Chapter 1

Introduction to theory and experimental methods

In this chapter all necessary concepts needed to understand the present work will briefly be introduced. The first three subsections (1.1 - 1.3) are intended to explain what a crystal is, how it is usually described and what happens if you break it, i.e. create a surface. Once a surface is created a method to describe it is needed as well, which will be given. The following two subsections are about the kinematic diffraction theory (1.4) in general as well as the theory of operation of LEED and, in particular, SPA-LEED (1.5). The next section deals with the theory of electrons in lattices in preparation of the Peierls distortion. The last subsection (1.7) focuses on phase-transitions in general as well as the in this work witnessed Peierls transition.

1.1 Crystals, symmetry and order

Before going into detail on how a crystal and it's surface can be described, I would like to address the question: *What is a crystal?* Or to be more precise: *How can a crystal be defined?* The quest of finding an answer to these, rather simple looking, question will lead to another question. A crystal's definition can be found in the *International Tables of Crystallography, Volume A, Chapter 8.1, Basic Concepts*. It goes as follows:

> *Crystals are finite real objects in physical space which may be idealized by infinite three-dimensional periodic ‚crystal structures‘ in point space. Three-dimensional periodicity means that there are translations among the symmetry operations of the object with the translation vectors spanning a three-dimensional space. Extending this concept of crystal structure to more general periodic objects and to n-dimensional space, one obtains the following definition:*
> *Definition: An object in n-dimensional point space E^n is called an n-dimensional crystallographic pattern or, for short, crystal pattern if among its symmetry operations*

> *(i) there are n translations, the translation vectors $t_1, ..., t_n$ of which are linearly independent,*
>
> *(ii) all translation vectors, except the zero vector 0 , have a length of at least $d > 0$.*
>
> *Condition (i) guarantees the n-dimensional periodicity and thus excludes subperiodic symmetries like layer groups, rod groups and frieze groups. Condition (ii) takes into account the finite size of atoms in actual crystals.*
>
> - International Tables of Crystallography A, IUCr [39]

According to this a fundamental property of any *crystal* is the presence of a *periodic structure*, leading to a long-range *order*. In 1982 Shechtman *et al.* unintentionally opened a discussion on the validity of this definition with a publication titled: *Metallic phase with long-ranged orientational order and no translational symmetry* [87]. Giving rise to the question: *Can there be order devoid of symmetry?* Roughly ten years later a preliminary definition was proclaimed by the Commission on Aperiodic Crystals of the International Union of Crystallography (IUCr).

> *In the following by ‚crystal‘ we mean any solid having an essentially discrete diffraction diagram, and by ‚aperiodic crystal‘ we mean any crystal in which three-dimensional lattice periodicity can be considered to be absent.*
>
> - Commission on Aperiodic Crystals, IUCr [46]

As a matter of form the answers to the solicited questions:

> *Yes, there can be order despite the lack of symmetry!*
>
> *If it shows a discrete diffraction image it is considered a crystal!*

The IUC's preliminary definition is rather pragmatic and is being discussed. There are some as interesting as amusing letters on this discussion printed in the *Zeitschrift für Kristallographie 222 (2007), pp. 308-319*, which I recommend for further reading. Since no *aperiodic crystal* has been under investigation in this work henceforth *crystal* refers to a periodic structure with long-range order. I would like to close this section with a quotation taken from one of the letters mentioned above:

> *Throughout it all I wondered, who cares? Whatever its label, Pluto still circles the sun, and planetary scientists still study it.*
>
> - Marjorie Senechal, Zeitschrift für Kristallographie 222 (2007), p. 311, [86]

1.2 Lattice, basis and reciprocal space

Having defined what hereby is meant with crystal, the subsequent question can be approached. *How can a crystal be described?* Two things are needed two describe a crystal or better a crystalline structure. The *lattice* and the *basis* or *pattern*. The lattice describes the long-range order in a crystal for example SC (simple cubic), BCC (body centred cubic) or FCC (face centred cubic). In three dimensions the lattice consists of three, so called, primitive vectors, each of it lying in a different plane, which span the lattice. Within the definition of a crystal given by the IUCr a primitive vector is a special translational vector, as it is the smallest. All other translational vectors a integral multiples of the primitive vector. The first to publish this notation was Auguste Bravais in 1850 [11], hence it is called a *Bravais lattice* and is mathematically described by with the lattice points $\vec{R}_n$ defined as

$$\vec{R}_n = n_1\vec{a_1} + n_2\vec{a_2} + n_3\vec{a_3} \tag{1.1}$$

whereby n_i can be any integer and $\vec{a}_i$ is one of the primitive vectors. This makes a lattice to be an infinite array of points in space. The Bravais lattice can by described as a function of the position vector $\vec{r}$ by a delta function and the Bravais lattice $\vec{R}_n$ itself, i.e.

