

Electron Diffraction and Crystal Structure

1. Introduction

In classical mechanics we describe motion by assigning momenta to point particles. In quantum mechanics we learn that the motion of particles is also described by waves, with the crucial parameters of the two viewpoints related through the de Broglie relation:

$$\lambda = \frac{h}{p} \quad [1]$$

where p is the momentum, λ is the wavelength, and h is Planck's constant

$$h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s} = 4.136 \times 10^{-15} \text{ eV} \cdot \text{s}.$$

To observe wave-like behavior, we require some kind of grating where the “distance between slits” is of order the wavelength. At typical laboratory energies, the electron's de Broglie wavelength is of order one Angstrom (10^{-8} cm), about the same size as the interatomic spacings in common crystals. The regular atomic arrays in crystals are thus perfectly scaled gratings for creating a “matter wave” diffraction pattern, measuring their wavelength, and verifying Eq. 1. As an added bonus, with the principle verified, the diffraction patterns then become powerful tools for the study of crystal structure.

In this experiment, you will use a cathode ray tube with a graphite crystal target that shows the diffraction pattern on the screen. You will verify the de Broglie relation, and analyze crystal structures, including measurement of the inter-atomic distance in the crystal.

2. Basic Principles

a. The de Broglie Wavelength vs. Voltage

In the cathode ray tube the electron is accelerated through high voltage V . Its energy and momentum are then given by

$$E = \frac{p^2}{2m} = eV \quad [2]$$

Solving for the momentum, and substituting into Eq. 1 gives:

$$\lambda = \frac{h}{\sqrt{2eVm}} \quad [3]$$

You should verify for yourself that this can be re-written in the practical form

$$\lambda(\text{Angstroms}) = \sqrt{\frac{151.3}{V(\text{volts})}} \quad [4]$$

Thus, a 150 V electron has a de Broglie wavelength of 1 Angstrom, and the wavelength should vary in inverse proportional to the accelerating voltage.

b. Crystal Lattice Spacing

A crystal is a very regular array of atoms. The regularity can be quantified in terms of certain small patterns of atoms, called **unit cells**, which are repeated over and over again. Since the vertices of

the unit cell are atoms, the size of the unit cell is related to the inter-atomic spacing, or **lattice constant**, which is usually called **a**.

This experiment will be done with a graphite (carbon) crystal that has a hexagonal structure. For a simple hexagonal crystal such as graphite, the lattice is as shown below. The (100) and (110) planes, which respectively give rise to the inner and outer rings in the electron diffraction tube, are shown at right; the ratio of the d-spacings $d_{100}/d_{110} = \sqrt{3}:1$. These spacings have been defined in terms of the unit vectors **a** and **b** where $a = b$ in the case of the hexagonal structure. The indices (100), (110), etc. are known as Miller indices.

