Neutron and X-ray Scattering of Quantum Materials

PHYS-640

Week 2 solutions

1: The monochromator

(a) Exercise 9.P.1 in the neutron notes.

1.

2. Inserting $d = n\frac{2\pi}{\tau}$ and $\lambda = \frac{2\pi}{k}$ in Bragg's law yields:

$$n\lambda = 2d\sin\theta \quad \Rightarrow \quad n\frac{2\pi}{k} = 2n\frac{2\pi}{\tau}\sin\theta \quad \Leftrightarrow \quad \frac{1}{k} = 2\frac{1}{\tau}\sin\theta \quad \Leftrightarrow \quad \tau = 2k\sin\theta$$

3. From momentum conservation shown we have $\tau = \mathbf{k}_i - \mathbf{k}_f$. This is illustrated in Fig. 1. Now consider the right-angled triangle shown with red in Fig. 1 and use that for diffraction $k_i = k_f = k$:

$$\sin\theta = \frac{\tau/2}{k} \quad \Leftrightarrow \quad \tau = 2k\sin\theta$$

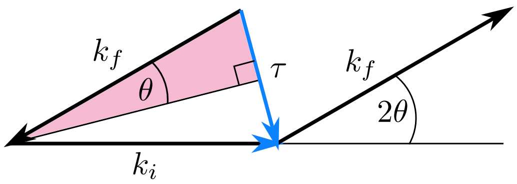

Figure 1: Sketch to help get to Bragg's law from momentum conservation.

4. First we need to convert the neutron energy to momentum:

$$E = \frac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad k = \frac{\sqrt{2mE}}{\hbar}.$$

The scattering angle can be found from Bragg's law:

$$\tau = 2k\sin\theta \quad \Rightarrow \quad 2\theta = 2\arcsin\left(\frac{\tau\hbar}{2\sqrt{2mE}}\right).$$

Then plugging in the numbers we get the scattering angle for PG (002) is $2\theta = 74.2°$.

(b) Sometimes Si (111) is chosen instead of PG (002) for monochromating the neutron beam. Calculate the structure factor for the Si (nnn) reflections for $n = 1, 2, 3, 4$.

Silicon has the diamond structure which is two interlaced face-centered cubic lattice with the second lattice displaced by $(1/4, 1/4, 1/4)$ with respect to the first one. That gives us 8 atoms per unit cell with the following coordinates given in the basis of the cubic lattice:

$$\begin{aligned}
\boldsymbol{\Delta}_1 &= (0,0,0), & \boldsymbol{\Delta}_5 &= (1/4,1/4,1/4),\\
\boldsymbol{\Delta}_2 &= (1/2,1/2,0), & \boldsymbol{\Delta}_6 &= (3/4,3/4,1/4),\\
\boldsymbol{\Delta}_3 &= (0,1/2,1/2), & \boldsymbol{\Delta}_7 &= (1/4,3/4,3/4),\\
\boldsymbol{\Delta}_4 &= (1/2,0,1/2), & \boldsymbol{\Delta}_8 &= (3/4,1/4,3/4).
\end{aligned}$$

The structure factor is then evaluated for reflections of the type $\mathbf{q} = (nnn)$ as given in reciprocal lattice units:

$$\begin{aligned} F(nnn) &= \sum_{j=1}^{8} b_j \, \mathrm{e}^{i2\pi(n,n,n)\cdot\Delta_j} \\ &= b_{\mathrm{Si}} \left(1 + 3\mathrm{e}^{i2\pi n} + \mathrm{e}^{i2\pi n(3/4)} + 3\mathrm{e}^{i2\pi n(7/4)}\right) \\ &= b_{\mathrm{Si}} \left(1 + 3\mathrm{e}^{i2\pi n} + \mathrm{e}^{i2\pi n(3/4)} + 3\mathrm{e}^{i2\pi n(3/4)}\mathrm{e}^{i2\pi n}\right), \end{aligned}$$

where $b_j = b_{\mathrm{Si}}$ is the same for all atoms in the unit cell. Since n is an integer then $e^{i2\pi n} = 1 \;\forall\; n$ and we get:

