

Structure characterization

Alessio Cimma

March 24, 2025

Contents

1	10-03-25: — Introduction	1
1.1	Radiation diffusion	1
1.2	Description of the Wavefunctions	2
1.3	Fourier transform & Bragg's law	3
2	13-03-25: — Scattering	4
3	17-03-25: — Diffraction	5
4	18-03-25: — Reconstructing crystal structure	6
4.1	Structure solving	6
4.2	Anomalous scattering	7
5	24-03-25: — Single crystal & powder diffraction	8

1 10-03-25: — Introduction

Crystals are ordered structures. Let's start from 2D crystals. The elementary cell is the smallest space we can consider to include all the features of the cell and by just applying traslation we can obtain the whole crystal. We can use vectors like \vec{a} and \vec{b} to represent all the possible location of atoms in the elementary cell. They are called **Lattice Vectors**.

Lattice traslation vectors: They are linear combinations of \vec{a} , \vec{b} and so on:

$$\vec{v} = n\vec{a} + m\vec{b} + p\vec{c} \quad (1)$$

Where n , m and so on are integers, they identify all the origins of the elementary cells. This means that by identifying a certain feature in the elementary cell and applying the Lattice Traslation Vectors we find the same feature in another elementary cell, which leads to the **Lattice Traslation Invariance**, defined as:

$$\Phi(\vec{x}) = \Phi(\vec{x} + \vec{T}) \quad (2)$$

All crystals MUST satisfy this property.

Crystal site: We can think about the crystal as a series of potential wells, where atoms are located. Once we accept this view, the actual atom inside the well, is not very important, the important thing is the position, so we can obtain a solid solution as a mixture. So we describe the well as the probability of a site being occupied from an element or another. This is called occupancy of a site.

1.1 Radiation diffusion

During scattering processes, we can have different behaviours:

- Inelastic, meaning that $E_f \neq E_i$.
- Elastic, meaning that $E_f = E_i$ (most frequent and subject of the course).

We need to introduce momentum as:

$$\vec{K}_i = \frac{2\pi}{\lambda_i} \vec{\tau}_i = \frac{\vec{\tau}_i}{\lambda_i} \quad (3)$$

Where $\vec{\tau}_i$ has modulus 1 and direction of the incident ray, while $\vec{\tau}_f$ is always 1, but in the direction of the scattered direction. The momentum transfer is $\vec{Q} = \vec{K}_f - \vec{K}_i$, which will be 100% in case of elastic scattering.

De broglie: We can use photons, which have the following relation with energy. This is done to show that we can use pretty much everything that interact with the sample.

$$P\lambda = h \quad (4)$$

$$e = \frac{hc}{\lambda} \quad (5)$$

So now we are interested in how we can express the probability of a certain scattering transition. We want to know the direction and intensity change. As always, probability will be given by:

$$\int_{\text{crystal}} \Psi_i^*(\vec{x}) I(\vec{x}) \Psi_s dV \rightarrow |\langle i|I|f \rangle|^2 \quad (6)$$

How can we describe the interaction?

Electron density:

$$\rho(\vec{x}) dV = \delta n_e \quad (7)$$

Larmor Formula: Aimed to describe how a particle behave when struck from an ELM wave. The power irradiated from the particle once it was moved from the wave is:

$$P \propto q^2 \vec{a}^2 \quad (8)$$

Where a is the acceleration. So what happens to a small Power?

$$\delta P \propto \partial q^2 \vec{a}^2 \quad (9)$$

$$\vec{a} = \frac{\vec{F}}{m} = \frac{\vec{E} \delta q}{\delta m} \quad (10)$$

$$\frac{\delta q}{\delta m} = \frac{e \delta n}{m_e \delta n} = \frac{e}{m_e} \quad (11)$$

$$\delta P \propto \rho(\vec{x})^2 dv dv \quad (12)$$

This means the the power or radiation will be bounded to the probability that the radiation will interact with the sample.

$$P \leftrightarrow \sum_{\vec{K}_f} P_{\vec{K}_i \rightarrow \vec{K}_f} \quad (13)$$

So in the Eq.6 we can subtitute the I with the $\rho(\vec{x})$.

1.2 Description of the Wavefunctions

Let's start from a simple plane wave.

- Starting incident radiation:

$$e^{2\pi i \vec{k}_i \vec{x} - i\omega t} \quad (14)$$

- Exiting scattered radiation:

$$e^{2\pi i \vec{k}_f \vec{x} - i\omega t} \quad (15)$$

So the final expression is:

$$P_{\vec{K}_i \rightarrow \vec{K}_f} \propto \left| \int \rho_{\vec{x}} e^{2\pi i \vec{Q} \vec{x}} dV \right|^2 \quad (16)$$

Nodes: We can collapse an entire elementary cell into a node, a geometrical point that will contain the information of the position of the elementary cell in the space. This helps us, because we can rewrite our \sum as a summation of nodes, where each node will have always the same term inside of it. So we'll need to add an additional \vec{x} which will position us in the correct spot inside the elementary cell. Remember that $d\vec{y}$ means integration over the elementary cell. But this means that we no longer need all the terms that traslate us between elementary cells, we already calculated what is their value.

