0.1 X-ray Diffraction

0.1.1 Scattering at Lattices

To elucidate the working principles behind X-ray diffraction (XRD) as a measurement method, a brief description of reciprocal space and constructive interference will be provided. Those derivations are based on Ashcroft and Mermin (1976) [1].

A periodic point-like structure with translational symmetry ("BRAVAIS lattice") can be described by three vectors $\mathbf{a}_i$ that span a so-called "unit cell". Every lattice point $\mathbf{R}$ is a linear combination of those unit cell vectors. For such a lattice, there exists a so-called "reciprocal lattice", which consists of all vectors $\mathbf{K}$ satisfying the condition[1]:

$$e^{i\langle \mathbf{K},\mathbf{R}\rangle} = 1\,. \tag{1}$$

This is again a BRAVAIS lattice with unit cell vectors $\mathbf{a}_j^*$:

$$\mathbf{K}_{hkl} = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^*\,. \tag{2}$$

It follows that for any i, j:

$$\langle \mathbf{a}_i^*, \mathbf{a}_j\rangle = 2\pi\delta_{ij}\,, \tag{3}$$

with the KRONECKER delta δ_{ij}. A major application of reciprocal space vectors is their ability to describe lattice planes. Any lattice plane can be described by the shortest possible reciprocal space vector $\mathbf{K}_{hkl}$ perpendicular to it. Consequently, the lattice plane is denoted by (hkl). The distance between equivalent lattice planes can be calculated via $d_{hkl} = |\mathbf{K}_{hkl}|^{-1}$.

With those preliminarities, the conditions for constructive interference during diffraction of radiation at BRAVAIS lattices can be derived. Consider two scattering centers separated by $\mathbf{d}$. Now consider incoming radiation with wave vector $\mathbf{k}$:

$$\mathbf{k} = \frac{2\pi}{\lambda}\hat{\mathbf{n}}\,, \tag{4}$$

with wavelength λ and direction $\hat{\mathbf{n}}$. For the case of elastic scattering, the outcoming wave vector $\mathbf{k}'$ has the same wavelength λ but different direction $\hat{\mathbf{n}}'$. The phase difference of two photons scattered at the 1st and 2nd scattering center, respectively, can be calculated from their path difference, which reads

$$\langle \mathbf{d}, \hat{\mathbf{n}}\rangle + \langle -\mathbf{d}, \hat{\mathbf{n}}'\rangle\,. \tag{5}$$

Constructive interference occurs, if the phase difference is an integral multiple of the wavelength, so it must follow that

$$\langle \mathbf{d}, (\hat{\mathbf{n}} - \hat{\mathbf{n}}')\rangle = m\lambda \tag{6}$$

$$\Leftrightarrow \langle \mathbf{d}, (\hat{\mathbf{k}} - \hat{\mathbf{k}}')\rangle = 2\pi m\,, \tag{7}$$

with $m \in \mathbb{N}$. Comparing with (1) reveals that $\hat{\mathbf{k}} - \hat{\mathbf{k}}'$ is a reciprocal space vector, because the separation $\mathbf{d}$ of the two scattering centers is a lattice vector. So constructive interference (observing a reflex) occurs if and only if the scattering geometry (determined by

[1] The definition of $\mathbf{K}$ by (1) is a consequence of demanding that the plane wave described by $f_{\mathbf{K}}(\mathbf{r}) = \exp(i\langle \mathbf{K}, \mathbf{r}\rangle)$ has the same symmetry as the BRAVAIS lattice [1].

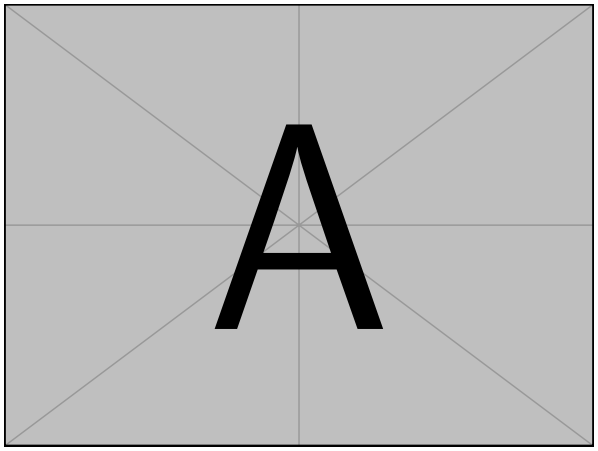

Figure 1: *Here comes an ashcroft-like image for the scattering geometry to derive Equ. (5)*

angle of incidence and refraction, as well as wavelength) matches the lattice symmetry in the sense that there is a corresponding lattice translation vector $\mathbf{d}$ fulfilling Equ. (7). So from the "position" of reflexes, one can deduce the lattice symmetry.

Note that this description of X-ray scattering is equivalent to the Bragg condition:

$$m\lambda = 2d_{hkl}\sin(\theta)\,, \tag{8}$$

where the angle of incidence θ and λ are contained in $\hat{\mathbf{k}} - \hat{\mathbf{k}}'$. Furthermore, when a lattice point is not equivalent to a single atom, but represents several scattering centers, an additional geometrical structure factor has to be taken into account to determine whether a certain geometry allows reflexes. This is important, e.g., for structures with trigonal symmetry. They are described with a conventional hexagonal unit cell, although not every plane (hkl) exhibits constructive interference.

0.1.2 X-rays

Atomic distances in solids are of the order of several Å, so the radiation for probing those structures must have a similar wavelength, which turns out to be X-rays [2]. The following description of X-rays is based on Spieß (2009) [3].

The basis of any X-ray tube are high-energy electrons which are produced by thermionic emission in a cathode, which is usally made out of tungsten[2]. An electric field of several kV accelerates the electrons to the anode, where they are stopped such that around 99 % of their kinetic energy dissipates. The momentum change of electrons, which are charged particles, leads to emission of *bremsstrahlung*. Furthermore, the electrons ionize atoms of the anode material which leads to unoccupied electron states. If those states are filled by electrons with higher quantum number n, the difference in energy of those levels is emitted as radiation with a discrete spectrum, called characteristic X-ray. Important for this work is a part of the characteristic spectrum, called K-radiation, which originates in occupation of empty $1s$-orbitals. The occupying electron must come from an orbital with angular momentum quantum number $l = 1$, i.e.

[2]Tungsten is the element with the second highest melting point of around 3400 °C. This ensures a low contamination of the anode with cathode material.

a p-orbital, because Δl cannot be zero. The radiation is termed Kα- or Kβ-radiation, if the previous orbital was $2p$ or $3p$, respectively. Furthermore, one distinguishes Kα_1- and Kα_2-radiation, depending on the magnetic quantum number of the previous orbital, which can be $\frac{3}{2}$ or $\frac{1}{2}$, respectively. Kα-radiation is desired for probing crystal structures.

Bibliography

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[2] George F. Harrington and José Santiso. "Back-to-Basics tutorial: X-ray diffraction of thin films". In: *Journal of Electroceramics* 47.4 (2021), pp. 141–163. ISSN: 1385-3449, 1573-8663. DOI: 10.1007/s10832-021-00263-6.

[3] Lothar Spieß, ed. *Moderne Röntgenbeugung: Röntgendiffraktometrie für Materialwissenschaftler, Physiker und Chemiker*. 2., überarb. und erw. Aufl. Studium. Wiesbaden: Vieweg + Teubner, 2009. 564 pp. ISBN: 978-3-8351-0166-1.