

X-Ray Diffraction and Scanning Probe Microscopy

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CURRICULUM SUGGESTIONS

TOPICS

Structure of the Atom

Nature of Light

Atomic Theory

Quantum Mechanics

Structure of Matter

Solids

Crystals

Crystal Structure

Shapes of Molecules

Electrical Interactions

VSEPR Theory

OVERVIEW

This unit could stand by itself with a scope limited to the theory behind diffraction of electromagnetic radiation, in general, and the use of X-ray diffraction, specifically, to determine the structure of materials. The same could be said for scanning probe microscopy. The unit could, however, also be used to supplement an existing chemistry curriculum and to provide a way to introduce or reinforce the above topics. In the suggestions that follow, when a specific investigation or activity is used as an example, it refers not only to the activity referenced, but also to the background information that is included in the Introduction to the unit and the Teacher Notes for that activity. These suggestions are illustrative not exhaustive.

SUGGESTIONS

Investigation 1 -----This investigation can be used to introduce the nature of light. Examples would include: velocity, frequency, and wavelength relationships; electromagnetic spectrum; properties of light, such as reflection, refraction, diffraction, and interference; dimensional analysis.

Investigation 2 ----- This investigation can be used to teach crystal structures, which are often included in a unit on the phases of matter. It could also be used in conjunction with the VSEPR theory of bonding to reinforce the concepts of molecular shapes as a consequence of electrical interactions between bonded and lone pairs of electrons. The investigation should provide the students with an understanding of how we know the shapes of molecules.

Investigation 3 ----- This investigation can be used to make the inherently abstract nature of topics related to quantum mechanics more concrete. By seeing that the theory of quantum mechanics can be used to create a real instrument that can, in turn, be used to image atoms, students should be able to see the practical consequences of this topic.

Activity 1 -----This activity is intended to weave Investigations 1-3 into the fabric of everyday life. By having students research the current literature and other information sources, it is hoped that they will see that these concepts are not just something that is studied in a chemistry class, but have applications that make a difference to our quality of life.

Sample Lesson Plan

DAY 1 50 min	<p>Present the material included in the background information for this unit. Specifically, discuss the nature of light and some of the properties it exhibits, including reflection, interference, and diffraction.</p> <p>Here are two suggestions for conveying an understanding of interference:</p> <ol style="list-style-type: none">1. Included in Appendix F are two circular wave patterns emanating from point sources from which overheads can be made. As the two overheads are superimposed, the wave patterns interfere with one another and the regions of constructive and destructive interference become quite obvious as lighter and darker lines, respectively, that radiate away from the two sources.2. Borrow a signal wave generator and two speakers from the physics department. Set the speakers on either end of the demonstration table and connect them to the generator. Select a “comfortable” tone and have the students walk back and forth across the room at varying distances from the speakers. Instruct them to locate regions where the sound is louder (the waves are constructively interfering) and softer (the waves are destructively interfering). If you have them stop in these “dead” spots and map their location relative to the speakers, they will notice that they are standing in straight lines that radiate away from both speakers in the same way that was illustrated by the overheads.
DAY 2 35-40 min	<p>Discuss diffraction in some detail. It might be a good idea to issue ordinary diffraction gratings to the students and have them look at a light source (incandescent, fluorescent, gas discharge tubes, or a LED).</p> <p>Make sure they are aware of the “rainbow” of colors produced by the incandescent source (a topic of discussion at another time) and particularly the series of bright lines and dark spaces produced by the other sources.</p>
10-15 min	<p>Pre-lab Investigation 1. Emphasize that the students are now going to see how the property of diffraction may be used as a tool to discover the existence of certain patterns or arrangements of atoms within materials.</p>
DAY 3 50 min	<p>Have the students do Investigation 1.</p>
DAY 4 25 min	<p>Discuss the results of Investigation 1. Since it is critical that the students have “good” data, show overheads of the figures included in the</p>

“Notes for the Instructor” for this investigation or use a pocket laser and display the patterns as a demonstration.

25 min

Have the students begin Investigation 2.

DAY 5

50 min

The students should finish Investigation 2. You should also discuss their results thoroughly (See “Notes for the Instructor” for this investigation).

