

PHYS-E0411 Advanced Physics Laboratory  
Photonic bandgap materials

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# 1 Introduction

Various optical phenomena are caused by scattering of light: for example the blue colour of the sky, the white colour of milk and the colours of a rainbow. The colour of the sky is due to light scattering from air molecules, whose size is much smaller than the wavelength of light. These small particles scatter light in all directions, but the amount of scattering is larger for shorter wavelengths, which means that blue light is scattered the most. The light coming from the sky is normally scattered, which is why sky has a blue colour. The behavior is described by Rayleigh scattering.[1] Milk is white, because it consists of colloidal particles, whose size is of the order of the wavelength of light. Scattering from such particles can be understood by examining the Mie solution to Maxwell's equations.[1] In general, particles whose size is larger than the wavelength of light, scatter light in all directions almost equally. That is why colloidal dispersions such as milk or paint look white. The colour of a rainbow is caused by dispersion of light from rain drops. The wavelength of incident light determines to which angle it is refracted to. Shorter wavelengths get refracted to smaller angles, which causes the spectrum of light being displayed on a rainbow.

Photonic bandgaps occur in materials where the structure of the material causes constructive and destructive interference of the scattered light. Scattering accompanied with interference behaviour is called diffraction. Some examples of photonic bandgap (PBG) materials found in nature are the vivid colours of the eye in a peacock feather, the green iridescent colour of certain beetles, the blue colour of certain butterflies and the colours of the mineral opal (see Fig. 1).[2, 3] Usually colours are caused by molecules, which absorb light, but these "structural colours" are caused by forbidden solutions of the Maxwell's equations. In all of the examples above, the colour displayed is caused by destructive and constructive interference taking place from an ordered, periodic structure and not by absorption of light. These structural colours are usually highly angle dependent and they often exhibit a metallic glow.

## 1.1 Photonic crystals and semiconductors

The main feature of PBG materials is the periodic modulation of refractive index along one, two or three directions of space. If the scattering centers are regularly arranged in a medium, light is coherently scattered. In this case, interference will

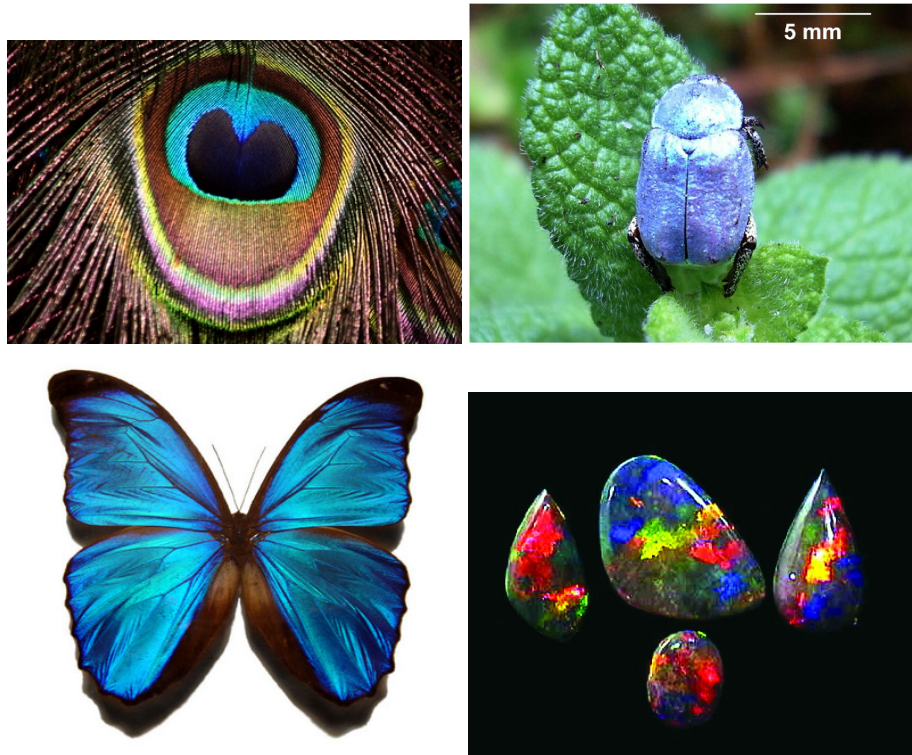


Figure 1: Many colours in nature are caused by photonic bandgaps. Examples of these are the eye in a peacock feather, shells of certain beetles, the wings of the Blue Morpho butterfly, and the mineral opal.

eventually cause that some frequencies will not be allowed to propagate, giving rise to forbidden and allowed bands. What is more, by introducing defects in the PBG materials, we can introduce allowed energy levels in the gap in analog to doping of semiconductors with impurities.[4] All these facts permit to establish a parallelism between the formalism used for electrons in ordinary crystals and that for photons in PBG materials.