$$\rho(\vec{r}, \vec{R}_n) = \sum_{n=1}^{N} \delta(\vec{r} - \vec{R}_n), \tag{1.2}$$

which can be interpreted as the probability to find a lattice point at a given position, hence it is labelled ρ. In total there are 14 different Bravais lattices. The rhombohedron spanned by the three primitive vectors is called *primitive unit cell*. Its volume V_{uc} can be calculated by

$$V_{uc} = \vec{a_1}(\vec{a_2} \times \vec{a_3}).$$

A unit cell is called primitive when it contains only one lattice point, i.e. when it is spanned by the primitive vectors, see left hand side of Figure 1.1. A special primitive unit cell is the *Wigner-Seitz cell*. Any point within the Wigner-Seitz cell is closer to the lattice point in its centre than it is to the neighbouring lattice points, see right hand side of Figure 1.1. Though the mathematical description of this kind of tessellation of an euclidean space dates further back, *Eugene Paul Wigner* and *Frederick Seitz* where the first to apply it in the field of physics [113].

In order to create a crystal one needs a *basis* or *pattern* which describes the position of the atoms attached to each point $\vec{R}$ given by the lattice. Figure 1.2 shows a lattice, a basis and the crystal described by them.

Practically every author of every book concerning solid state physics puts the cart before the horse by introducing the reciprocal lattice at this point. Despite knowing better and the lack of a good reason I will do so as well. The reciprocal lattice $\vec{G}_{hkl}$ can be written as:

$$\vec{G}_{hkl} = h\vec{g_1} + k\vec{g_2} + l\vec{g_3}. \tag{1.3}$$

Where (h, k, l) are the miller indices. Like their real-space counterparts $(\vec{a_1}, \vec{a_2}, \vec{a_3})$ the primitive reciprocal vectors $(\vec{g_1}, \vec{g_2}, \vec{g_3})$ are linear independent of each other and can be

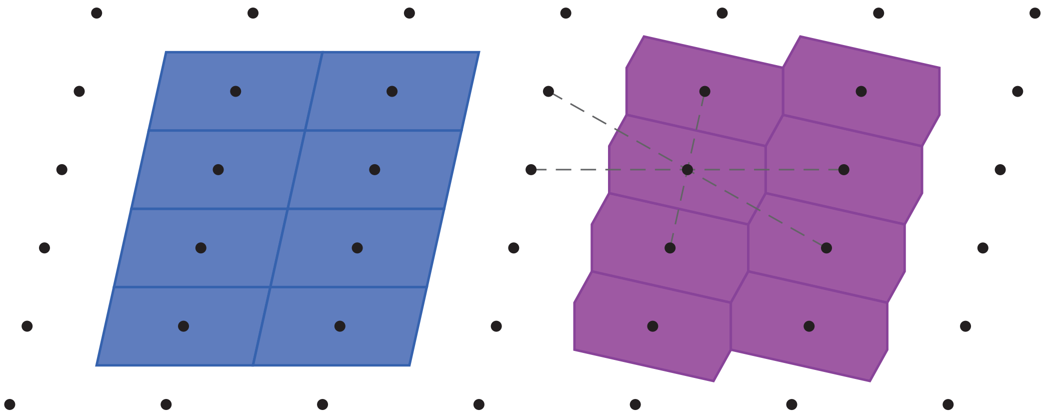

Figure 1.1: Primitive unit cells. The blue coloured diamonds mark the primitive unit cells spanned by the primitive vectors, whereas the magenta coloured polygons mark the Wigner-Seitz cells. The boundaries of the polygon are perpendicular to the lines (dashed) connecting neighbouring lattice points and intercept them in the middle.

