



Keble College - Hilary 2012
Section VI: Condensed matter physics
Tutorial 2 - Lattices and scattering

Please leave your work in the Clarendon laboratory's 'J' pigeon hole by 5pm on Monday of 4th week.
Suggested reading: Hook & Hall 1.1-1.5, 11.1-11.2; Kittel 1, 2; Ashcroft/Mermin 4, 5.

The underlying microscopic periodicity of a solid is essential to many of its properties. In the next tutorial we will assume that atoms undergo small oscillations around a regular structure and derive quantised excitations called phonons which determine the atomic contribution to the heat capacity of a solid. In the later tutorials we will see how the periodicity of the potential in which electrons move is fundamental to electronic transport properties such as conductivity. In preparation, in this tutorial we will learn the formal language describing lattice structure. We will also see how to determine this lattice structure through scattering experiments.

1 Direct lattice and crystal structure

1. Direct lattice:

- (a) *Definitions* — Explain the following in any order: *lattice*, *lattice vector*, *primitive lattice vectors*, *unit cell*, *primitive cell*, *Wigner-Seitz cell*, and *conventional cell*.
- (b) *Examples of conventional cells* — Draw the conventional cells for *simple cubic*, *body centred cubic* and *face centred cubic* lattices in both plan view and 3D. How many lattice points are there in each conventional cell? Identify them.
- (c) *Example of the Wigner-Seitz cell* — A 2D lattice has primitive vectors $a\mathbf{i}$ and $1.5a\mathbf{j}$. Show how to construct the Wigner-Seitz cell in this case. What special property of the Wigner-Seitz cell makes it useful?

2. Crystal structure:

- (a) *Definitions* — Explain the terms *basis* and *crystal structure*, and how the lattice and basis together form the crystal structure. Given the crystal structure, is the choice of lattice and basis unique?
- (b) *Examples* —
 - i. Give and draw a lattice and basis that together describe the CsCl crystal structure.
 - ii. Now consider the Fe crystal structure. First give and draw a bcc lattice with a basis that together describe this structure. Second give and draw a cubic lattice with a basis that together describe the same structure.
 - iii. Similarly, give and draw two lattice-basis pairs that together describe diamond structure, and a lattice, basis and sub-basis that together describe the same structure.

[Note: Be sure to realise that you write the coordinates describing a basis, this refers to some basis (there are two different uses of the word basis here) of vectors \mathbf{e}_i and some origin, i.e. (x, y, z) denotes the point $x\mathbf{e}_1 + y\mathbf{e}_2 + z\mathbf{e}_3$ with respect to the origin. Usually, the lattice point is assumed to be the origin. However, the basis vectors \mathbf{e}_i are not necessarily the primitive lattice vectors for the lattice you are using, e.g. when you are using a bcc lattice you usually use the primitive lattice vectors of the conventional cubic lattice as basis vectors in terms of which to describe the locations of atoms in the basis. Make sure you understand what you are writing down, and write it down clearly.]

The direct lattice, basis and crystal structure describe the arrangement of atoms in a solid and are therefore important for a number of reasons. In the next tutorial we will see how the periodicity of this arrangement and the number of atoms in the basis determines the type of collective vibrational motion the atoms may undergo. In tutorial 5 we will see how the arrangement of atoms, e.g. the number of nearest neighbours, can influence the magnetic properties of a solid.

2 Reciprocal lattice

3. (a) *Definitions* — Define the set of reciprocal lattice vectors $\{\mathbf{K}\}$ in terms of the set of direct lattice vectors $\{\mathbf{R}\}$. [Hint: Your answer should be an equation involving a scalar product.] Explain what is meant by the n -th Brillouin zone.
- (b) *Useful choice of primitive reciprocal lattice vectors* — Let \mathbf{a}_i ($i = 1, 2, 3$) be primitive lattice vectors of the direct lattice. Show that if we define \mathbf{b}_i by

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)},$$

with cyclically permuted expressions for \mathbf{b}_2 and \mathbf{b}_3 , \mathbf{b}_i constitute primitive lattice vectors of the reciprocal lattice. Show that for this choice of primitive reciprocal lattice vectors, $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$. Is this choice of primitive reciprocal lattice vectors unique? Do all choices satisfy $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$?

- (c) *Volume* — If a primitive cell of the direct lattice has volume Ω , what is the volume of a primitive cell of the reciprocal lattice?
- (d) *Example* — Using this choice of primitive reciprocal lattice vectors or otherwise, construct the reciprocal lattice and first two Brillouin zones for the 2D lattice in Qu. 1(c).

The reciprocal lattice is one of the most important concepts in this course. We will see in tutorial 3 and 4 that vibrational modes and electron eigenstates are both described by some wavevector \mathbf{k} in reciprocal space. The invariance of reciprocal space under translations by a reciprocal lattice vector follows from the invariance of the equations of motion in real space under translations by a direct lattice vector. The structure of the reciprocal lattice will therefore be vital in understanding the properties of solids, e.g. the overlap of the Fermi surface with a Brillouin zone boundary causes a solid to be an insulator or semi-conductor rather than a metal.