Fig. 2 shows examples of band structures for semiconductor and for a photonic crystal. For semiconductors, there is a gap between certain energy levels, which is marked white in the figure. This is called the electronic band gap and it is what gives semiconductors their unique properties. Electrons with certain energies are not allowed to propagate through the structure.

The figure on the bottom in Fig. 2 is a band structure for a fictional photonic crystal. A frequency ( $\omega$ ) range where there exists no bands spreads out through the entire x-axis. This is called a photonic band gap and it is marked white in the figure. The band structure is similar to the electronic band structure of the semiconductor. Comparing the electronic and photonic band structures, it is

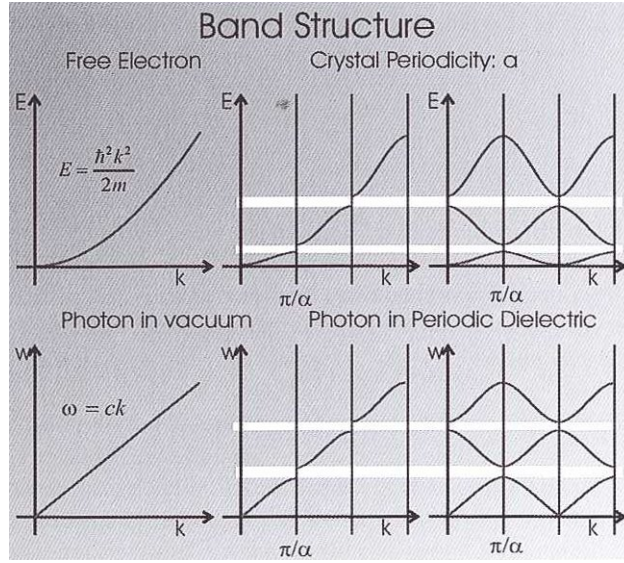


Figure 2: Examples of band diagrams for free electrons and electrons confined in a crystal lattice (top) and for photons in vacuum and in a periodic dielectric. [5]

easy to understand why PBG materials are sometimes called semiconductors of light.

In figure 3, it is shown how the calculated energy band gap is related to the measured optical response in reflectance, transmittance and diffuse intensity in an artificial opal -type PBG structure.

## 1.2 Artificial opals

Spherical particles of the same size can spontaneously self-assemble into well-ordered crystalline materials. They form lattices of spheres that are arranged in a cubic close packed structure. The structure resembles that of the mineral opal. Such a material behaves as a Bragg reflector and is a three-dimensional photonic bandgap material or a *photonic crystal*. It reflects light of a specific wavelength. In other words, it behaves as a mirror for a narrow wavelength range but is like a window for the other part of the spectrum.

Scattering from opaline structures is described by the following Bragg's equation modified for optical region,

$$\lambda = 2d_{111} (n_{\text{eff}}^2 - \sin^2 \theta_i)^{1/2} , \quad (1)$$

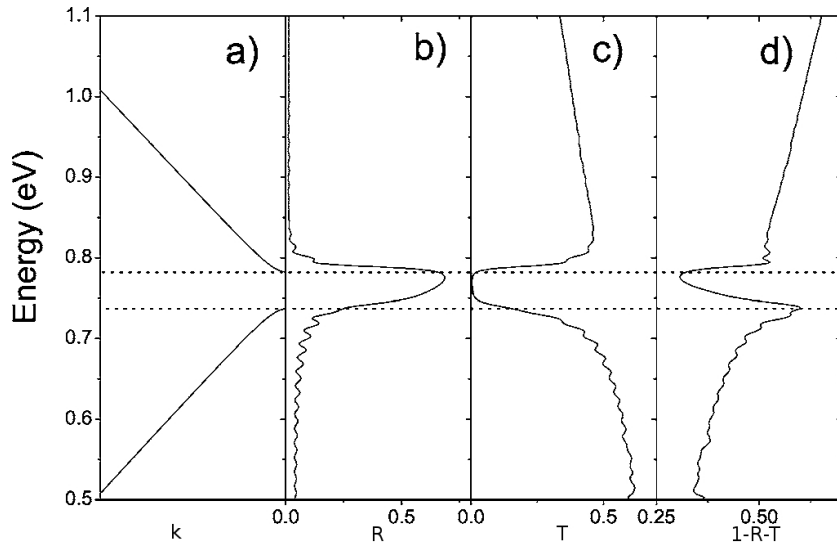


Figure 3: Optical response of an artificial polystyrene opal. a) Calculated energy bands, b) reflectance, c) transmittance and d) diffuse intensity. [6]