- DAY 6**
50 min
- During this class discussion, emphasize that what students have done so far is to investigate a technique for the collection of indirect evidence about shapes that may be contained within a material. What is needed is direct proof for the existence of those patterns. This should lead into a discussion of the theory behind scanning probe microscopy (SPM). The background information and several of the Appendices deal with this and related topics.
- DAY 7**
50 min
- Have the students do Investigation 3.
- DAY 8**
50 min
- Discuss Investigation 3 and have the students begin Activity 1. Depending upon your technology resources, arrangements for LMC/computer lab time will need to be made in advance. Many students will be able to complete this assignment outside of class time.
- DAY 9**
50 min
- The students should continue with Activity 1, and the worksheet should be completed by the end of this period.
- DAY 10**
- Unit exam.

X-Ray Diffraction and Scanning Probe Microscopy (SPM)

Overview

This module is designed to introduce students to two major tools that are used to determine the structure of matter and to reinforce concepts associated with electromagnetic radiation. Historically, X-ray and related diffraction methods have provided a great deal of information about crystalline materials ranging from gold to table salt to DNA, in which the atoms or molecules are arranged in a repeating pattern. Because the wavelength of X-rays and the spacing between atoms in a crystal are comparable, the phenomenon of diffraction occurs. From the pattern of diffraction spots, scientists work backward to identify what atoms are present in the crystal and how they are arranged relative to one another. This experiment is expensive and dangerous to demonstrate in a classroom, as X-rays are a highly energetic form of electromagnetic radiation.

To circumvent this problem, the experiment is scaled up in this module. Instead of using X-rays having wavelengths on the order of an angstrom, visible light with wavelengths of thousands of angstroms is employed. Similarly, instead of atoms spaced by angstroms, arrays of dots or lines on a 35-mm slide are spaced by many thousands of angstroms. Making these two modifications again leads to diffraction, as the wavelength and feature spacing are sufficiently close in scale to create observable effects. Thus, when these slides are used to view point sources of light like LEDs or flashlight bulbs, diffraction patterns (optical transforms) that mimic those that would be produced by shining X-rays on crystals can be observed. (It is also possible to shine pocket laser beams through these slides to create the same effect.) The trigonometric equations underlying both X-ray diffraction and the optical transforms (Fraunhofer diffraction) and their algebraic simplification (optical transforms) can be presented at the teacher's discretion.

Students have an opportunity to see how diffraction patterns are affected by the nature of the corresponding arrays and, in particular, to discover the “reciprocal lattice effect,” in which small spacings on the array become large diffraction spacings and vice versa. The experiment also provides an opportunity to explore the electromagnetic spectrum and spectral composition of various lighting sources, as different colors of light affect the size of the diffraction pattern.

A recent breakthrough has been the use of scanning probe microscopes to image individual atoms on the surfaces of solid materials. Students have an opportunity to “image” the magnetic fields of refrigerator magnets with a probe tip cut from the magnet; and to “image” an electrically conducting surface using the probe of a simple multi-meter. These experiments mimic scanning methods that use probe tips of atomic sharpness that are moved across a surface in atomic-scale increments. The variations in forces between tip and surface provide atomic-level topographic information. The cover of the “Exploring the Nanoworld” kit is an image of pairs of silicon atoms, obtained using a scanning tunneling microscope, representing one instrument of scanning probe microscopy.

X-Ray Diffraction and Scanning Probe Microscopy

X-Ray Diffraction

Diffraction can occur when electromagnetic radiation interacts with a periodic structure whose repeat distance is about the same as the wavelength of the radiation. Visible light, for example, can be diffracted by a grating that contains scribed lines spaced only a few thousand angstroms apart, about the wavelength of visible light. X-rays have wavelengths on the order of angstroms, in the range of typical interatomic distances in crystalline solids. Therefore, X-rays can be diffracted from the repeating patterns of atoms that are characteristic of crystalline materials.

Electromagnetic Properties of X-Rays

The role of X-rays in diffraction experiments is based on the electromagnetic properties of this form of radiation. Electromagnetic radiation such as visible light and X-rays can sometimes behave as if the radiation were a beam of particles, while at other times it behaves as if it were a wave. If the energy emitted in the form of photons has a wavelength between 10^{-6} to 10^{-10} cm, then the energy is referred to as X-rays. Electromagnetic radiation can be regarded as a wave moving at the speed of light, c ($\sim 3 \times 10^{10}$ cm/s in a vacuum), and having associated with it a wavelength, λ , and a frequency, ν , such that the relationship $c = \lambda \nu$ is satisfied.