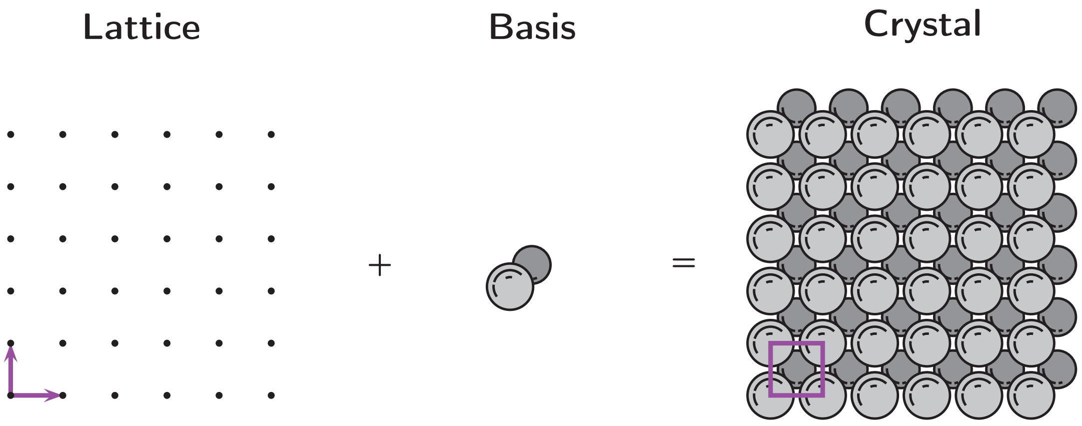

Figure 1.2: Construction of a generic crystal by lattice and basis. From left to right: The underlying lattice (⁚⁚) and its primitive vectors (↑→, not necessarily perpendicular to each other). The basis consisting of two atoms (●). The resulting crystal and its primitive unit cell (□).

calculated from the primitive real-space vectors using:

$$\vec{g_1} = \frac{2\pi}{V_{uc}}(\vec{a_2} \times \vec{a_3}),\ \vec{g_2} = \frac{2\pi}{V_{uc}}(\vec{a_3} \times \vec{a_1}) \text{ and } \vec{g_3} = \frac{2\pi}{V_{uc}}(\vec{a_1} \times \vec{a_2}).$$

The Wigner-Seitz cell of the reciprocal lattice is called *Brillouin zone* (BZ) named after Nicolas Lèon Brillouin, who developed this concept and published it in 1930 [12]. Though of no major importance in real-space, the Wigner-Seitz cell in reciprocal space, i.e. Brillouin zone, is of utmost importance, since it contains information about whether a crystal is of a conducting, semi-conducting or insulating nature.

1.3 Surface reconstructions

> *God made the bulk; the surface was invented by the devil.*
>
> \- Wolfgang Pauli

Let's have a look at the devils work! Since this work is about surface science and mass is not infinite, we usually examine crystals that have finite dimensions. The perfect symmetry of a crystal is broken right where it ends, at its surface.

In order to minimize it's free energy the surface reconstructs itself in a totally new - and most of the time a lot more complicated - way than the bulk crystal. A, so called, *surface reconstruction* evolves. There are other ways to change the face of a surfaces once it has been created. One is to deposit atoms on the surface which, most of the time, leads to a different reconstruction again because of natures pet issue the energy minimization. Heat can lead to a change of the surfaces reconstruction as well. In order to allow for discussions about surfaces the following question has to be answered: *How can a surface reconstruction be described?*

1.3.1 Park & Madden's notation

A possible way to describe a reconstruction is given by Park and Madden [72]. The simplest surface, i.e. the one with the smallest primitive unit cell, is the bulk terminated surface. As a surface is two-dimensional the translational vectors $\vec{T}$ can be described by a linear combination of two linear independent primitive vectors:

$$\vec{T} = n_1\vec{a_1} + n_2\vec{a_2}.$$

Depending on the surface normal the two vectors may even be two of the primitive vectors of the lattice. For instance in case of a (100) surface of a simple cubic crystal the two primitive lattice vectors lying in the surface plane are the two primitive vectors describing the translational symmetry of the bulk terminated surface. By undergoing a reconstruction the surface enlarges its unit cell in order to lower the surface energy.