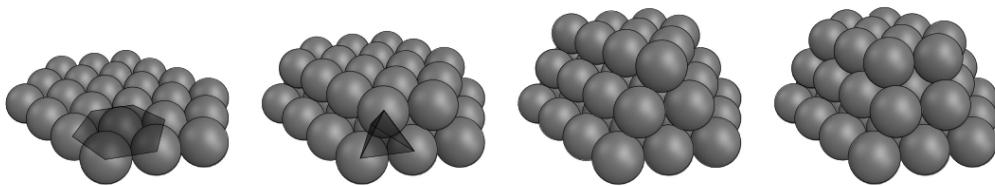


Figure 4: Stacking of the 111 planes of a fcc crystal (first three images) and stacking of the hcp structure. Take note of the hexagonal arrangement of the spheres on a single layer and the tetragonal packing of the second layer.

in which  $\lambda$  is the wavelength of light in free space,  $d_{111}$  is the spacing between the 111 crystal planes,  $n_{\text{eff}}$  is the effective (average) refractive index of the assembly (also including the void space) and  $\theta_i$  is the angle (calculated from the normal of the plane) of the incident beam.

### 1.3 Close-packing of spheres

Close-packed structures are the most effective way of filling space with spheres. A single layer of spheres is closest-packed with a hexagonal coordination of each sphere. The second layer of spheres is placed in the indentations left by the first layer so that three spheres on the bottom layer and one sphere on top will form

a regular tetrahedron.

When a third layer of spheres is placed in the indentations of the second layer there are two choices. The third layer can lie in indentations directly in line with the 1st layer. Layer ordering may be described as ABA and the forming structure is called hexagonal close-packed (hcp). Alternatively the third layer can lie in the other indentations leaving it staggered with respect to both previous layers. Layer ordering may be described as ABC. The forming structure is called face centered cubic or fcc (see Fig. 4). Self-assembled hard spheres have been shown to usually pack into the fcc structure with the 111 lattice plane parallel with the substrate.

An alternative way to demonstrate the fcc structure is via its unit cell. A primitive unit cell is the smallest piece of space which describes the structure unambiguously. Usually structures are demonstrated by using (non-primitive) cubic unit cells, which are more easy to understand visually. The non-primitive cubic unit cell for the fcc structure is shown in Fig. 5. The figure on the left shows the location of the spheres with respect to the unit cell. The 111 planes in the unit cell are also shown. The figure on the right shows the actual unit cell when it is close-packed with spheres.

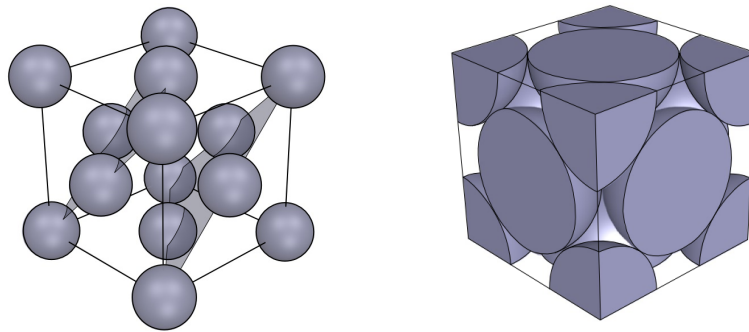


Figure 5: The (non-primitive) unit cell of a fcc structure (on the left) and the close-packing of the unit cell (on the right).

The filling factor is the ratio between the space occupied by the spheres divided by the size of the unit cell. There are several ways to calculate the filling factor, but probably the easiest way is by considering the cubic unit cell of the structure.

## 1.4 Effective medium approximations

The calculation of refractive indices for different inhomogeneous materials is done by using effective medium approximations (EMAs). These can be quite tricky to calculate and several different models have been introduced. Different models have applications where they give good results.

