X-Ray Diffraction and Scanning Probe Microscopy

x-ray diffraction provides indirect evidence for the existence of atoms

How it works
shine x-rays on/through crystals
- various diffraction patterns result
- different patterns provide indirect evidence for atoms

currently, map out atoms' placement, using scanning probe microscopy (SPM)

SPM includes:
1. scanning tunneling microscopes (STM)
2. atomic force microscopy (AFM)

Optical transform experiments- use light which is safer than x-rays to see diffraction patterns (mimic x-rays & crystal patterns)

- x-rays used because their wavelengths are on the order of an angstrom-same size as the spacings between atoms in a crystal; therefore, diffraction occurred

- the patterns of spots could be used to work backward to identify what atoms are present in the crystal & how they are arranged relative to one another

problem: x-rays are expensive & dangerous
- solution: light rays & arrays of dots or lines on 35mm slides can simulate x-rays & crystalline arrangements (light's wavelength & slide spacings are comparable = diffraction)

Diffraction- the scattering of light from a regular array, producing constructive & destructive interference

Need to know about light to understand

Light
Controversy: Newton = light is tiny particles; others = light is a wave

Modern View = both particles & waves

light consists of quanta- discrete bundles of energy
- amount of energy dependent on color of light

Picture of a wave –crest/trough/wavelength identified wavelength- distance between 2 neighboring peaks or troughs (λ)

frequency- the # of peaks that pass a given pt. each second measured in cycles/second (Hertz(Hz))

wave velocity- the distance a peak moves in a unit of time

$v = f\lambda$ velocity = (frequency)(wavelength)

Wave transparencies

-overlap transparencies to see constructive & destructive interference

-as centers get further apart more interference occurs

Diffraction occurs when wavelength of light = distance between spacings of a structure

X-ray (λ = angstrom) = distance between atoms in a crystal

visible light = spacing on 35 mm slide = diffraction grating

diffraction pattern mathematically related to arrangement of atoms in structure which causes scattering

<u>How a diffraction pattern is made</u>

constructive & destructive interference occurs when electromagnetic radiation from several sources overlaps at the same time

<u>constructive interference</u>- waves moving in step(in phase)

<u>destructive interference</u>- waves moving out of phase (one max. & one min. meet up)

interference occurs in waves scattered by atoms in crystal $\rightarrow$ diffraction pattern

Purpose: provide info. about structures of crystalline solids

data used to determine molecular structures b/c relative atomic positions determined

therefore, evidence & indirect proof of atoms-periodic repeating atomic arrangement in crystals

symmetry of pattern = symmetry of atomic packing

intensity of diffracted light depends on arrangement & # of atoms in unit cell

<u>Electromagnetic spectrum</u>- spectrum of all radiation which travels at the speed of light & includes visible light, x-rays, ultraviolet light, infrared light, radio waves, etc.

c = speed of light = 3.00×10^8 m/s (through air in a vaccuum)

For light $v = f\lambda \rightarrow c = f\lambda$

visible part of spectrum consists of many wavelengths of light

longest λ = red = f lowest   shortest λ = violet = f highest

What type of relationship exists between f & λ? Inverse

-full spectrum not seen when look at a light source
-if look through a diffraction grating, see <u>bright-line spectrum</u>- each element has its own unique set of lines

-scientists measure the λ's of the lines in the bright-line spectrum
-use $c = f\lambda$, you can find the f

Planck also derived a formula that expresses the energy of a single quantum $E = hf$

h = Planck's constant = 6.6×10^{-34} Joule/Hertz

Example Problems

1. Calculate the frequency of a quantum of light (photon) with a wavelength of 6.0×10^{-7}m.

$c = f\lambda$
$3.00 \times 10^{8}\text{m/s} = f(6.0 \times 10^{-7}\text{m})$
$f = 5.0 \times 10^{14}$hertz

2. Calculate the energy of a photon of radiation with a frequency of 8.5×10^{14}Hz.

$E= hf$
$E = (6.6 \times 10^{-34}\text{ Joule/Hertz})(8.5 \times 10^{14}\text{Hz})$
$E = 5.6 \times 10^{-19}$ Joules

3. What is the velocity(m/s) of a wave with a frequency of 550 Hz and a wavelength of 2.40 millimeters?

1320mm/s → 1.320 m/s

Slide = array = dots

Diffraction w/LED = pattern = spots

Horizontal array produces a vertical pattern

Why? In a horizontal array of lines, distance between them represents a repeat distance or interplanar spacing, d. If monochromatic light (light in only 1 wavelength) is shone on slide, constructive interference occurs. Since there is a finite repeat distance in the vertical direction, there is both constructive and destructive interference in this direction. Hence, a series of bright spots and dark spaces is produced. In the horizontal direction the repeat distance is infinite so only destructive interference takes place and only dark spaces are produced.