3 Families of planes, Miller indices and reciprocal lattice vectors

4. (a) *Families of planes and the direct lattice* — Any infinite family of parallel equally spaced planes of which one contains the origin (referred to as a family of planes) can be defined in the following way: for every integer n there is a plane containing all three points $n\mathbf{a}_1/h$, $n\mathbf{a}_2/k$ and $n\mathbf{a}_3/l$, where \mathbf{a}_i are primitive lattice vectors of the direct lattice. As such, we denote the family of planes by a Miller index (hkl) . Alternatively, the family can be defined as the equally spaced planes, with one plane containing the origin and its adjacent plane intercepting the axes defined by $\hat{\mathbf{a}}_1$, $\hat{\mathbf{a}}_2$, $\hat{\mathbf{a}}_3$ at a_1/h , a_2/k and a_3/l , respectively. Assume that every lattice point lies on one of the planes (this can be included in the definition of a family of planes as used in this course), and use this to show that h , k and l are integers.
- (b) *Families of planes and the reciprocal lattice* — Another way of defining a family of planes (hkl) is by the equations $\mathbf{K}_{(hkl)} \cdot \mathbf{r} = 2\pi n$, for all integers n . Show that the spacing between the planes is given by $d_{(hkl)} = 2\pi/|\mathbf{K}_{(hkl)}|$. Use the fact that every lattice point lies on one of the planes to show that $\mathbf{K}_{(hkl)}$ must be a reciprocal lattice vector. Use this and

the definition in part (a) to show that $\mathbf{K}_{(hkl)} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$, where \mathbf{b}_i are primitive reciprocal lattice vectors obeying $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$.

- (c) *Families of lattice planes* — Show that $h' = mh$, $k' = mk$ and $l' = ml$, where m is an integer, denotes another family of planes ($h'k'l'$) that are parallel to the first family but whose spacing is changed as $d_{(h'k'l')} = d_{(hkl)}/|m|$. Then show that a family of planes (hkl) is a family of lattice planes iff h, k, l have no common factors, and in the process define what is meant by a family of lattice planes. Therefore show there is a unique two-way correspondence between a family of lattice planes and the shortest reciprocal lattice vector in a given direction.
- (d) *Example* — For the lattice in Qu. 1(c), draw the families of planes with Miller indices (11), (20) and ($\bar{1}2$), and the reciprocal lattice vectors to which they correspond. Which are families of lattice planes?

We have discussed families of planes, their spacing and their relation to the reciprocal lattice vectors. The reason for this is that, while it is not practical to obtain the direct or reciprocal lattices directly from experiments, it is possible to obtain the spacing and sometimes orientations of families of planes. The discussion in the previous section then tells us how to infer from this the form of the direct and reciprocal lattice. Before practicing making such inferences, we will first look at how the spacing and orientations of lattice planes may be measured.

4 Scattering principles and experimental methods

5. Incident X-rays or neutrons are scattered and constructively interfere at certain angles characteristic of the crystal. The expected peaks are given by Bragg's law

$$n\lambda = 2d_{hkl} \sin \theta,$$

where n is a positive integer, λ is the wavelength of the incident radiation, $d_{(hkl)}$ is the spacing of the family of planes (hkl) from which the X-rays or neutrons are scattered and θ is the scattering angle.

- (a) *Bragg formulation* — Derive Bragg's law using geometrical arguments in terms of families of lattice planes.
- (b) *Von Laue formulation* — Derive Bragg's law by first using simple scattering and interference arguments, where each lattice point is considered to be an identical scatterer (see e.g. page 97 of Ashcroft and Mermin), to derive the Laue condition.
- (c) *Structure factor and atomic form factor* — Again using simple scattering arguments, where this time scattering is from atoms forming the basis and atomic constituents, explain what is meant by the terms *structure factor* and *atomic form factor*, respectively. How does the X-ray atomic form factor vary with θ and Z for a typical atom, where Z is the number of electrons?

Let us now treat scattering more formally. In this approach (which is closely related to the lecturer's approach), we use that for small interactions between the crystal and a particle incident on it, the probability of later observing the particle with wavevector \mathbf{k}'' far away from the crystal is the modulus squared of

$$\Psi \propto \int V(\mathbf{r}) e^{-i(\mathbf{k}'' - \mathbf{k}') \cdot \mathbf{r}} d^3\mathbf{r},$$

where \mathbf{k}' is the initial wavevector of the radiation and $V(\mathbf{r})$ is the potential felt by the particle. This comes from Fermi's Golden Rule with the assumption that neither the state of the crystal nor the internal state of the particle is excited by the interaction (elastic scattering).