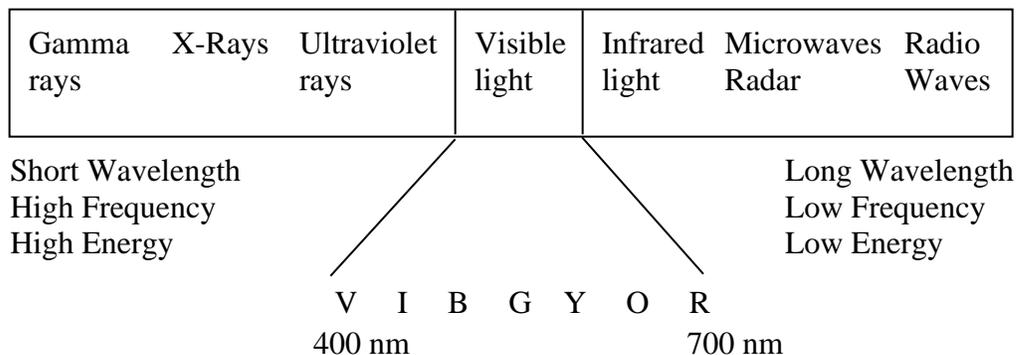


Figure 1. Electromagnetic spectrum. The colors of the visible range of the spectrum are abbreviated violet (V), indigo (I), blue (B), green (G), yellow (Y), orange (O), and red (R).

X-Rays and Crystalline Solids

In 1912, Maxwell von Laue recognized that X-rays would be scattered by atoms in a crystalline solid if there is a similarity in spatial scales. If the wavelength and the interatomic distances are roughly the same, diffraction patterns, which reveal the repeating atomic structure, can be formed. A pattern of scattered X-rays (the diffraction pattern) is mathematically related to the structural arrangement of atoms causing the scattering.

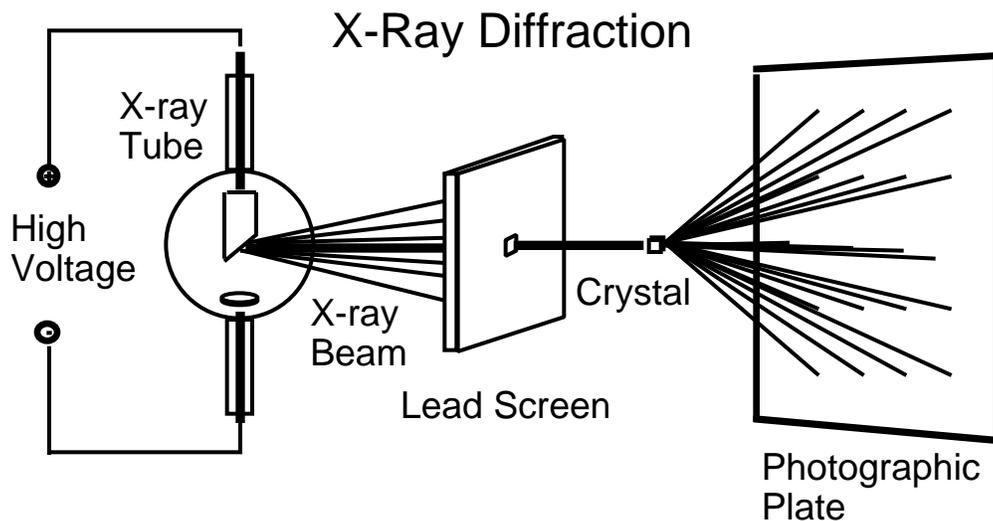


Figure 2. A schematic of X-ray diffraction.

When certain geometric requirements are met, X-rays scattered from a crystalline solid can constructively interfere, producing a diffracted beam. Sir Lawrence Bragg simulated the experiment, using visible light with wavelengths thousands of times larger than those of X-rays. He used tiny arrays of dots and pinholes to mimic atomic arrangements on a much larger scale. Optical transform experiments, in which visible light is diffracted from arrays, yield diffraction patterns similar to those produced by shining X-rays on crystalline solids. However, the optical transform experiment is easier and safer than X-ray experiments and can be used in the classroom.

How Diffraction Patterns are Made

When electromagnetic radiation from several sources overlaps in space simultaneously, either constructive or destructive interference occurs. Constructive interference occurs when the waves are moving in step with one another. The waves reinforce one another and are said to be in phase. Destructive interference, on the other hand, occurs when the waves are out of phase, with one wave at a maximum amplitude, while the other is at a minimum amplitude. Interference occurs among the waves scattered by the atoms when crystalline solids are exposed to X-rays. The atoms in the crystal scatter the incoming radiation, resulting in diffraction patterns. Destructive interference occurs most often, but in specific directions constructive interference occurs. See APPENDIX A for a more detailed explanation.