$$F(nnn) = 4b_{\mathrm{Si}} \left(1 + \mathrm{e}^{i(3/2)\pi n}\right),$$

and we can calculate the structure factor for $n = 1, 2, 3, 4$:

$$\begin{aligned} F(111) &= 4b_{\mathrm{Si}} \left(1 + \mathrm{e}^{i(3/2)\pi}\right) = 4b_{\mathrm{Si}}(1 - i), \\ F(222) &= 4b_{\mathrm{Si}} \left(1 + \mathrm{e}^{i3\pi}\right) = 0, \\ F(333) &= 4b_{\mathrm{Si}} \left(1 + \mathrm{e}^{i(9/2)\pi}\right) = 4b_{\mathrm{Si}}(1 + i), \\ F(444) &= 4b_{\mathrm{Si}} \left(1 + \mathrm{e}^{i6\pi}\right) = 0. \end{aligned}$$

For this family of planes we can recognise a pattern: $F(nnn) = 0$ for n even and $F(nnn) = 4b_{\mathrm{Si}}\,(1 + i^n)$, i.e finite, for n odd.

(c) Can you think of why Si (111) is sometimes a better choice for the monochromator?

The $\lambda/2$ contribution to the beam is totally killed by the structure factor.

2: The crystal structure of Po and NaCl

(a) Calculate the structure factor for Po and NaCl.

Both have simple cubic structure but for NaCl it is necessary to define a basis with 8 atoms in the unit cell:

$$\begin{aligned} \boldsymbol{\Delta}_1^{\mathrm{Na}} &= (0, 0, 0), & \boldsymbol{\Delta}_5^{\mathrm{Cl}} &= (1/2, 0, 0), \\ \boldsymbol{\Delta}_2^{\mathrm{Na}} &= (1/2, 1/2, 0), & \boldsymbol{\Delta}_6^{\mathrm{Cl}} &= (0, 1/2, 0), \\ \boldsymbol{\Delta}_3^{\mathrm{Na}} &= (0, 1/2, 1/2), & \boldsymbol{\Delta}_7^{\mathrm{Cl}} &= (0, 0, 1/2), \\ \boldsymbol{\Delta}_4^{\mathrm{Na}} &= (1/2, 0, 1/2), & \boldsymbol{\Delta}_8^{\mathrm{Cl}} &= (1/2, 1/2, 1/2). \end{aligned}$$

For Po there is just a single atom in the unit cell positions at $(0, 0, 0)$ so the structure factor becomes:

$$F_{\mathrm{Po}}(\tau) = b_{\mathrm{Po}},$$

which means that $F_{\mathrm{Po}}(\tau)$ is in fact independent on τ. The structure factor for NaCl more involved:

$$\begin{aligned} F_{\mathrm{NaCl}}(\tau) = \sum_{j=1}^{8} b_j \, \mathrm{e}^{i\tau\cdot\Delta_j} = b_{\mathrm{Na}} &\left(1 + \mathrm{e}^{i\pi(H+K)} + \mathrm{e}^{i\pi(K+L)} + \mathrm{e}^{i\pi(H+L)}\right) \\ &+ b_{\mathrm{Cl}} \left(\mathrm{e}^{i\pi H} + \mathrm{e}^{i\pi K} + \mathrm{e}^{i\pi H} + \mathrm{e}^{i\pi(H+K+L)}\right). \end{aligned}$$

This is only finite if H, K, L are all odd or all even. Any other combination gives $F_{\text{NaCl}}(\tau) = 0$.

(b) What is the main difference between the two examples?

For the simple cubic Bravais structure of Po, all Bragg reflections are allowed. NaCl, other the other hand, needs to be described using a basis and this leads to restrictions on the combination of H, K and L.

(c) Index the powder diffraction pattern of NaCl in Fig. 2.

