PHS 460
X-ray crystallography and structural analyses 3 units

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Recommended text books: Introduction to Solid State Physics- C. Kittel; Solid State Physics- N. W. Ashcroft and D. Mermin; and of course the web, you may check wikipedia

Highlights

Crystal morphology, crystal optics, classification of crystals, x-ray diffraction methods, theory and applications, polarization, interference, dispersion in crystals, single crystals and polycrystalline structure

Few terms:

- Crystallography is the science of the study of macroscopic crystal.
- Term “crystal” refers to the structure and symmetry of materials.
- The advent of the x-ray diffraction, makes it possible to study the atomic arrangements of atoms in crystalline materials.

We can now define a crystal:

As a region of matter within which atoms are arranged in a three-dimensional (translational) periodic array”,

With this orderly arrangement known as the crystal structure.

Therefore, X-ray crystallography is study of discovering and describing the crystal structure.

Before we go on to discuss Crystal Morphology, let us look at the elementary definition of crystal structures:

- **Crystal structure**

Crystal structure is an arrangement of atoms (or molecules in crystalline materials).

A crystal structure is composed of an array, which is a set of atoms arranged in a particular way, and a lattice.

Crystal structure = (Bravais) lattice + basis

The arrays in crystalline materials form patterns that are located upon the points of a lattice.

The array of points are repeated periodically in three dimensions and the points can be thought of as forming identical small boxes.

The lengths of the edges of a unit cell and the angles between them are known as the lattice parameters or lattice constants (a, b, c). The symmetry properties of the crystal are embodied in its space group.

We can define a Bravais lattice in terms of the lattice parameters a, b, c and angle theta of the unit cell.

Crystal structure = (Bravais) lattice + basis

The lattice has the same translational symmetry as the crystal structure.

It is invariant under rotation of pi and 2*pi about any lattice point.

Note that for a cubic crystal structure, the lattice parameters are equal i.e. the lengths of the unit cells a=b=c, while this is not true for non-cubic systems.

A crystal structure with its symmetry play a role in determining many of its physical properties, such as cleavage, electronic band structure, and optical properties.

- **We shall return later to discuss in more detail, the concept of crystal structure.**

Primitive translation vectors

Let us consider a 2D crystal with lattice parameters a1 and a2 with angle theta.

So that, a1 = a1x(along x-direction) + a1y(along y-direction)
And a2 = a2x(along x-direction) + a2y(along y-direction)

The primitive translation vectors mirrored in the x-axis, along the Cartesian x, y axes will be:
a1(prime) = a1x(along x-direction) – a1y(along y-direction)
And a2(prime) = a2x(along x-direction)- a2y(along y-direction)

Note that “along the x-direction and along the y-direction” represent unit vectors

If the resulting lattice is invariant under the reflection then a1(prime) and a2(prime) are lattice vectors too.

For a BCC, the primitive translational vectors are: a(prime) = a/2 (x(cap) + y(cap) - z(cap)), b(prime) = a/2 (-x(cap) + y(cap) +z(cap)), c(prime)= a/2(x(cap)-y(cap)+ z(cap))

For an FCC, we have a(prime)= a/2(x(cap) + y(cap)), b(prime) = a/2(y(cap) + z(cap)), c(prime) = a/2(z(cap) + x(cap))

Here, the cap means unit vectors along the x, y and z axes.

Lattice planes and directions

From a previous course on Introductory Solid State Physics, we all know Miller Indices and these are used to obtain planes and directions

At this point, we can now give a clear and broad definition of X-ray crystallography:

It is a method of determining the arrangement of atoms within a crystal, in which a beam of X-rays strikes a crystal and diffracts into many specific directions.

The angles and intensities of the diffracted beam produces a three-dimensional picture of the density of electrons within the crystal (on a photographic film).

This allows to determine the electron density and the mean positions of the atoms in the crystal. Also, the chemical bonds, the degree of disorder and various other information can be obtained.

Since many materials can form crystals — such as salts, metals, minerals, semiconductors, as well as various inorganic, organic and biological molecules

X-ray crystallography has been fundamental in the development of many scientific fields.

The method also revealed the structure and functioning of many biological molecules such as DNA.

X-ray crystallography is still among the major methods for characterizing the atomic structure of new materials.

X-ray crystal structures can also account for unusual electronic or elastic properties of a material.

Shed light on chemical interactions and processes, or serve as the basis for designing pharmaceuticals against diseases.

As we will learn in the later part of this course,

There are many different methods of X-ray diffraction.
The condition for constructive interference in crystal planes is the Bragg's Law:

Which states n*lambda = 2d*sin(theta).

We all are aware of this Law from previous courses (PHS 360 and PHS 362)

However, the processes involved in any X-ray diffraction measurement is that a:

crystal is mounted on a rotating spindle of some kind

rotated gradually while being bombarded with beam of X-rays

producing a diffraction pattern of regularly spaced spots *reflections (pattern on a photographic screen)*.