Purpose of X-Ray Diffraction

Diffraction data has historically provided information regarding the structures of crystalline solids. Such data can be used to determine molecular structures, ranging from simple to complex, since the relative atomic positions of atoms can be determined. X-ray diffraction provided important evidence and indirect proof of atoms.

Diffraction patterns constitute evidence for the periodically repeating arrangement of atoms in crystals. The symmetry of the diffraction patterns corresponds to the symmetry of the atomic packing. X-ray radiation directed at the solid provides the simplest way to determine the interatomic spacing that exists. The intensity of the diffracted beams also depends on the arrangement and atomic number of the atoms in the repeating motif, called the unit cell. (See "Memory Metal" module, Appendix A for more information about unit cells.) Thus, the intensities of diffracted spots calculated for trial atomic positions can be compared with the experimental diffraction intensities to obtain the positions of the atoms themselves.

From this as well as other indirect methods such as stoichiometric relationships and thermodynamics, evidence of atoms was obtained. However, a direct way to image atoms on the surfaces of materials now exists. Developed in the mid-1980's, the scanning tunneling microscope (STM) permits direct imaging of atoms.

Scanning Probe Microscopy (SPM)

Scanning Probe Microscopy (SPM) includes Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM), and a variety of related experimental techniques. These are experimental methods that are used to image both organic and inorganic surfaces with (near) atomic resolution. In a scanning tunneling microscope a sharp metal tip, terminating ideally in a single atom, is positioned over an electrically conducting substrate, and a small potential difference is applied between them. The gap between the tip and the substrate surface is made large enough that electrical conduction cannot occur; yet, it is small enough to let electrons tunnel (a quantum mechanical phenomenon) between the tip and the surface. Tunneling probability decays exponentially with increasing tip-to-surface separation. Thus, 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 atomic-scale increments across the surface, a process called rastering. Scanning is more commonly done by adjusting the tip-to-surface separation so as to maintain a constant tunneling current, thereby preventing the tip from crashing into the surface. In either mode of operation a “map” of the sample surface with atomic resolution results.

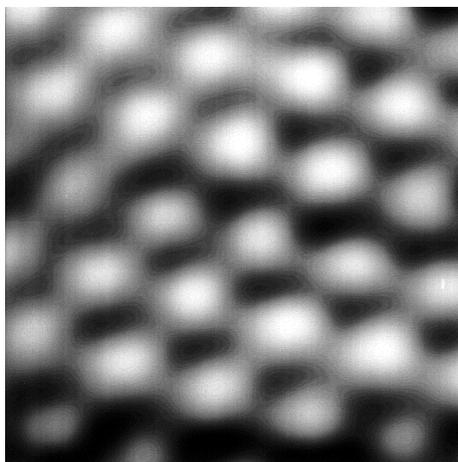


Figure 3. The STM image of a close-packed layer of Ag atoms. (Photograph courtesy of Robert Hamers.)

Atomic Force Microscopy (AFM)

In an atomic force microscope the surface topography is mapped by measuring the mechanical force between tip and surface rather than the electrical current flowing between them as the STM does. Since force is used to create the images rather than the electrical current, the AFM can be used to image both conducting and non-conducting substrates. To measure the interatomic force, the tip of the AFM is mounted on the end of a small cantilever. As the interatomic force varies, the deflection of the lever can be sensed by bouncing a laser beam off the back of the lever and measuring displacements with a pair of photosensors