We know that only combinations of H, K, L all odd or all even will give intensity in the diffraction pattern of NaCl. The first one of these would be (111) so we can use Bragg's law to calculate the corresponding scattering angle, 2θ. In general we have:

$$|\tau| = 2k \sin\theta \quad \Rightarrow \quad \frac{2\pi}{a}\sqrt{H^2+K^2+L^2} = \frac{4\pi}{\lambda}\sin\theta \quad \Rightarrow \quad \sin\theta = \frac{\lambda}{2a}\sqrt{H^2+K^2+L^2}, \tag{1}$$

where we used $k = \frac{2\pi}{\lambda}$ and $|\tau| = \frac{2\pi}{a}\sqrt{H^2+K^2+L^2}$ for a cubic system. For $H = K = L = 1$ and $a = 5.59$ Å yields a scattering angle of $2\theta = 27.61°$. That corresponds very nicely to the first peak observed in Fig. 2. Table 1 gives a list of allowed Bragg peaks and their calculated scattering angles and they are all marked in Fig. 2.

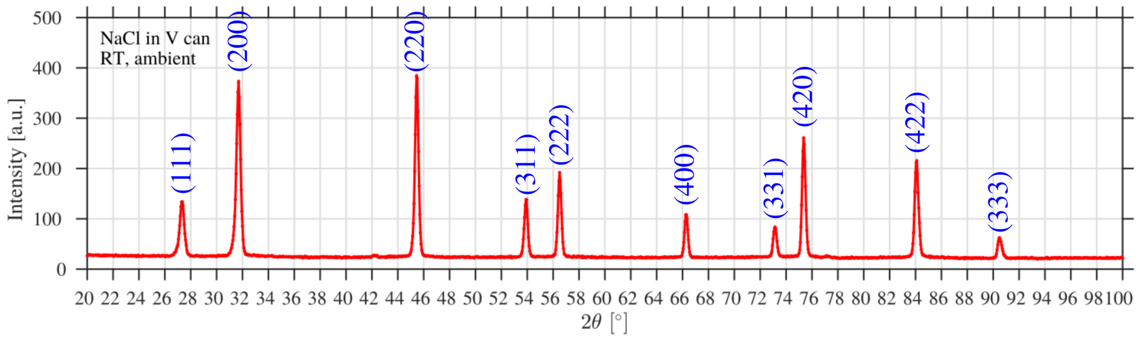

Figure 2: Neutron powder diffraction pattern on NaCl measured at room temperature (RT) and ambient pressure on the D20 diffractometer at the ILL. The wavelength used was $\lambda = 1.54$ Å.

(HKL)	2θ (°)
(111)	27.61
(200)	31.98
(220)	45.86
(311)	54.37
(222)	57.00
(400)	66.87
(331)	73.80
(420)	76.05
(422)	84.88
(333)	91.41

Table 1: Calculated scattering angles for allowed Bragg reflections for NaCl measured with $\lambda = 1.54$.

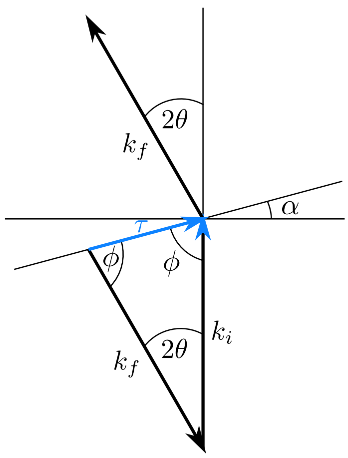

Figure 3: Sketch to assist calculation of the scattering angle for momentum transfers of the type $\tau = (0K0)$ in Exercise 3(c).

(d) NaCl is sometimes used as a pressure gauge when doing neutron scattering experiments under pressure. Using the equation of state (EoS) published by Brown *et al.* (https://doi.org/10.1063/1.371596, also on moodle), what is the change in scattering angle, 2θ, of the first Bragg peak when applying 3 GPa of hydrostatic pressure?

First we need to know by how much the NaCl lattice is squeezed. Reading off Table II in the paper by Brown *et al.* in the column for 300 K (room temperature) we see that the relative volume change at 3.07 GPa is $v_r = (V_0 - V)/V_0 = 0.0944$, meaning just short of 10%. With this we can find the lattice constant under 3 GPa pressure:

$$v_r = \frac{V_0 - V}{V_0} = \frac{a_0^3 - a^3}{a_0^3} = 1 - \left(\frac{a}{a_0}\right)^3 \quad \Rightarrow \quad a = a_0\sqrt[3]{1 - v_r}.$$

Plugging that into Eq. (1) and using $a_0 = 5.59$ Å as and $H = K = L = 1$ for the first Bragg peak yields a scattering angle of $2\theta = 26.69°$. That is a change in the position of the (111) peak of 0.91° and that is detectable in neutron diffraction experiments.