The geometrical relation between bulk terminated and reconstructed surface can be described by a matrix M:

$$\begin{array}{l} \vec{b_1} = m_{11}\vec{a_1} + m_{12}\vec{a_2} \\ \vec{b_2} = m_{21}\vec{a_1} + m_{22}\vec{a_2} \end{array} \Leftrightarrow \begin{pmatrix} \vec{b_1} \\ \vec{b_2} \end{pmatrix} = M \begin{pmatrix} \vec{a_1} \\ \vec{a_2} \end{pmatrix},$$

$$M = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix}.$$

Where $\vec{a}_i$ are the translational vectors of a bulk terminated and $\vec{b}_i$ the translational vectors of the reconstructed surface. The determinant of the matrix M can be used to describe the relationship between the bulk terminated and the reconstructed surface.

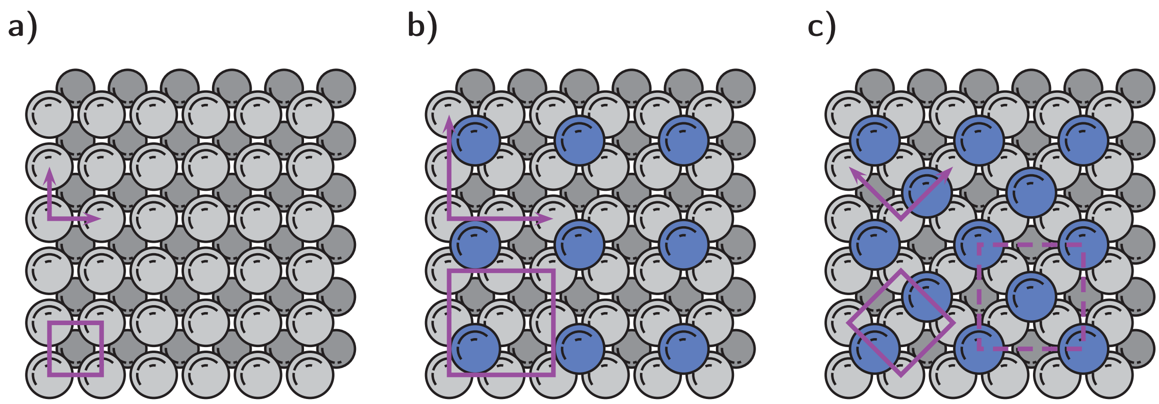

Figure 1.3: View on top of a fcc(100) surface. **a)** Bulk terminated fcc(100) surface. The primitive unit cell (□) is depicted in magenta as well as primitive unit vectors (↱). In Wood's notation a surface of that kind shows a (1×1) reconstruction. **b)** The blue balls (●) indicate some kind of adsorption. The adsorbates change the periodicity into a (2×2) reconstructed surface. **c)** In this case there are two ways to describe the reconstruction: c(2×2) (unit cell denoted by ⬚) or ($\sqrt{2}\times\sqrt{2}$)R45 (primitive unit cell denoted by □). The ‚c‘ prior to the periodicity denotes the *centred* unit cell.

```
If( $\det M \in \mathbb{Z}$ )
        it is called $simple$
else if( $\det M \in \mathbb{Q}$ )
        it is called $coincident$
else
        it is called $incommensurate$
endif.
```

Though it is a precise method, it is not very convenient, as the determinant itself only carries information about the ratio between unit cell sizes and writing the complete matrix is laborious. In most books and publications as well in this work a different notation is used:

1.3.2 Wood's notation

Due to its convenience, Wood's notation [115] is by far more common. Within this notation a reconstruction is given by:

$$X(hkl)(a_1 \times a_2)R\phi - A$$

Where X denotes the substrate and (hkl) are the miller indices indicating the surface normal in terms of the crystal axis. a_1 and a_2 indicate the length of the unit cell vectors in units of the underlying substrate surface unit cell vectors. Sometimes the adsorbate reconstruction is rotated compared to the substrate reconstruction which is indicated by the presence of R followed by the degree of rotation ϕ. Finally the adsorbate is given by