A simple EMA, which is based on taking a weighed average of the individual dielectric constants, can be used to describe the effective dielectric constant of an artificial opal structure,

$$\epsilon_{eff} = \Phi_A \epsilon_A + \Phi_B \epsilon_B , \quad (2)$$

where  $\Phi_A$  and  $\Phi_B$  are the volume fractions of domains  $A$  and  $B$ , and  $\epsilon_A$  and  $\epsilon_B$  are their dielectric constants, respectively. The relation between the dielectric constant and the refractive index,  $n$ , for dielectrics is  $\epsilon = n^2$ .



## 2 Measurements and equipment

### 2.1 UV-Vis-NIR spectrophotometry

The instrument used for measuring the PBG samples is a UV-Vis-NIR spectrophotometer (*Perkin-Elmer Lambda 950 UV-Vis-NIR spectrophotometer*). It measures the transmission, absorption, or reflection spectrum of a sample. Usable wavelength range is 175–3300 nm. Sample is usually either a liquid or a solid film. A simplified block diagram for the device is shown in Fig. 6.

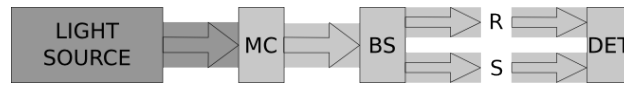


Figure 6: A simplified schematic representation of the UV-Vis-NIR spectrophotometer. Light source is a tungsten or deuterium lamp, MC is the monochromator, BS is the beam splitter, R and S refer to the reference and sample, respectively, and DET is the detector.

The light source emits at a broad wavelength range and it is either a tungsten or a deuterium lamp. The wanted wavelength is then selected with a monochromator (MC), which lets only a narrow wavelength range pass. After the monochromator, the beam splitter (BS) splits the light beam into two similar beams. Then the light passes through a series of mirrors, slits and beam masks before entering the sample compartment, where lies the sample (S) and the reference sample (R). The sample changes the intensity of the beam and the resulting intensity is recorded with the detector (DET). Before the measurements, the full intensity baseline is gathered. The response from the sample is then compared to this baseline intensity and the absorption, transmission, or reflection values are determined from the relative intensity. The effect of substrates or solvents can be reduced by placing a reference sample at the reference beam. The program automatically reduces the effect of the reference from the measured data.

Transmission or transmittance is a value, which tells how large percentage of the emitted intensity is transmitted through the sample to the detector,

$$T = \frac{I}{I_0}, \quad (3)$$

where  $I_0$  is the baseline intensity. The absorption or absorbance is a logarithmic

quantity, which tells how strongly the sample absorbs the incoming light. Absorbance value of zero corresponds to a transmittance value of 100%, value of one corresponds to  $T=10\%$ , two corresponds to  $T=1\%$ , and so on. Our spectrometer can measure absorbance values up to 4, but the best results are achieved when the absorbance is in the range from 0 to 1.

In a system where there are two absorbing media, such as a sample and a substrate, the transmittance can be divided into two parts. Before the sample the intensity of the beam is  $I_0$ . After the sample the intensity becomes  $I_s = T_s I_0$ , where  $T_s$  is the transmittance of the sample. After the substrate the intensity becomes  $I = T_{\text{substr}} I_s = T_s T_{\text{substr}} I_0$ , and the overall transmittance of the system is thus  $T = T_s T_{\text{substr}}$ . By measuring the spectrum of the substrate separately, the transmittance of the sample can be extracted from the measured spectrum.

## 2.2 Optical microscopy

The instrument used for analyzing the structure of the PBG samples is a polarized light microscope (*Leica DM4500*). The microscope is equipped with objectives ranging from 5x to 40x which result in magnifications ranging from 50x to 400x. The microscope is also equipped with polarizers which can be used to study e.g. the birefringence of samples. However, in this work, the polarizers are not necessarily needed. Images of the samples can be obtained by using the software-controlled camera that is attached on the microscope. The assistant will give instructions on how to use the microscope.