3: Time-of-flight neutron Laue diffraction with $LiFePO_4$

(a) Calculate the structure factor for $LiFePO_4$ (atomic positions are uploaded on moodle). You probably want to write a little script for this rather than doing it by hand. Which are suitable Bragg peaks to use for aligning the sample in the (b, c)-plane?

An example of a script has been uploaded to moodle. The space group of $LiFePO_4$ is *Pnma* which has the following conditions for Bragg reflections:

- For $(0KL)$ type reflections, $H + K$ must be even
- For $(H00)$, $(0K0)$ and $(00L)$ type reflections, H, K and L must be even
- For $(HK0)$ type reflections, H must be even

Which peak that are suitable for aligning the sample depends on the wavelength used at the given diffractometer but (020) and (002) would work on most instruments.

(b) Assume a (↑↑↓↓) arrangement of spins in the unit cell. Is this structure commensurate or incommensurate? Which Bragg peak positions are suitable to look for this magnetic structure?

It is a commensurate structure since the magnetic unit cell is equal to the nuclear one. The magnetic ion positions in one unit cell are:

$$\Delta_1 = (1/4+\delta, 1/4, 1-\epsilon), \quad \Delta_2 = (3/4-\delta, 3/4, \epsilon), \quad \Delta_3 = (3/4+\delta, 1/4, 1/2+\epsilon), \quad \Delta_4 = (1/4-\delta, 3/4, 1/2-\epsilon),$$

where $\delta = 0.0322$ and $\epsilon = 0.0284$. To simplify the calculations somewhat we can translate origo by $(1/4, 1/4, 0)$ such that instead the positions are:

$$\Delta_1 = (\delta, 0, 1-\epsilon), \quad \Delta_2 = (1/2-\delta, 1/2, \epsilon), \quad \Delta_3 = (1/2+\delta, 0, 1/2+\epsilon), \quad \Delta_4 = (-\delta, 1/2, 1/2-\epsilon),$$

and we recognise the almost face-centered arrangement of the ions. The magnetic structure factor is then:

$$F_M(\tau) = \sum_{j=1}^{4} s_{j,\perp}\, \mathrm{e}^{i\tau\cdot\mathbf{\Delta}_j} = S\Big(\mathrm{e}^{i2\pi\left[\delta H + (1-\epsilon)L\right]} + \mathrm{e}^{i2\pi\left[(1/2-\delta)H + 1/2K + \epsilon L\right]}$$
$$- \mathrm{e}^{i2\pi\left[(1/2+\delta)H + (1/2+\epsilon)L\right]} - \mathrm{e}^{i2\pi\left[-\delta H + 1/2K + (1/2-\epsilon)L\right]}\Big).$$

We here assumed $|s_{j,\perp}| = S$ for all four sites. The minus sign on the two last terms then reflect the fact that ions 3 and 4 are "down". Bragg peaks that would have intensity in case of this magnetic structure would be for example (001) and (110). Here the former has zero nuclear intensity whereas the latter is also a nuclear Bragg peak.

(c) In a time-of-flight Laue diffraction experiment performed on the NOBORU instrument at J-PARC, the single crystalline sample is oriented as shown in Fig. 4(a)-(b). Show that Bragg