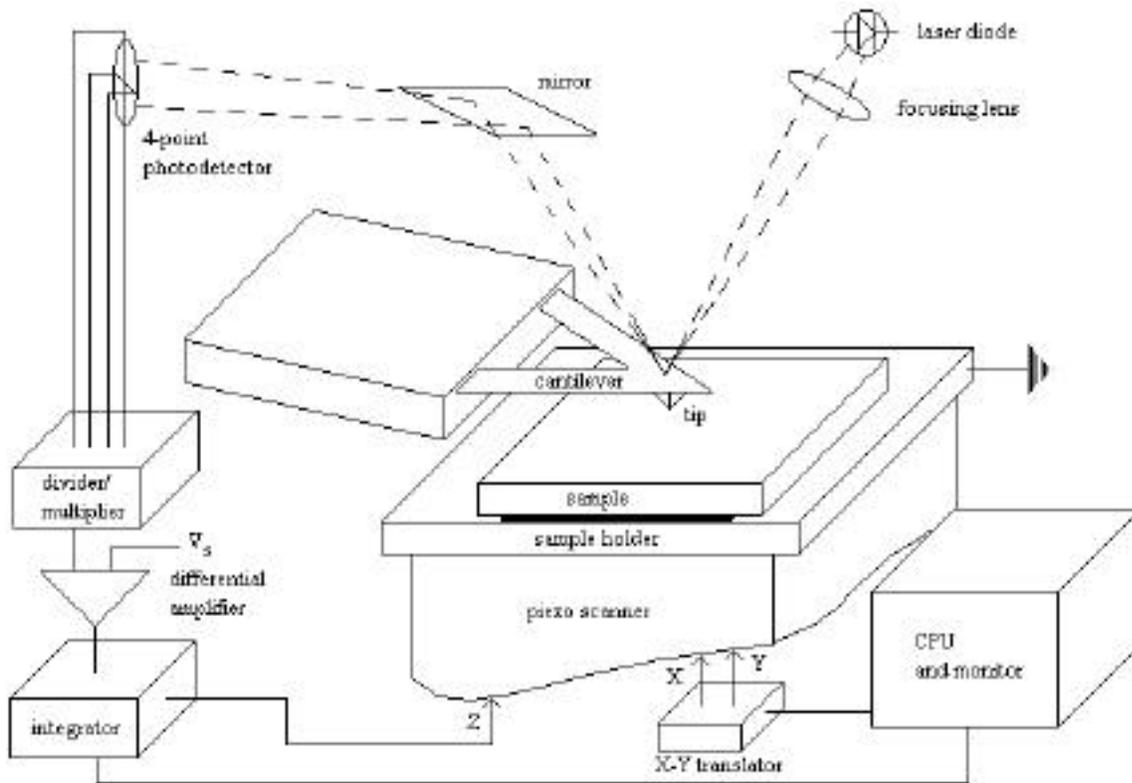


Figure 4. In AFM, small forces are measured between the tip and the sample during scanning. These forces cause vertical movement of the cantilever, which is monitored by a laser beam that is reflected from the top cantilever surface.

Electrons and the Scanning Tunneling Microscope (STM)

Gert Binnig and Heinrich Rohrer were awarded the Nobel Prize in Physics, in 1986, for the development of the scanning tunneling microscope. They were also jointly honored with Ernst Ruska for their work on the development of electron microscopy.

To gain a better understanding of how the scanning tunneling microscope works, the behavior of electrons in metals and other electrically conducting material needs to be considered. Electrostatic forces acting between the electrons and the nuclei of atoms hold the atoms of a metal together. Core electrons are bound tightly to individual nuclei. However, the valence electrons that are farthest from the nuclei feel a relatively weak electrostatic attraction and are free to move about in the space between the nuclei. Since these electrons carry or conduct the electric current, they are referred to as conduction electrons. The large numbers of valence electron orbitals overlap and provide a continuous distribution of states available to the conduction electrons, called a band, that extends over the entire solid. Each orbital can be occupied by a pair of electrons with opposite spin, and they are filled in order from lowest to highest orbital in energy. The Fermi energy (E_F) is the energy of the most weakly bound electrons. The electrons at the Fermi energy are held in the metal by an energy barrier. Classically, these electrons can never leave the metal unless they are given enough energy to go over this potential barrier. Quantum mechanically, however, electrons near the Fermi energy can tunnel through the potential barrier.

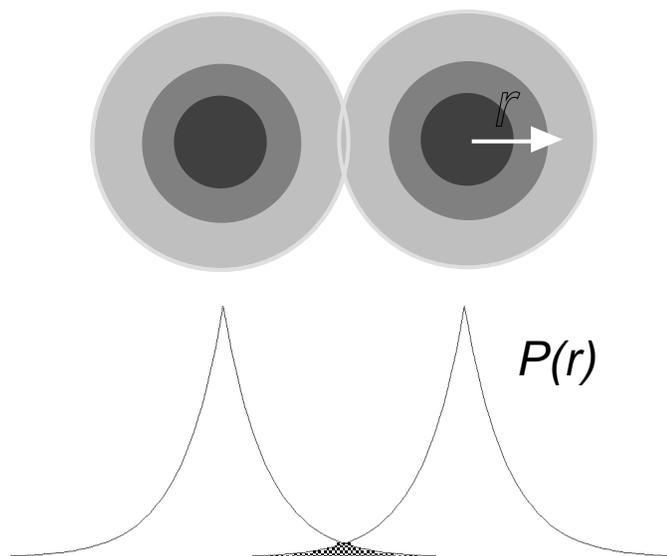


Figure 5. Two atoms with their electron probability clouds slightly overlapping. In the top part of the figure, the atoms are represented as spheres with overlapping volumes. In the bottom part of the figure, the graphical representations of the electron probabilities (as a function of distance from the nucleus) are seen to overlap.