### 3 Lab instructions

1. Make the colloidal crystal samples.
  - At all times, when working in the lab, use protective glasses and gloves. You will receive them from the assistant.
  - Take five glass slides, clean them with ethanol and dry them. Save one slide as a reference.
  - Attach a silicone mold (a “well”) to the four of the glass slides. Press firmly and observe the attaching from the back side of the slide.
  - Using a “Finn-pipette”, cast predefined volumes of the dispersions in the wells. You’ll receive instructions on how to use the pipettes.
  - Let the drops dry on a hot plate set to about 60 degrees.
2. Measure the transmission spectra of your colloidal crystals.
  - There is a predefined method, “PBG 2015” in the software that you will use.
  - Measure the full intensity and dark baselines.
  - Measure the UV-vis-NIR transmittance spectra of all samples to that sample is perpendicular to the beam ( $0^\circ$  angle).
  - Measure spectra of one of the samples at  $0^\circ$ ,  $8^\circ$ ,  $16^\circ$ ,  $24^\circ$  and  $32^\circ$  angles.
  - Measure also the clean glass slide at  $0^\circ$ ,  $8^\circ$ ,  $16^\circ$ ,  $24^\circ$  and  $32^\circ$  angles.
3. Investigate the structure of your PBG materials with an optical microscope (Leica DM4500).
  - You’ll receive instructions on how to use the microscope.
  - Acquire representative optical microscope images of all your samples. Use the same settings (zoom, light intensity, direction of light) for all samples for easier comparison.
  - Remember to insert scale bars into the images.

## 4 Prerequisite questions

You need to write down short answers to all of the questions below in order to do the lab work.

1. What is the analogy between atomic crystals and photonic crystals? How about X-ray diffraction and the photonic bandgap effect? What is different?
2. What is the analogy between semiconductors and photonic crystals?
3. What does “structural colour” mean? What is the difference between the colour from *e.g.* some blue flower compared to the blue colour from the Blue Morpho butterfly?
4. In the lab work, the colloidal dispersions contain a certain number of polystyrene (PS) particles per millilitre. One way of preparing colloidal crystals is just to evaporate the water out from the dispersions. This is done by pouring the dispersion in a circular pool with diameter of 20 mm. Calculate how much dispersion (volume) is needed to fill the pool with ten layers of the spheres (i.e. calculate how many particles are needed to make one monolayer and use the particle concentration to calculate the needed volume). Fill the calculated values in the table below. Assume that spheres are packed in hexagonally arranged layers and use the particle diameters given in the second column.

material	size from DLS/nm	particles/ml	volume for 10 monolayers
PS	$202 \pm 11$	$5.6 \cdot 10^{11}$	
PS	$356 \pm 14$	$1.0 \cdot 10^{11}$	
PS	$465 \pm 11$	$4.6 \cdot 10^{10}$	
PS	$505 \pm 8$	$3.1 \cdot 10^{10}$	

## 5 Report

Describe photonic bandgap materials in general and make an analogy between semiconductors and photonic crystals. Also mention the basic similarities and differences between X-ray scattering from crystals and light scattering from photonic crystals. Why are PBG materials interesting? Think of some applications. Note that the properties of a PBG can be changed by external stimuli, such as pH, temperature, humidity, electric field, ...

Describe the structure of an artificial opal and calculate the filling factor for the close packed fcc structure. Locate the 111 planes in the unit cell of the structure (draw a picture) and calculate the interplane distance,  $d_{111}$ , with respect to the diameter of the spheres,  $D$ . Derive the optical Bragg equation for the structure by assuming that the light is reflected from 111 crystal planes, whose spacing is  $d_{111}$ . Hints on how to do this are given in App. A. By using the effective medium approximation, calculate the effective refractive index for the colloidal crystals. Your samples consist of polystyrene, whose refractive index  $n = 1.59$  [8].

Briefly describe the UV-Vis-NIR spectrophotometer and its operational principle. What quantity does the spectrometer measure? How are values such as transmittance or absorbance extracted from the measured data? What is the relation between absorbance, transmittance, and reflectance?

The particle manufacturer has determined the size of the particles by dynamic light scattering (DLS). Read an article named "A comparison of atomic force microscopy (AFM) and dynamic light scattering (DLS) methods to characterize nanoparticle size distributions". Describe briefly, what is DLS based on. What are the pros and cons of DLS? What other methods are there to determine the size of such nanoparticles?

Measure the particle sizes from the electron microscope images found on the exercise web page. A good program to use is ImageJ (<http://rsb.info.nih.gov/ij/>). If needed, the assistant can give advise on using ImageJ. Measure at least 20 particles from each sample and calculate the average size and also the standard deviation of the size. Remember to describe the process and put your data in a table. Include also the particle sizes supplied by the manufacturer (page 12). Which particle sizes data (DLS or electron microscopy) should you use in the data analysis in this work? Justify your choice.