As spacing of array decreases, distance between spots in pattern increases.

$d\sin\varphi = n\lambda$ -regions of constructive interference are further separated

Reciprocal lattice effect- the spacings of spots in the diffraction pattern very inversely with the feature spacing in the array that produced it

-size of diffraction pattern also depends on wavelength of light used to produce it

systematic absences- when every other diffraction spot is eliminated by placing an identical atom at the center of each simple cube in the array

Scanning Tunneling Microscope

How it works:
- sharp metal tip, ending in a single atom, is placed over an electrically conducting substrate
- a small potential difference is applied between them
- gap between tip & substrate surface large enough so electricity can't flow between them, but small enough to let electrons tunnel between tip & surface

tunneling- the movement of an electron due to its wave nature through a classical barrier-the electron "jumps from surface to tip"

- as the distance between surface & tip increases, tunneling capability decreases
- the spatial arrangement of atoms on the surface is determined by the variation in tunneling current sensed by the probe tip as it moves in very small steps across the surface

rastering- scanning back and forth across the surface of a material

- scanning done by adjusting tip-to-surface separation to maintain a constant tunneling current (tip cannot crash into surface)

Atomic Force Microscopy (AFM)

How it works:
- surface mapped by measuring mechanical force between tip & surface
- since force used to create images, not electrical current, AFM used to map either conducting or non-conducting surfaces
- to measure interatomic force, tip is mounted on end of a small cantilever
- as it varies, lever deflections sensed by bouncing laser beam off the lever & measuring the displacements with a pair of photosensors

Understanding the Relationship between Electrons & STM

- electrostatic forces between electrons & nuclei hold metallic atoms together
- core electrons are bound tightly to nuclei & valance electrons that are farthest from the nuclei feel a weak electrostatic attraction & can move around in the space between the nuclei
- these electrons carry/conduct current = conduction electrons

conduction band- large numbers of valence electron orbitals that overlap & provide a continuous area for conduction electrons, extending over the solid

- each orbital can be occupied by a pair of electrons with opposite spins & are filled from low energy to high energy

Fermi energy- energy of the most weakly bound electrons

-electrons here are held in by an energy barrier

-classically, the electrons can never leave the metal unless they have enough energy to get over that barrier

-quantum mechanically, electronc near the barrier can tunnel through the barrier

Tunneling

-tip must be a few angstroms(10^{-8} cm) from the surface

-electrons are not confined to an area but are within a probability distribution

-therefore, edges of atom are indistinct

-electrons usually near the nucleus & electron probability distribution falls off rapidly as you get farther from the nucleus

-because the probability distribution falls off so rapidly, this tunneling current provides ssensitive probe of interatomic separation

-if two atoms close to one another, an electron from one atom can move through region of overlapping electron density to become a part of the other atom's electron cloud

Challenges for STM

1. vibrations because the separation between the sample & probe is small
   -easy to crash tip into surface, if surface not smooth on the atomic level
   -sneeze or motion in room can ruin experiment
2. probe sharpness determines how small a structure can be imaged on the surface
   -electrochemical etching can be used to sharpen the tip
   -must consist of single atom to detect individual atoms
3. position control
   -must be able to move in displacements of 0.1nm or less

-use a special type of piezoelectric ceramic material, which expands & contracts when appropriate voltages are applied

STM Tip

-terminates in a single atom

-composed of tungsten or platinum

-tungsten, if exp't. done in vacuum (easier to prepare single atom tip)

-platinum, if exp't. done in liquid or air (tungsten reacts too quickly)

-Pt & Pt-Ir alloys used more often because less reactive

STM Uses

Study physics of atoms at surfaces

Study properties of atomically "clean" surfaces or surfaces that have been modified

Study electrode surfaces

Image structures such as DNA and operating battery electrodes

Method for gene sequencing

Writing with atomic resolution

Move atoms

Demonstrates quantum mechanics

Create atomic-scale devices & new structures