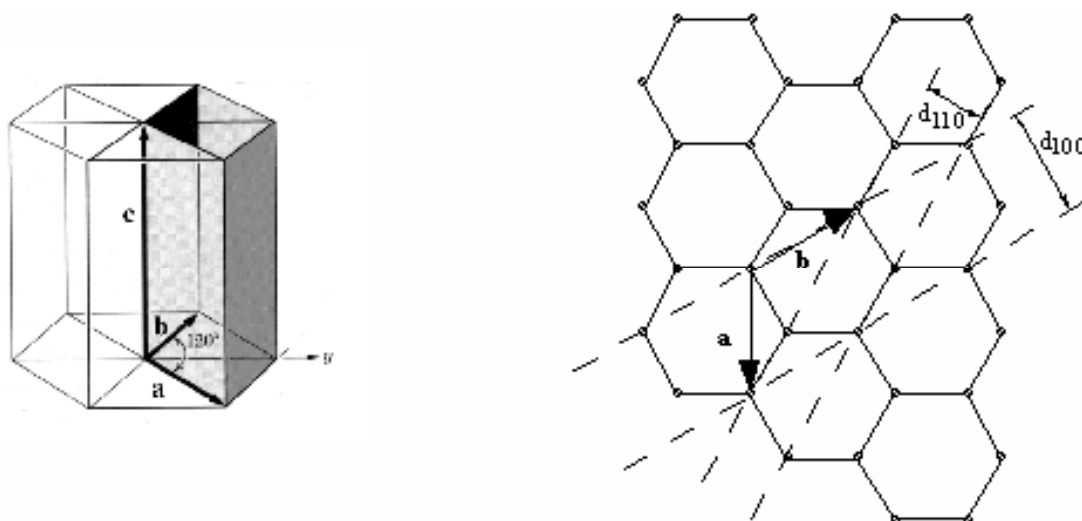


Figure 1: The unit cell and lattice spacings for graphite.

c. Bragg Reflection

A rigorous description of crystal diffraction starts with a plane wave of electrons, treats each atom as an individual source of re-scattered spherical waves, and solves the three-dimensional problem of summing over all the expanding wavefronts. The standard solution is very interesting and elegant application of crystallography and Fourier analysis. You may enjoy the treatment in Chapters 1-2 of **Kittel**, which start from the diffraction problem and build up a theory of crystal structure, or Chapter 4-6 of **Ashcroft and Mermin**, which start from crystallography and then develop an analysis of diffraction.

However, as is frequently the case, there is a somewhat heuristic description based on a simple physical model, which is easy to understand, and gets exactly the right answer. This picture was formulated by W.H. and W. L. Bragg (father and son) in 1913, in order to explain very sharp peaks observed at certain angles in the reflection of **x-rays** from crystals. This work won the Braggs the Nobel Prize in 1915.

Because it is really about the wave nature of the scatterer, the Bragg picture applies equally well to electrons. We think of the regular array in the crystal in terms of **planes** of atoms. Each plane reflects wave like a simple plane mirror, with the angle of reflection equal to the angle of incidence (a.k.a **specular reflection**).

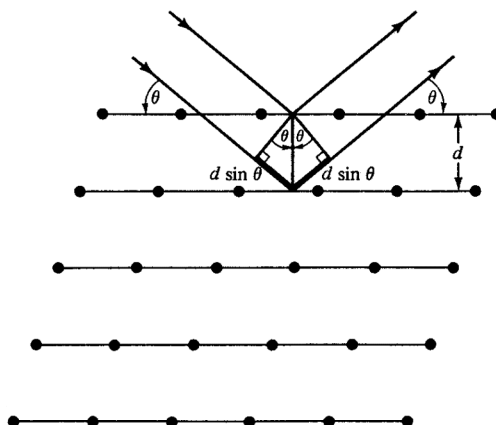


Figure 2 Bragg's picture of crystal diffraction as multiple specular reflections.

The sum of the reflections from a large number of parallel mirrors all separated by the same distance, **d**, will produce strong diffraction peaks when the angle between the beam and surface satisfies the **Bragg condition**

$$2d \sin \theta = n\lambda \quad [5]$$

In 1927, fourteen years after Bragg's work with x-rays, Davison and Germer, working at Bell Labs, observed a strong diffraction peak in electron scattering from nickel. The wavelength of the "electron wave", as calculated from the Bragg formula and the lattice constant of nickel, was exactly as predicted by de Broglie. This was verified shortly thereafter by G. Thompson in Scotland.

De Broglie got the Nobel Prize in 1929. Davison's result was completely accidental (see Serway for the funny story). Thompson, who verified that the electron was a wave, was the son of J.J. Thompson, who discovered that the electron was a particle! Davison and Thompson got the Nobel Prize in 1937.

d. The "Powder Method"

The Bragg picture tells us that a beam of fixed wavelength (i.e. fixed energy) striking a crystal at the right angle will have its reflection reinforced by constructive interference. The obvious experimental plan is to measure scattering intensity vs. angle. However, given a single uniform crystal, the not-so-obvious problem is how to sample *all* of the possible angles. One way to do this is to hold the detector fixed and rotate the crystal. Alternatively, one could vary the beam *energy*, hoping to hit the right wavelength for the unknown orientation of the crystal.