1.3 Fourier transform & Bragg's law

$$|\vec{K}_f| = |\vec{K}_i| = \frac{1}{\lambda} \quad (17)$$

If the line connecting the incident and scattered vector were connected, their module would be Q , so:

$$\frac{|\vec{Q}|}{2} = \frac{1}{\lambda} \sin(\theta) \quad (18)$$

Which is essentially the Bragg's law, stating that there's a limit angle during scattering and there's a max lenght of the vector Q :

$$|\vec{Q}| \leq \frac{2}{\lambda} \quad (19)$$

Monochromatic source: Until now we have supposed that the incident beam is characterized by just one wavelength (monochromatic condition). All our discussions will be in the frame of this setup, but it is not the only possible experimental configuration.

2 13-03-25: — Scattering

There's a long demonstration, you can see it in the Obsidian files, but overall it's explaining how to obtain values like energy and periodicity from crystal coordinate system. It also explains how electrons tends to accumulate in specific regions, which are responsible of the scattering of photons, and it is what we actually are able to see.

3 17-03-25: — Diffraction

From now on we will consider Diffraction \equiv Diffusion operated by a periodic system. Important, to calculate the reciprocal vectors you can use:

$$\vec{a}^* = \frac{\vec{b} \wedge \vec{c}}{V} \quad (20)$$

Intensity considerations: We get the intensity from the number of counts over a time times the area. This means that that is proportional to the probability of scattering at a certain factor, giving us the structure factor $F(\vec{H})$ (which is related to the crystalline structure and Bragg's law). Seguendo gli appunti su Obsidian, arriviamo inoltre a parlare del Debye-Waller factor ($\sim e^{-B_j \vec{H}^2}$), which takes into account the atomic vibration.

4 18-03-25: — Reconstructing crystal structure

$$I_{\text{Theor.}}(\bar{H}) \sim |F(\bar{H})|^2 \frac{V_{\text{cry}}}{V_{\text{EC}}^2} K(2\theta) \quad (21)$$

By comparing experimental and theoretical value, we find that it is necessary to add a scale factor that takes into account all the factors of the real world that can change the value.

$$I_{\text{Exper.}}(\bar{H}) \sim \underbrace{|F(\bar{H})|^2 \frac{V_{\text{cry}}}{V_{\text{EC}}^2} K(2\theta)}_{\text{Depends on the crystal}} \cdot \underbrace{\mathcal{S}_{\text{scale}}}_{\text{Depends on the setup}} \quad (22)$$

We can obtain Ω , which is the resulting sum of all the different errors generated by the approximation of our mathematical model. If we try to minimize Ω , we obtain the most optimal setup.

$$\Omega = \sum_{\bar{H}} \frac{[I(\bar{H})_{\text{Theo}} - I(\bar{H})_{\text{Expe}}]^2}{\sigma^2(\bar{H})} \quad (23)$$

We can change the position, the scale, the B_j factor to approximate better our crystal model, also known as ‘*Structure refinement*’.

4.1 Structure solving

We can start from examining the electron density (invariant in the lattice), obtaining the Fourier coefficients that gives us structure factors and hkl . The problem is that the Intensity is proportional to the square of the structure factor, and this one is a complex function, so we encounter the ‘phase problem’, because we don’t know how to calculate it. There are 3 methods to solve this:

MEM (Maximum Entropy Method): We consider which function maximize the entropy of the function:

$$\Omega = \sum_{j=1}^{Pixels} \rho_j \ln(\rho_j) = \text{Entropy} \quad (24)$$

This is calculated for each point in our lattice, meaning we try to calculate the best possible electron density, which is the one whose value (totally unknown) maximize the previous expression. We also have some CONSTRAINTS:

- $\rho_j \rightarrow F_{\text{Theo}}(\bar{H})$: You must know the number of electrons in the elementary cell (you know the composition of the crystal).
- $|F_{\text{Theo}}(\bar{H})| = |F_{\text{Exp}}(\bar{H})|$: You must know that the factor structure has the same modulus (you don’t know the phase tho).

Charge flipping: I assume that the modulus is equal, but i still don’t know the phase, so what i do is to take a guess function that change sign each time it is negative. Considering this as a new factor structure i repeat everything again until I reach the correct representation of the crystal structure.

Direct methods: It's a set of methods with a common basic idea, but we will not investigate them.

4.2 Anomalous scattering

We start from the Larmor Law:

$$\mathcal{P} \propto q^2 \bar{a}^2 \tag{25}$$

5 24-03-25: — Single crystal & powder diffraction

Experimental setup of XRD.