Tunneling

The quantum mechanical phenomenon called tunneling is possible when the tip is only within a few angstroms (10^{-8} cm) of the surface. Tunneling is the term used to describe the movement of an electron through a classical barrier, which is possible only due to its wave nature and hence impossible in classical physics. To understand this better, consider only one atom. The electrons surrounding the atomic nucleus are not confined to a hard shell but are within a varying probability distribution. This causes the edges of the atom to be indistinct. When the quantum mechanical equations describing the probability of the electron locations are solved, it is found that the electron spends most of its time near the nucleus, and the probability distribution falls off exponentially as the distance from the nucleus increases. Because the electron probability distribution falls off so rapidly with distance from the nucleus, this tunneling current provides a very sensitive probe of interatomic separation. If two atoms are within angstroms of each other, an electron from one atom can move through the region of overlapping electron density to become part of the other atom's electron cloud. See **APPENDIX B** for more on tunneling.

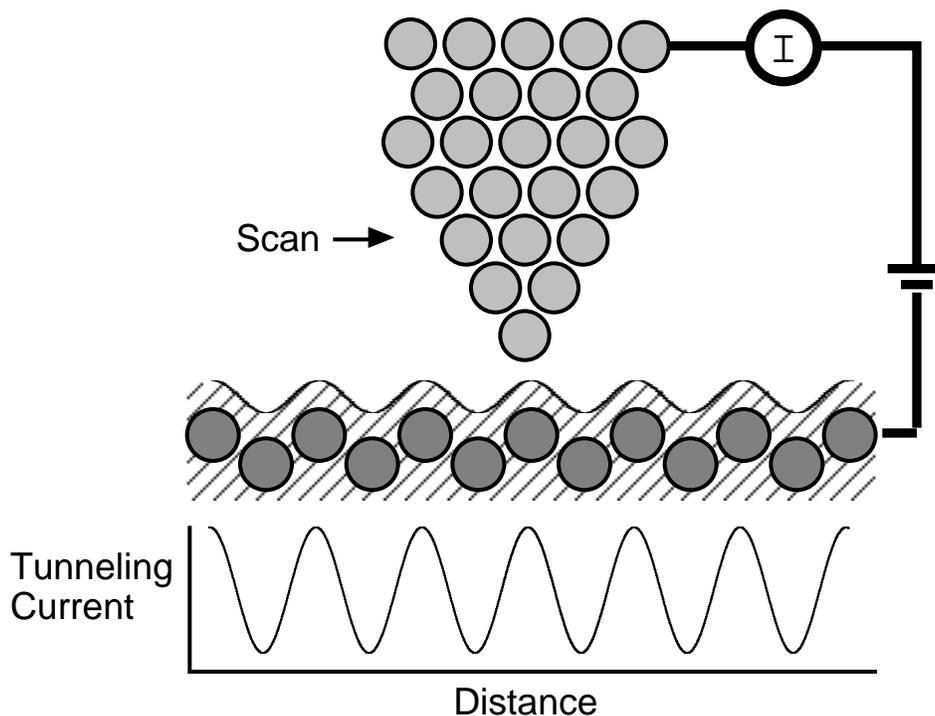


Figure 6. A plot of tunneling current as a function of horizontal probe tip position. The absolute vertical position is held constant. When the tip is nearest the surface atoms, the current is highest. The wavy line above the shaded circles represents the contour of the surface.

Challenges for STM

Theoretically, STM can be used to image individual atoms on the surface; in practice, however, three challenges arise. The first challenge, vibrations, are important because the separation between the sample and probe is so small. Since the tip is only a few angstroms from the surface, it is easy to crash it into the sample unless the substrate is smooth on the atomic scale. For such a small separation, any minor perturbation such as vibrations set up by a sneeze or motion in the room can jam the probe into the sample and ruin the experiment. As a result, careful engineering is necessary to make the instrument rigid and to isolate it from external disturbances. Another problem, probe sharpness, determines how small a structure can be imaged on the surface. Electrochemical etching can be used to sharpen the end of a metal wire to a radius of about 1000 nm. A probe with such a large surface area would allow tunneling to occur over a large region of the sample surface. In order to detect individual atoms, the probe tip must be comparable in size to an atom. Thus, the probe tip must ideally consist of a single atom. The final problem is that of position control. In order to move the probe with controllable displacements of 0.1 nm (1 angstrom) or less, a special type of piezoelectric ceramic material is used. This material expands and contracts on a scale of angstroms when appropriate external voltages are applied to pairs of electrodes on its opposite faces. Therefore, a probe attached to a piece of piezoelectric ceramic can be moved with great precision by application of external voltages. See **APPENDIX C** for how to resolve these challenges.