The problem is nicely finessed by the idea, due to Debye and Scherrer, to use a powder or *polycrystalline* sample. A poly-crystal is a conglomerate of a large number of small crystal domains, where each domain is large enough to embody the "true" crystal structure, but all of the domains are oriented randomly with respect to each other. (Why would crystals form in this way?) A beam incident on a bulk sample will find many domains oriented at the correct Bragg angle for the beam energy. Think through the simple geometry of this and convince yourself that the locus of the strongly reflected wave will be a *cone with half-angle equal to twice the Bragg angle*.

The situation is shown schematically on the left in Figure 3. This technique also naturally projects a diffraction *pattern* onto a screen, for easy analysis via photograph or similar technique.

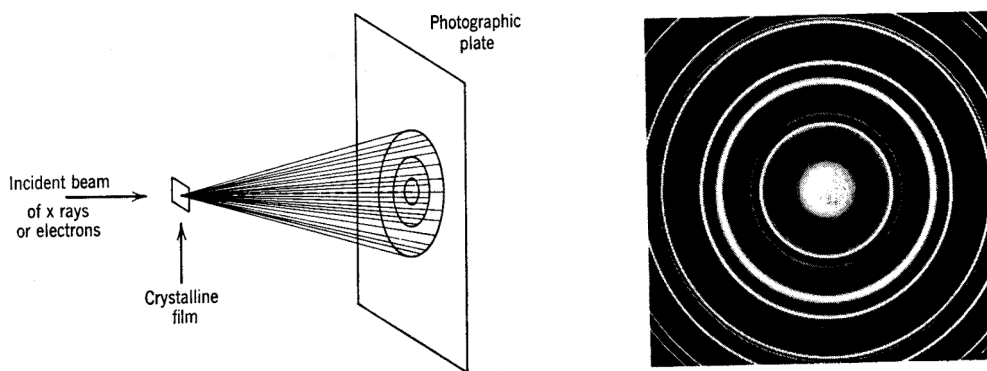


Figure 3 Left: The Debye-Scherrer technique. Right: The diffraction pattern of Au. (Eisberg & Resnick)

The diffraction maximum traces a circle in the projection plane. The circle is the base of a cone whose half-angle is given by

$$\alpha = 2\theta_{\text{Bragg}} = \tan^{-1} \left[\frac{R}{L} \right] \quad [6]$$

where R is the radius of the circle, and L is the distance from the target to the screen. Combining this with the Bragg condition, and assuming $R \ll L$ gives

$$\frac{dR}{L} = n\lambda = \frac{nh}{\sqrt{2eVm}} \quad [7]$$

and thus, if L and λ are known, measurement of the radius yields d , the distance between Bragg planes. Electron diffraction becomes a tool for measuring inter-atomic distances in crystals and, as we will see, the rich detail of crystal structure. Debye won the Nobel Prize in 1936.

e. Some Crystallography

A pattern using polycrystalline gold is shown on the right of Fig. 3. The prediction of a circular diffraction pattern is correct, but there are many maxima. We must conclude there are many different Bragg planes with different separations. In fact, this is a simple consequence of the fact that in a fixed lattice structure, there are many ways to “draw planes”. A two dimensional example is shown in Fig. 4 below. Besides the obvious “horizontal and vertical” rows as in Fig. 2, we can draw a set of planes where each atom is “2-down and 1-over” from its neighbor. The distance $\mathbf{d}$ between these planes is different from the distance $\mathbf{a}$ between atoms, leading to a different Bragg angle, and thus a different ring radius compared to the situation shown in Fig. 2. Each of the many other ways to make planes (“2-down, 2-over”, etc.) leads to a different $\mathbf{d}$, a different circle, and the possibility of the complex pattern in Figure 3.

The three dimensional version of the array in Fig. 2 is called a simple cubic array. There are two other kinds of cubic arrays, face-centered, and body-centered, shown in Fig. 5. And there are many other kinds of non-cubic crystal arrangements (hexagonal-close-packing, diamond, etc.), as well as the possibility of mixing up different atomic species (leading to periodic patterns in $\mathbf{a}$). The ways to “draw” Bragg planes are different in all these structures, and electron (or x-ray) diffraction is a method of choice for understanding and distinguishing them.

