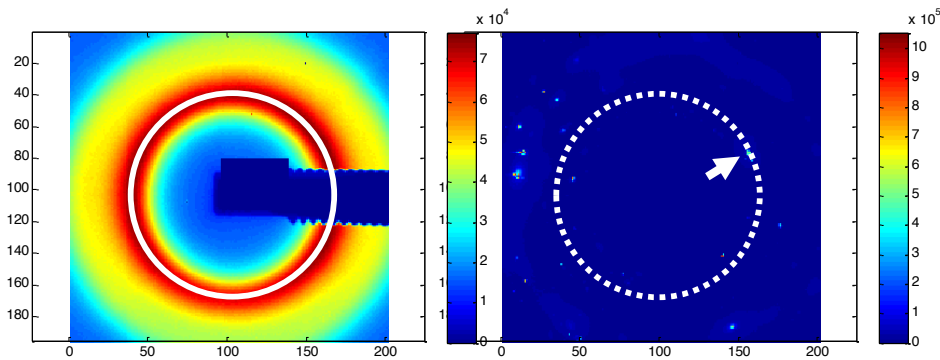
$4\theta \approx 32/250$ or $\theta=32 \text{ mrad}$;

$n\lambda = 2d \sin \theta \rightarrow n = (2 * 58.38 * 0.032 / 1.24) \rightarrow n \sim 3$

Problem 2: From the link henke.lbl.gov/optical_constants find the transmission of 1mm water at 10 keV.

Diffraction from water/ice

In our experiment we will use a Eiger area detector, with a pixel size of $75 \mu\text{m}$. The Eiger detector will first be used to acquire diffraction images from a liquid sample, in the present case simply water. A water drop is hanging from a thin capillary by virtue of the surface tension. The diameter of the drop is larger than the X-ray beam, so it provides a window-less sample. The figure below on the left shows an example of a typical diffraction pattern from water. Subsequently, one can blow cold nitrogen gas onto the water drop so that it freezes to ice. The ice is actually a powder of crystallites, albeit with much fewer crystals than the AgBehenate sample, and you observe the Bragg spots on the Eiger detector. An example of a typical diffraction picture is shown in the right figure below.



15 keV, 40 mm distance, water

**Same, but frozen to ice
(NB colorbar up by 10x)**