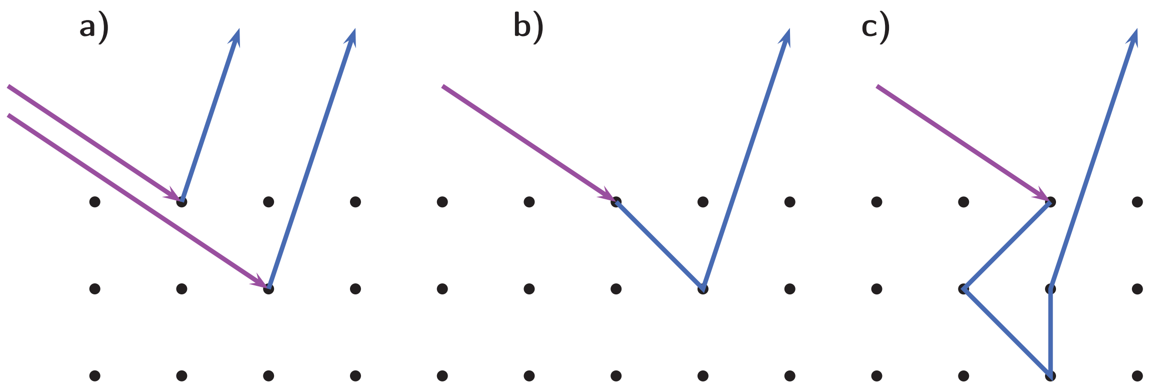

Figure 1.4: Generic scattering paths of electrons or waves, respectively. **a)** Single scattering; the probe interacts only once with the sample or lattice. **b)** Double scattering; the probe interacts twice with the sample. **c)** Multiple scattering; the probe interacts multiple times with the sample. Incident paths are depicted in magenta. Paths after the first scattering event are depicted in blue.

A. In some cases Wood's notation is not bijective, e.g. see Figure 1.3 c). Despite this, given minor drawback, this is the notation being used throughout this work.

Sometimes Wood's notation gets abbreviated. Especially when it comes to this work's subject the (8×2) reconstruction, which is often denoted as a (8×'2') or a (8×„2“) reconstruction. The quotation or single quotation marks are supposed to indicate the striped nature of the reconstruction. I will refrain from doing so.

1.4 Kinematic theory of diffraction at ...

> *Obviously, even allowing for a refraction and change of wavelength due to inner potential, a purely kinematic theory of electron diffraction is incomplete; indeed it is great good luck that it explains as much as it does, for a proper dynamic theory is far harder.*
>
> - Sir George Thomson, Contemporary Physics 9, p. 13, [101]

So far notations for the description of surfaces and lattices have been introduced. This section will focus on the question: *How does a diffraction pattern look like for a given crystal or surface structure?* One of the simplest approaches is the Kinematic Diffraction Theory. In Figure 1.4 some distinctive ways for probes to reach the detector are shown. Only the case shown on the left, i.e. the single scattering path, is taken into account. Though later electrons will be used for probing and since diffraction is an interference phenomena, it has to be explained using waves.

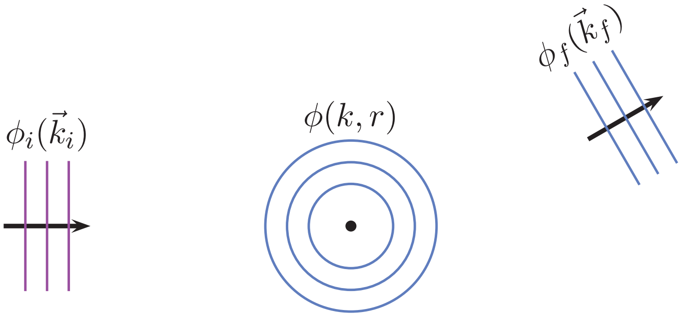

Figure 1.5: Scattering at a singe atom. The incident plane wave $\phi_i(\vec{k}_i)$ is scattered at a atom. Resulting in a spherical wave $\phi(k,r)$ being emitted by the scatterer. Far away from the emitter the spherical wave can be approximated by another plane wave $\phi_f(\vec{k}_f)$. This approximation is justified in an experimental context where the aperture of the detector is small compared to the distance between sample and detector. Wave fronts are depicted by blue and magenta lines, respectively.