Understanding the physical correspondence between the diffraction pattern and crystal structure requires a formalism for describing the crystal lattice. The careful treatment of this problem is a

fascinating mathematical exercise, the basis of crystallography, and the starting point of solid-state physics. We urge you to study the treatment in the references.

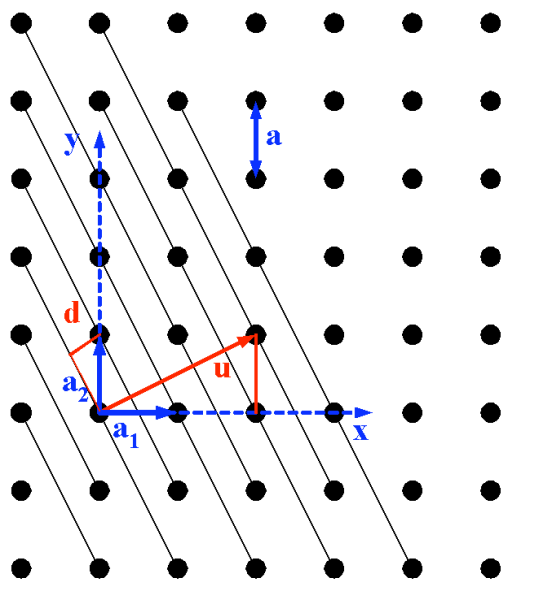


Figure 4 A Bragg plane in a 2-D “cubic crystal”, and its normal vector $\mathbf{u}$, whose numerical coordinates in the $\mathbf{a}_1 \mathbf{a}_2$ basis are the Miller indices.

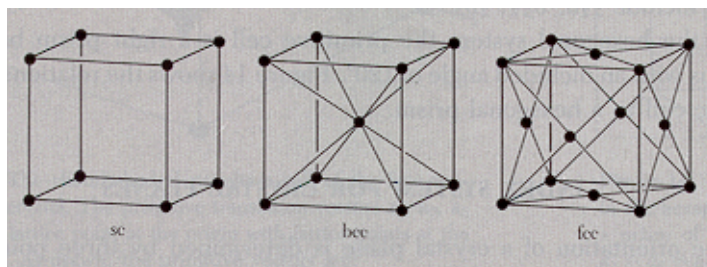


Figure 5 Unit cells of the Simple Cubic, Body Centered Cubic, and Face Centered Cubic Arrays (Kittel)

For now, however, we lay out a simple, physically appealing construction, with some implied terminology from crystallography. We are interested to specify the “Bragg planes” and the distance between these planes. A plane is specified by its normal vector. Consider the two-dimensional representation shown in Fig. 4. The lattice constant is a . The **unit-cell** for this lattice is a square of side a . The **primitive-vectors** are vectors of “unit-length” a , defining coordinate axes in directions along the sides of the primitive cells. The Bragg planes for “2-down and 1-over” are shown. The perpendicular vector to these planes, $\mathbf{u}$, is “2-over and 1-up”. In the business, this is called the “(2,1) plane”. The numbers 2 and 1 are called **Miller indices**. In three dimensions, the Miller indices for a Bragg plane are the smallest set of integers (h, k, l) that specify the direction of the normal vector in the basis defined by $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$. Some examples for the simple cubic lattice are shown in Fig. 6.