The STM Tip

The tip is prepared so that it terminates in a single atom. The tip is usually composed of tungsten or platinum. If the experiment is performed in a vacuum, tungsten is the preferred material because it is relatively easy to prepare a single-atom-terminated tip. If the STM experiment is to be performed in a liquid or in air, tungsten reacts too quickly. Therefore, Pt or

Pt-Ir alloys are preferred even though it is more difficult to prepare tips with these materials, and they generally are not as atomically sharp. See **APPENDIX D** for more about the STM tip.

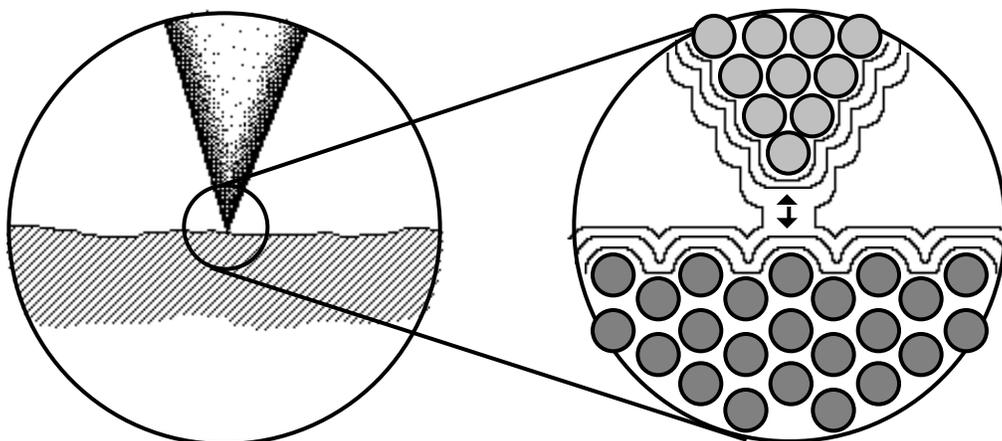


Figure 7. A sketch of an atomically sharp tip near a surface (left-hand picture) and a blow-up (right-hand picture) of the atoms of the tip (grey circles) and the surface (black circles).

Uses and Capabilities of STM

The STM has many uses. It is used in fundamental studies of the physics of atoms at surfaces. STMs can be constructed to be compatible with high-vacuum conditions, which are used to study the properties of atomically “clean” surfaces or surfaces that have been modified in some controlled way. The STM can also be used to study electrode surfaces immersed in liquid electrolytes. In addition to these scientific applications, the STM has a wide range of potentially practical applications. The STM can image structures ranging from DNA in a biological environment to the surface of an operating battery electrode. The application of the STM to biological molecules has been proposed as a method of gene sequencing. See **APPENDIX E** (part 1) for specifics on imaging. Research is currently being done to demonstrate the ability to write with atomic resolution. Features a few nanometers wide have been written by using the probe to scratch or dent the surface directly or by using the tunneling current to locally heat the surface of a substance. The probe has even been used to move individual atoms so as to form a word. See **APPENDIX E** (part 2) for specifics on moving atoms. Scanning tunneling microscopy is a practical demonstration of quantum mechanics. Scanning probe microscopy techniques may be used to create atomic-scale devices and new structures. For example the STM has been used to prepare a “nanobattery,” which consists of two copper pillars and two silver pillars that are placed sequentially on a graphite surface by electrochemical reduction of solutions of copper sulfate and silver fluoride.