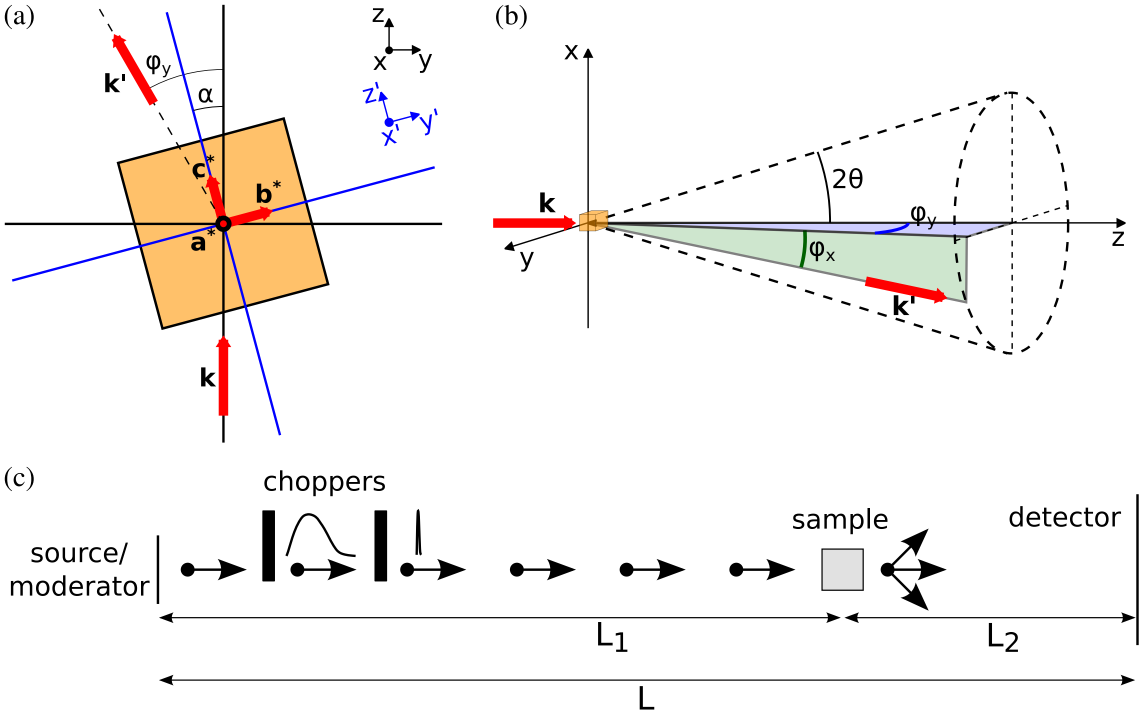

Figure 4: (a) Scattering geometry of the time-of-flight Laue diffraction experiment. The crystal is rotated an angle α with respect to the incoming beam. The scattered neutrons have a scattering angle φ_y with respect the z-axis. (b) The Debye cone with opening angle 4θ. The angle of the scattered neutrons with respect to the horizontal plane is φ_x. (c) Overall setup at NOBORU for time-of-flight neutron diffraction.

reflections in the $(0K0)$ direction scatter with the angle 2α in the horizontal plane.

The Bragg peaks of the type $(0K0)$ are rotated α with respect to the y-axis as seen in Fig. 4(a). Using the sketch shown in Fig. 3 and the isosceles triangle formed of τ, $\mathbf{k}_i$ and $-\mathbf{k}_f$ we immediately see that:

$$180^\circ = 2\phi + 2\theta \quad \Rightarrow \quad 2\theta = 180^\circ - 2(90^\circ - \alpha) = 2\alpha.$$

(d) The distance from the source to the sample is $L_1 = 14$ m and from the sample to the detector is $L_2 = 1.5$ m, see Fig. 4(c), and the rotation of the crystal was $\alpha = 7^\circ$. What is the flight times for the nuclear Bragg reflection (020) and the magnetic Bragg reflection (010)?

We use first use Bragg's law $|\tau| = 2k\sin\theta$ together with $k = \frac{2\pi}{\lambda}$ to find the necessary wavelength to hit reflections along $(0K0)$:

$$K\frac{2\pi}{b} = \frac{4\pi}{\lambda}\sin\theta \quad \Rightarrow \quad \lambda = \frac{2b}{K}\sin\theta$$

Then we can use $t = \alpha L\lambda$ with $\alpha = 252.7\,\mu\text{s/m/Å}$ (apologies for another α) to calculate the time-of-flight:

$$t = \alpha L\frac{2b}{K}\sin\theta.$$

Plugging in $L = 14 + 1.5$, $b = 6.01$ Å and $\theta = 7^\circ$ we get $t_{(010)} = 5.74$ ms and $t_{(020)} = 2.87$ ms.