Remember also to describe the sample preparation procedure!

Plot the spectra of the colloidal crystals (transmittance or absorbance) and locate the bandgap. You need to reduce the effect of the substrate from your spectra. Estimate the accuracy of the location of the bandgap. Discuss the sources for error in the measurements.

Plot the location of the bandgap (from UV-Vis-NIR) as a function of the particle size. Fit a straight line to your plot and estimate the error of the slope by drawing error lines. Plot also the theoretical response you calculated before. Does the theoretical curve fit nicely? Discuss the differences.

Plot the location of the bandgaps as a function of angle in a  $\lambda^2/\sin^2(\theta)$  -graph. You will end up with a straight line when you do this correctly. Remember to make error estimations with error curves. Again, you need to extract the error limits for the slope. Plot the appropriate theoretical curves and compare them to your measurements. Try to make the correlation better by varying some parameter. Again, justify your choice.

Finally, gather your results from transmission measurements in table form and discuss them.

Include also the optical microscope images to your report and analyze the images. What can you see in the images? Comment on the quality of your samples. Can you suggest improvements for the sample preparation procedure? Read section 3 from the review article "Self-Assembled Photonic Structures". Describe different colloidal photonic crystal preparation techniques introduced in the article. Discuss the pros and cons of different preparation techniques.

Send your report to the assistant (jukka.hassinen(at)aalto.fi) as .pdf and .txt files. To help archiving reports, the files should be named as "2015-group number-author's surname" (e.g. 2015-1-Meikäläinen). Files should not be larger than few MB.

## References

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## A How to derive the optical Bragg law?

Consider the situation described in Fig. 7. An incident beam with wavelength  $\lambda$  hits an array of spheres. Approximate the situation so that before the first layer there is only air,  $n = n_0 = 1$ , and after there is a material with a refractive index of  $n = n_{\text{eff}}$ . Scattering occurs from crystal planes with a spacing of  $d$ . What makes this situation different from scattering of X-rays from crystals, is that the optical refractive index must be taken into account. Write the optical path difference,  $\Delta$ , for the two waves going from  $A$  to  $D$  and  $A$  through  $B$  to  $C$ . The optical path is defined as the refractive index of the medium times the physical path.

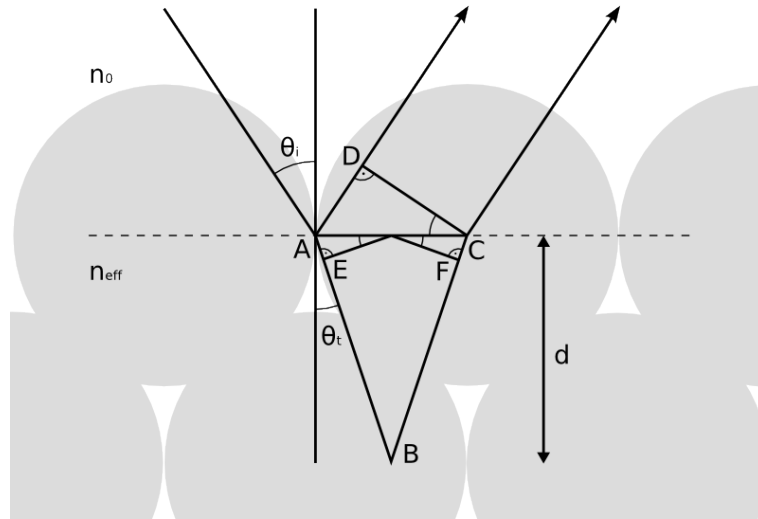


Figure 7: Scattering occurs from crystal planes. Also the refractive indices of the materials have to be taken into account.

Once you have formulated the path difference, divide the path  $ABC$  into four parts  $AE$ ,  $EB$ ,  $BF$ , and  $FC$ . Make use of trigonometric functions. You also need to use Snell's law at some point,

$$n_0 \sin \Theta_i = n_{\text{eff}} \sin \Theta_t , \quad (4)$$

and note that  $n_0 = 1$  for air. Scattering occurs when the path difference is an integer multiple of the wavelength of the incident light,

$$N\lambda = \Delta , \text{ where } N \in \{1, 2, 3, \dots\} . \quad (5)$$



Combine this solution with the scattering rule and you should end up with the optical Bragg law (Eq. 1).