We note that the potential must have the same translational symmetry as the the crystal, hence

$$V(\mathbf{r}) = \sum_{\mathbf{R}} v(\mathbf{r} - \mathbf{R}),$$

where the sum is over all direct lattice vectors \mathbf{R} and $v(\mathbf{r})$ is the potential due to a single primitive cell with its lattice point at the origin. If the particle is an X-ray and hence is scattered primarily by electrons, then

$$v(\mathbf{r}) \propto \sum_j \rho_j(\mathbf{r} - \mathbf{r}_j),$$

where the sum is over the atoms j making up the basis at positions \mathbf{r}_j , and $\rho_j(\mathbf{r})$ is the density of electrons around atom j if it were at the origin. For neutrons, which in the simplest case are scattered by nucleons,

$$v(\mathbf{r}) \propto \sum_j b_j \delta^3(\mathbf{r} - \mathbf{r}_j),$$

where we have approximated the nucleus of each atom by a delta function and b_j is the nuclear scattering length. Since the neutron-nucleon interaction is not quite as simple as that of the X-ray and electron, b_j is not so easy to define in terms of more fundamental quantities and must be found experimentally. It is, however, typically a real quantity.

6. (a) Consider the direct lattice to be a sum of delta functions in space, one at each lattice point, i.e.

$$L(\mathbf{r}) = \sum_{\mathbf{R}} \delta^3(\mathbf{r} - \mathbf{R}),$$

where the sum is over all direct lattice points \mathbf{R} . Show that $V(\mathbf{r}) = (L * v)(\mathbf{r})$ where the asterisk represents a convolution.

- (b) Let $G(\mathbf{k})$ be the normalised Fourier transform of $L(\mathbf{r})$,

$$G(\mathbf{k}) = \frac{\Omega}{(2\pi)^3} \int L(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}} d^3\mathbf{r} = \frac{1}{(2\pi)^3} \sum_{\mathbf{R}} e^{-i\mathbf{k} \cdot \mathbf{R}} = \sum_{\mathbf{K}} \delta^3(\mathbf{k} - \mathbf{K}),$$

where Ω is the volume of a primitive cell. Argue that $G(\mathbf{k})$ is the reciprocal lattice (in the same sense that $L(\mathbf{r})$ is the direct lattice).

- (c) Use the convolution theorem to show that for $\Delta\mathbf{k} = \mathbf{k}'' - \mathbf{k}'$

$$\Psi \propto G(\Delta\mathbf{k})S(\Delta\mathbf{k}),$$

where

$$S(\mathbf{k}) = \sum_j f_j(\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{r}_j},$$

and give $f_j(\mathbf{k})$ for both X-rays and neutrons and, for X-rays and $1/|\mathbf{k}|$ much larger than the size of an atom, give $f_j(\mathbf{k})$ in terms of the number of electrons Z .

- (d) Relate this result back to Bragg's law, the structure factor and the atomic form factor.
7. (a) Explain in reasonable detail how each of the (i) Laue photograph, (ii) rotating crystal, and (iii) powder methods is used to determine the spacing (and orientation) of families of lattice planes. For each method, describe which parameters are varied and how, the diffraction pattern obtained, for what purposes the method is especially useful, and list the factors that effect the intensity of the diffraction spots.
- (b) What are the relative advantages and disadvantages of X-rays and neutrons in determining crystal structure? Describe very briefly how each may be produced.

5 Inferring the lattice structure

8. Explain why X-ray diffraction may be observed in first order from the (110) planes of a crystal with a body-centred cubic lattice, but not with a face-centred cubic lattice. [Hint: In each case, draw the xy -plane plan view of the conventional cell and the planes.]

A collimated beam of monochromatic X-rays of wavelength 0.162 nm is incident upon a powdered sample of the cubic metal palladium. Peaks in the scattered X-ray pattern are observed at angles of 42.3° , 49.2° , 72.2° , 87.4° and 92.3° from the direction of the incident beam. Identify the lattice type, and calculate the nearest-neighbour distance. Check that this is consistent with the fact that the density and atomic mass of palladium is 12023 kg m^{-3} and 106.4, respectively.

9. In NaH crystals, the H atoms were thought to be displaced from the Na atoms either by $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ or by $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ to form the ZnS (zinc blende) structure or NaCl (sodium chloride) structure, respectively. [Note: Here, displacements are in terms of a conventional cubic primitive lattice vectors.] To distinguish these models a neutron powder diffraction measurement was performed. The intensity of the Bragg peak indexed as (111) was found to be much larger than the intensity of the peak indexed as (200).

Using the conventional cubic lattice, write down expressions for the structure factors S_{hkl} for neutron diffraction assuming NaH has (i) the sodium chloride (NaCl) structure, and (ii) the zinc blende (ZnS) structure. Hence, deduce which of the two structure models is correct for NaH.

[Hint: For neutrons, the atomic form factor is proportional to the nuclear scattering length. The nuclear scattering lengths of Na and H are $0.363 \times 10^{-5} \text{ nm}$ and $-0.374 \times 10^{-5} \text{ nm}$, respectively.]