The two-dimensional images taken at different rotations are converted into a three-dimensional model of the density of electrons within the crystal using the mathematical method of Fourier transforms (see the class Lecture Note for mathematical details)

Scattered wave amplitude

Recall, a crystal is invariant under any transformation of the form:

T = ua + vb + wc
Where u, v and w are integers.

The implication of this statement is that:

Properties of the system such as electron density, etc are invariant under T.

If the electron density is periodic with periods a, b and c,

Then, n(r + T) = n(r)

Means we can show that n(r) by Fourier Analysis must be equal n(r + T).

A few things on reciprocal and diffraction condition in reciprocal lattice are necessary here!

X-ray crystallography is related to several other methods for determining atomic structures.

Similar diffraction patterns can be produced by scattering electrons or neutrons (these can also be interpreted as a Fourier transform)

In cases where single crystals of sufficient size cannot be obtained, other X-ray methods can be applied to obtain less detailed information:

fiber diffraction, powder diffraction and small-angle X-ray scattering (SAXS)

- these methods are beyond the scope of the present course contents.

If the material under investigation is only available in form of nanocrystalline powders or suffers from poor crystallinity the methods of electron crystallography can be applied for determining the atomic structure.

Crystal Morphology

- As mentioned earlier, crystals are formed by repetition arrangements of atom in space (unit cells in 3-D space).

- Crystal morphology is also dependent upon the manner (*i.e.*, rate and direction) in which the crystal grows.
- Crystal formation can be divided into two stages:

(1) nucleation and (2) crystal growth.

- Nucleation and crystal growth are dependent upon:
- Temperature (T)
- Pressure (P)
- Composition (X) of the surrounding fluid/vapor

- Availability of surface area

Crystal growth involves:

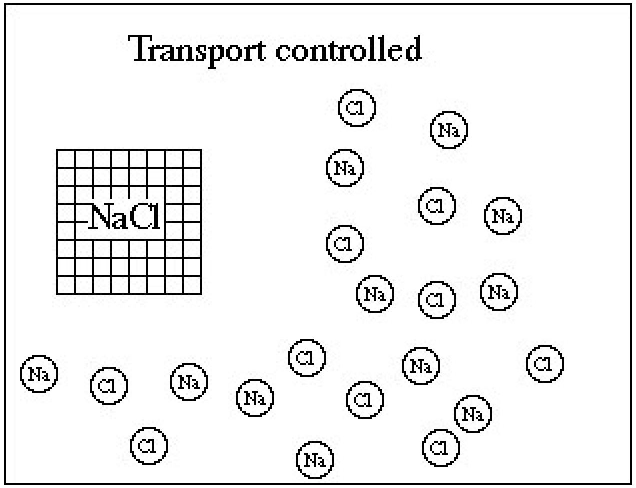
- The transport of ions to the surface of the crystal.
- Reactions at the surface.
- Removal of reaction products from the crystal.

(imagine an analogy of Frenkel and Schottky Defects in solid state physics)

Models for crystal growth

- **Transport-controlled** growth - growth is limited by the rate at which ions can migrate to the surface via diffusion and advection.

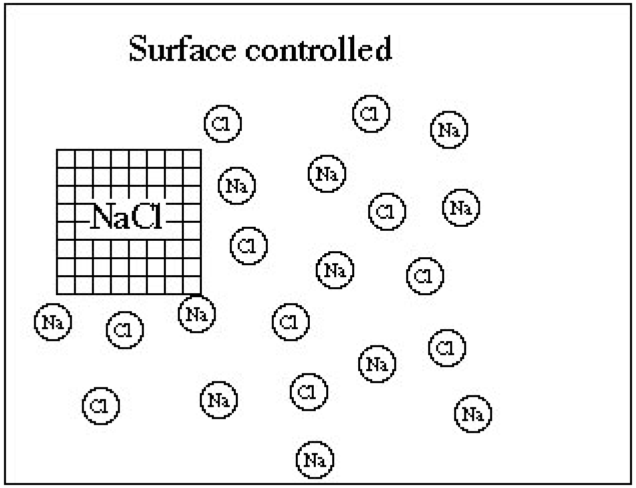
Transport-controlled growth



Surface-reaction controlled growth

- where growth is limited by the rate of reaction at the surface.

Surface-reaction controlled growth



Crystal optics

Branch of optics that describes the behaviour of light in anisotropic *media*

Anisotropic media-- light behaves differently depending on which direction the light is propagating.

In anisotropic material-- the index of refraction depends on both composition and crystal structure.

Crystals are often naturally anisotropic, and in some media (such as liquid crystals) it is possible to induce anisotropy by applying an external electric field.

Classification of crystal and the rest of the notes

The remaining parts of this notes are found in the class Lecture Notes. Which also contains the mathematical equations.