1.4.1 Single scatterers

Consider a plane-wave $\phi_i(\vec{k}_i)$ with wave vector $\vec{k}_i$ being elastically scattered by an atom placed at $\vec{r}_0$. The result is a spherical wave ϕ_f with wave number k_f being emitted from point $\vec{r}_0$ (see Figure 1.5). Since only elastically scattered electrons are taken into account the wave number does not change ($k_i = k_f = 2\pi/\lambda$). The amplitude of the emitted wave does not show a spherical symmetry. Depending on initial wave vector $\vec{k}_i$ and observed direction $\vec{k}_f$ the wave's amplitude varies. This variation originates in the scattering potential $V(\vec{r})$ of the scatterer, i.e. the atom, and is described by the so called *atom-form-factor* $f(k_i, k_f)$ which is given by

$$f(\vec{k}_i,\vec{k}_f) = \int \phi_f^* V(\vec{r})\phi_i \, \mathrm{d}^3r$$

where the initial wave

$$\phi_i = e^{i(\vec{k}_i\cdot\vec{r})}$$

and the final, i.e. scattered, wave

$$\phi_f = f(\vec{k}_i,\vec{k}_f)e^{i\vec{k}_f|\vec{r}-\vec{r}_0|}.$$

The atom-form-factor for electrons scattering at a single atom will mainly depend on the charge distribution $\rho(\vec{r})$ of the atom. The atom-form-factor is not our main interest, since we are interested in diffracting electrons at a lot of atoms and I will not go into further details. To make things short the scatterer is placed on the origin ($\vec{r}_0 = 0$). Furthermore, since any measurement will take place far away from the sample ($r \gg r_0$), the scattered spherical wave can be approximated by a plane wave, leaving ϕ_f to be:

$$\phi_f = f(\vec{k}_i,\vec{k}_f)e^{i\vec{k}_f\cdot\vec{r}}$$

This approximation is justified in an experimental context where the aperture of the detector ($\approx \mu$m) is small compared to the distance between sample and detector ($\approx$ dm). A simple and perhaps more accessible analogy to the diffraction of an electron wave at an atom is the diffraction of a laser beam at a slit. In case of a basis being the scatterer the atom-form-factor includes every atom within the basis.

1.4.2 Undistorted lattices

Instead of scattering at a single atom, consider the wave ϕ_i to be scattered at a basis, made of J different atoms. The scattered wave ϕ_f is then given by:

$$\phi_f = \sum_{j=1}^{J} f_j(\vec{k}_i, \vec{k}_f) e^{i\vec{k}_f \cdot \vec{r}}$$

The atom-form-factor f is now indexed to take into account that it is different for each species of atom in the basis. Notice that the different positions of the basis atoms which would lead to a phase shift of the scattered waves ϕ_f with respect to each other is completely ignored, i.e. implicitly included in the atom-form-factor f_j.

Consider a Bravais lattice $\vec{R}_n$ as in equation (1.1), choosing any point of the lattice as the origin, i.e. $\vec{r}_0$. The wave $\psi_{f,0}$ scattered at $\vec{r}_0$ is therefore

$$\psi_{f,0} = \sum_{j=1}^{J} f_j(\vec{k}_i, \vec{k}_f) \cdot e^{i\vec{k}_f \cdot (\vec{r} - \vec{r}_0)}.$$

Every point $\vec{R}_n$ of the lattice will emit a scattered wave $\psi_{f,n}$ similar to $\psi_{f,0}$. The difference between any scattered wave $\psi_{f,n}$ and the wave scattered at the origin $\psi_{f,0}$ is a phase factor, which is given by the difference of the dot-products $(\vec{k}_i \cdot \vec{R}_n)$ and $(\vec{k}_f \cdot \vec{R}_n)$. Introducing the scattering vector $\vec{k}_s$ which is given by $\vec{k}_s = \vec{k}_f - \vec{k}_i$, the phase factor is given by:

$$e^{i(\vec{k}_f \cdot \vec{R}_n - \vec{k}_i \cdot \vec{R}_n)} = e^{i\vec{k}_s \cdot \vec{R}_n}.$$

