Chemical Crystallography: Exercise No. 1

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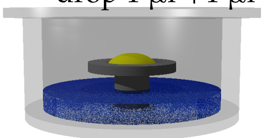
24th March 2022

1 Crystal growth



A sample is crystallised by vapour diffusion in a sealed container. Your sample is dissolved in pure EtOH at a concentration c. The mother liquor is a mixture of 7:3 (v/v) $H_2O/EtOH$. Before sealing the container, you mixed 1 µl of the sample with 1 µl of mother liquor in the table.

1. What is the content of the drop immediately after mixing?
2. What is the content of the drop after equilibration?
3. Estimate how long it takes to reach equilibrium
4. What measures are there to reduce the time for equilibration?

Make use of your common sense, rather than a pocket calculator!

2 Symmetry

A mirror seems to swap your hands: left hand becomes right and, and right hand becomes left hand. Why does the mirror not swap up and down?

3 Fractional Coordinates

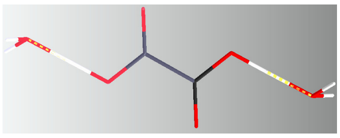
A crystal structure is fully described with the content of the unit cell. All other unit cells are identical. A place inside the unit cell has fractional coordinates between 0 and 1 ($0 \leq x, y, z < 1$). Often, however, some atoms have coordinates outside this range. The example of oxalic acid from lecture No. 1 contains the atom

```
C1   1 -0.045033   0.058931   0.051985  11.00000   0.00919
        ^^^ x ^^   ^^^ y ^^   ^^^ z ^^
```

One could replace the x-coordinate with $-0.045033 + 1 = 0.954967$, i.e. this atom line is crystallographically identical to

```
C1   1   0.954967   0.058931   0.051985   11.00000   0.00919
```

1. Why is it often reasonable to allow a few atoms with come coordinates outside the range between 0 and 1, as in this example for $C1$?



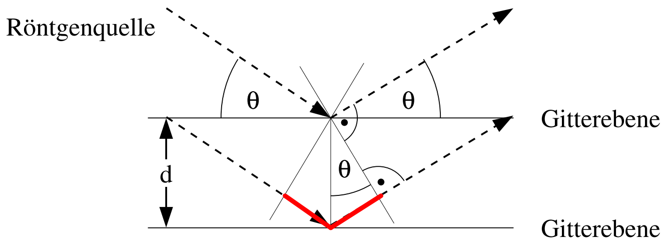
4 Bragg's Law

1. Make use of Bragg's law $\lambda = 2d \sin\theta$ to derive tha maximum possible resolution for a diffraction experiment.

$$d \geq \lambda/2 \tag{1}$$

   This maximum is also known in optics, e.g. for ligh microscopes.

2. Use the following drawing in order to derive Bragg's law $n\lambda = 2d \sin\theta$:



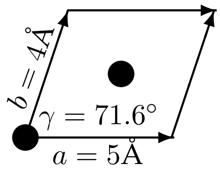
5 Diffraction theory

1. Based on the Laue equations,

$$\begin{aligned}
\vec{a} \cdot \vec{S} &= |\vec{a}||\vec{S}| \cos(\vec{a}, \vec{S}) = h \\
\vec{b} \cdot \vec{S} &= |\vec{b}||\vec{S}| \cos(\vec{b}, \vec{S}) = k \\
\vec{c} \cdot \vec{S} &= |\vec{c}||\vec{S}| \cos(\vec{c}, \vec{S}) = l
\end{aligned}$$

   show that there is always a reflection in direction of the direct beam $\vec{S}_{in}$! To do this, make a sketch to derive the scattering vector $\vec{S}$ under this condition.

2. The following "unit cell" has one atom at the origin $(0, 0, 0)$ and one atom of the same element type centred at the cell, $(0.5, 0.5, 0.5)$ (Note: The cartesian coordinates of this point are (3.12Å, 1.897Å, c)).



Both atoms emit a spherical wave with amplitude 1.

a) What is the amplitude of the reflections

  i. (1, 0,0)

  ii. (0,1,0)

  iii. (1,1,0)

b) The wavelength of the experiment is irrelevant for this question. Why is this so?

6 Resolution and crystal quality

The lecture showed drawings of the lattice planes in the context of Bragg's Law. The greater the distance of the next two lattice points, that define a plane, the better (numerically smaller) is the resolution d of these lattice planes.

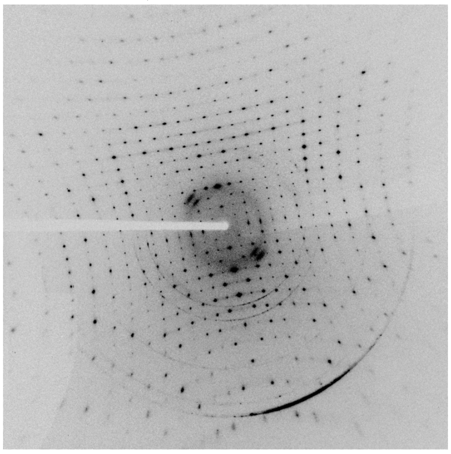
1. With your own words, describe what is meant by "resolution" of an optical instrument like a microscope or a telescope?

2. Discuss why a crystal is considered "high quality" when it diffracts to high resolution! Hint: Do not consider the answer to the previous question, but consider the arrangement of unit cells, that is necessary for a high-resolution lattice plan!

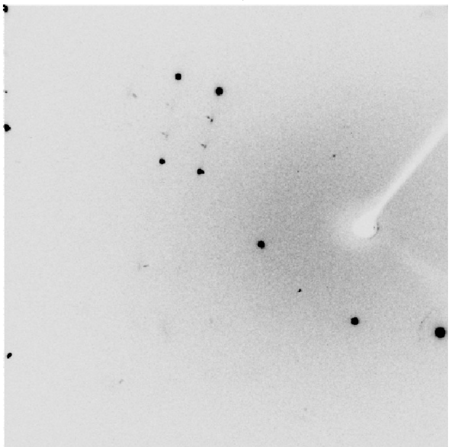
7 Diffraction images

The following two diffraction images were shown during the lecture:

$14.2 \times 16.2 \times 27.9$ Å^3
$\alpha = \gamma = 90°, \beta = 87.9°$



$10.56 \times 11.64 \times 16.14$ Å^3
$\alpha = \beta = \gamma = 90°$



The unit cell dimensions are more or less comparable. Yet, the left images shows many more reflections. What are the possible causes for this?

8 Diffraction geomerty

An area detector with a circular area and a diameter of 20 cm is placed such that the direct beam hits the centre of the detector, i.e. $2\theta = 0°$). The distance between the detector and the crystal is 5 cm. What is the maximum possible resolution for this geometry for:

1. a copper source ($\lambda = 1.54$ Å)
2. a silver source ($\lambda = 0.559$ Å)
3. synchrotron radiation at $\lambda = 1.0$ Å?