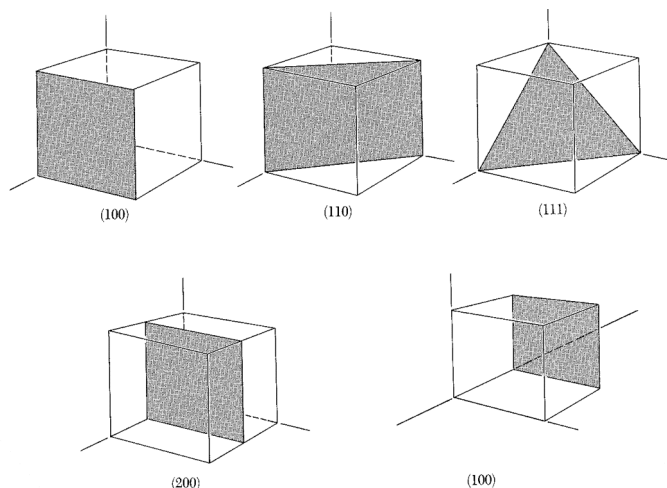


Figure 6 Some Bragg planes of the SC lattice (Kittel)

Having a way to label the planes, the remaining problem in understanding the diffraction pattern is to specify the distance, d , between the planes. The general solution is an elegant exercise in crystal symmetry and Fourier analysis, and is discussed in the references.¹

3. Experimental Technique

a. Apparatus

The electron diffraction tube is a small cathode ray tube (CRT) similar to that in a small (old-fashioned) TV set. The electrons pass through a target that consists of graphite, only a few molecular layers thick, vapor-deposited on a micromesh nickel grid. The target is crystalline in tiny regions, so a "powder" diffraction pattern results, seen as a pair of rings around a central spot on the luminescent screen. See diagram below. The distance between the target and phosphor screen is $L = 13.5$ cm.

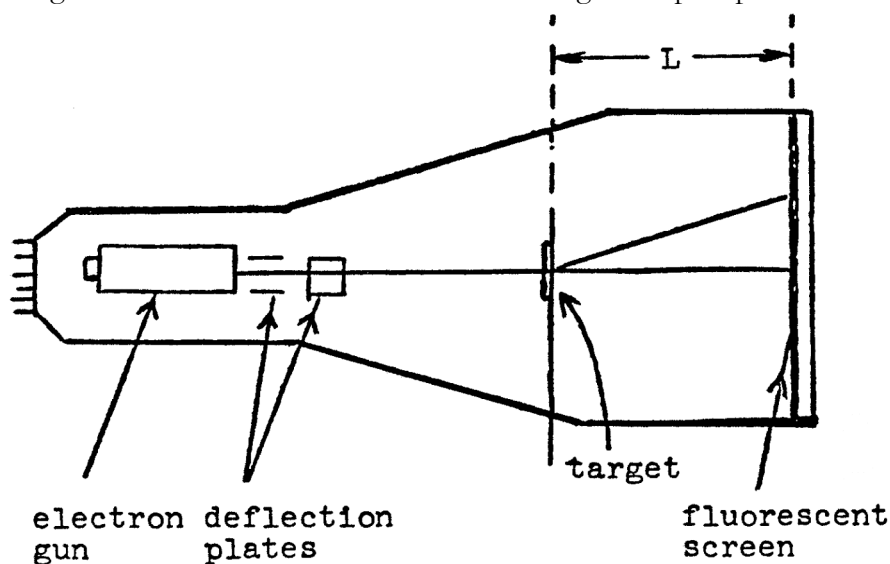


Figure 1 Schematic of the CRT tube

¹ The normal vector, $\mathbf{u}$, is an element of the **reciprocal lattice**. An interference maximum will occur if the change in the electron wave-vector $\Delta\mathbf{k}$ is a vector of the reciprocal lattice! See Ashcroft and Mermin or Kittel.

b. Experimental Procedure

- i. Familiarize yourself with the apparatus, a Leybold electron diffraction tube with a graphite target. A power supply provides high voltage that can be varied between 0 and 5 kV. Set the high voltage to 0 with the slider control before turning on the power. Change the HV and understand qualitatively the response of the electron beam. Determine the lowest voltage for which patterns can be obtained. Measure the radius R of the two rings from the graphite target for 5 or more voltages between about 2 and 5 kV. A good way to do this is to place a piece of masking tape across the tube face and mark the center and radii on the tape. You can use the clip-on magnet on the neck of the tube to center the spot. To prevent overheating the target or burning out the phosphor on the screen, please turn the HV down when you are not actually making measurements. You'll need to turn the room lights off to see the rings clearly.
- ii. Check the calibration of the HV meter using a high-voltage probe (if available).

c. Analysis of Data

Plot R vs. $V^{-1/2}$ including estimated uncertainties for both sets of rings. [Don't forget that (0,0) is a point also!]