The scattering vector $\vec{k}_s$ represents the change of the wave vector upon scattering. Hence the scattered waves are given by

$$\psi_{f,n} = \psi_{f,0} \cdot e^{i\vec{k}_s \cdot \vec{R}_n},$$

see Figure 1.6 for a schematic representation. The resulting wave ψ is the sum over all waves $\psi_{f,n}$ from all N lattice points, i.e.

$$\psi = \sum_{j=1}^{J} f_j(k_i, k_f) \sum_{n=1}^{N} e^{i\vec{k}_s \cdot \vec{R}_n} \cdot e^{i\vec{k}_f \cdot (\vec{r} - \vec{r}_0)}$$

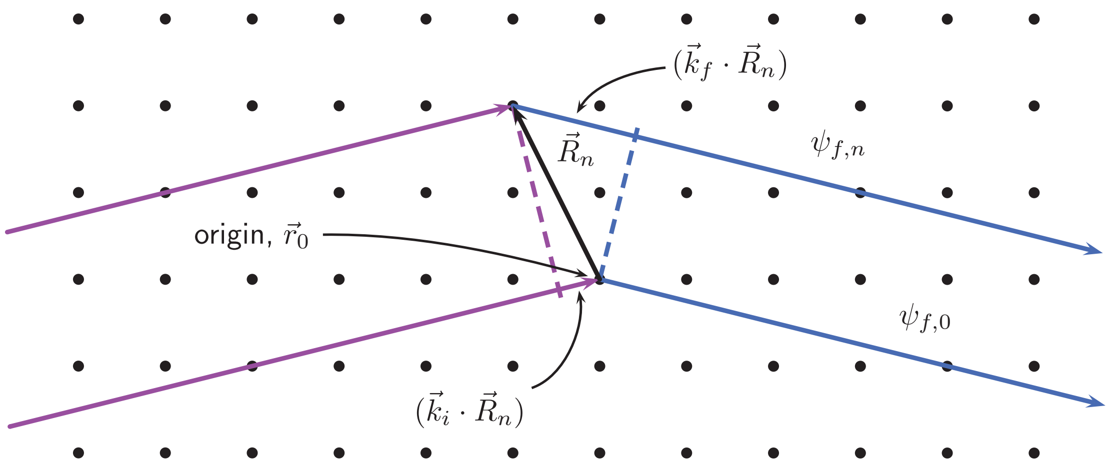

Figure 1.6: The wave vector ($\vec{k}_i$, ↗) of the incident wave ends on two lattice points (•) at which the wave is scattered. The scattered waves ($\psi_{f,0}$ and $\psi_{f,n}$) are depicted for a generic wave vector ($\vec{k}_f$, ↗). The only difference between the two scattered waves at the point of measurement is a phase shift in between them. Remember that the point of measurement is infinitely far away compared to the lattice vectors.

The intensity I of the diffracted wave is proportional to the density of the wave function ψ, i.e. its magnitude squared:

$$I \propto |\psi|^2 = \psi\psi^* = \underbrace{\sum_{j=1}^{J}\sum_{l=1}^{J} f_j(\vec{k}_i, \vec{k}_f) f_l^*(\vec{k}_i, \vec{k}_f)}_{F(\vec{k}_i, \vec{k}_f)} \underbrace{\sum_{n=1}^{N}\sum_{m=1}^{N} e^{i\vec{k}_s(\vec{R}_n - \vec{R}_m)}}_{G(\vec{k}_s)}$$

I consists of two parts. The first part, depending on initial and final wave vector $\vec{k}_i, \vec{k}_f$, is called the *dynamical-form-factor* $F(\vec{k}_i, \vec{k}_f)$. The second part depends only on the positions of the unit cells, i.e. the lattice, and the scattering vector $\vec{k}_s$. This part is called the *lattice-form-factor* $G(\vec{k}_s)$.

$$I \propto F(\vec{k}_i, \vec{k}_f) G(\vec{k}_s)$$

The dynamical-form-factor $F(\vec{k}_i, \vec{k}_f)$ includes the atom-form-factor, multiple scattering processes within unit cell, position of atoms in the unit cells, etc. Unlike the lattice-form-factor the dynamical-form-factor will not play a major role for things to come.

The lattice-form-factor contains solely information about the lattice. Assuming a perfect, i.e. undistorted, Bravais lattice the positions $\vec{R}_n$ can be expressed by:

$$\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3,$$