Determine the two lattice spacings, d_{110} and d_{100} for graphite, and estimate their uncertainties.

4. References

C. Kittel, Introduction to Solid State Physics. This is a standard source book for Solid State. Chapters 1 and 2 of this book will make you an expert at this experiment. Chapter 1 is an introduction to crystal structure. Chapter 2 starts from diffraction and builds the necessary theory to understand it for cases beyond the cubic lattice.

N. Ashcroft and D. Mermin, Solid State Physics. This is the *other* standard source book for Solid State. Chapters 4 through 7 lay out the issues of crystallography and diffraction that concern us. A more sophisticated treatment than Kittel.

H.P. Myers, Introductory Solid State Physics. See Chapters 2 and 3 for crystallography and diffraction.

R. Eisberg and R. Resnick, Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles. This book has everything. The de Broglie hypothesis, "matter waves", and a short history of crystal diffraction experiments are discussed in Sec. 3.1. A nice quick overview of the principles of crystallography is given in Appendix Q.

R. Serway, C. Moses, C. Moyer, Modern Physics. Sec 4.2 has a nice discussion of the Davisson-Germer experiment, Bragg scattering, and "matter waves".

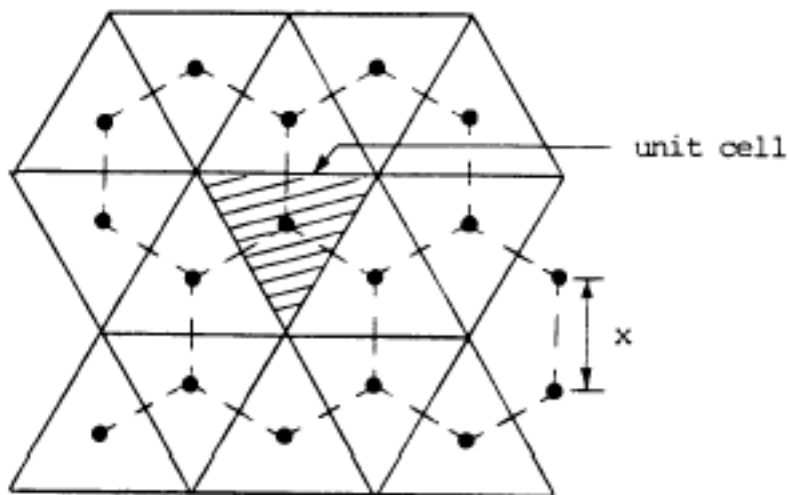
5. Questions

- (1) Estimate the error introduced into these measurements by the curvature of the tube face.
- (2) Are the data compatible with $R \propto V^{-1/2}$ as implied by Eq. 7? Have you verified the de Broglie hypothesis? Have you observed the wave nature of the electron? Discuss your results.
- (3) Compare the ratio of the two lattice spacings to that expected for a hexagonal lattice like graphite.
- (4) Graphite consists of layers of carbon atoms with an average separation between layers of $3.40 \text{ \AA}$. Assume that each layer has the hexagonal structure shown below. Use the following information to compute the nearest neighbor distance x between atoms within each carbon layer. A convenient choice of unit cell is the equilateral triangle shown below. Some useful numbers are:

N = Avogadro's Number = 6.02×10^{23} atoms/mole

W = Atomic weight of carbon = 12 g/mole

ρ = Density of graphite = 2.25 g/cm^3



Hexagonal structure of graphite

- (5) Calculate the average spacing between carbon atoms and compare it to the two measured lattice spacings and the nearest neighbor distance from Question 4.
- (6) What evidence has this experiment provided to demonstrate that the crystalline structure of graphite really is hexagonal?
- (7) Give one example of the electron showing its particle-like nature in this experiment. Give one example as to it showing its wavelike nature.