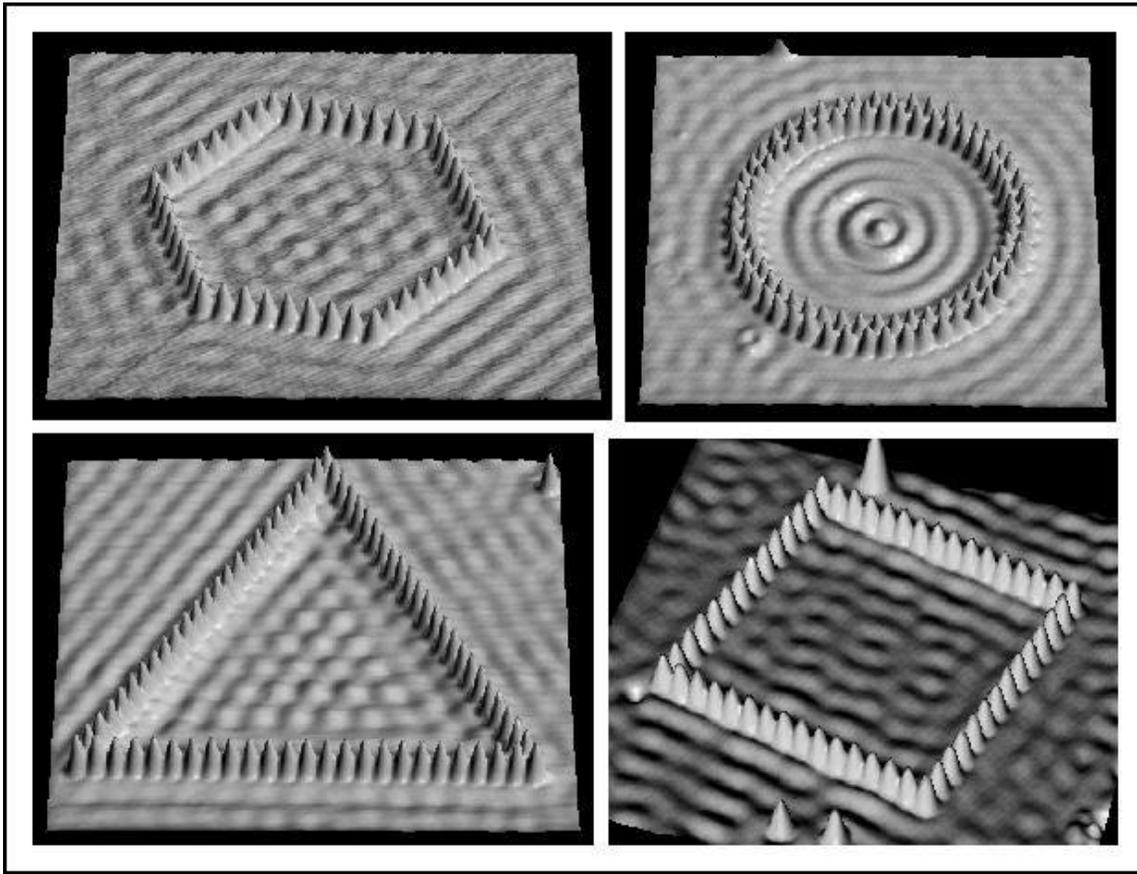


Figure 8. An example of the images that can be made with atoms using Scanning Tunneling Microscopy. The images shown are of iron atoms on copper.

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 ()

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
 $v = f \quad \text{velocity} = (\text{frequency})(\text{wavelength})$

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 (= 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

How a diffraction pattern is made

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

constructive interference- waves moving in step(in phase)

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

interference occurs in waves scattered by atoms in crystal 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

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

$c = \text{speed of light} = 3.00 \times 10^8 \text{ m/s}$ (through air in a vacuum)

For light $v = f \quad c = f$

visible part of spectrum consists of many wavelengths of light

longest = red = f lowest shortest = 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 bright-line spectrum- 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.

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

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

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

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

$$1320 \text{ mm/s} \quad 1.320 \text{ m/s}$$

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.

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

Reciprocal lattice effect- the spacings of spots in the diffraction pattern vary 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 & valence 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, electrons 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 sensitive 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

X-Ray Diffraction and Scanning Probe Microscopy

x-ray diffraction provides _____

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. _____ (STM)
2. _____ (AFM)

_____ - 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 _____
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 _____ & _____

-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)

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

Need to know about light to understand

Light

Controversy: Newton = _____ **Modern View** = _____
others = _____

light consists of quanta- _____

-amount of energy dependent on color of light

Picture of a wave –crest/trough/wavelength identified

_____ - distance between 2 neighboring peaks or troughs ()

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

_____ - the distance a peak moves in a unit of time
 $v = f$ velocity = (_____) (wavelength)

Wave transparencies

- overlap transparencies to see constructive & destructive interference
- as centers get further apart _____ interference occurs

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

X-ray (= 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

How a diffraction pattern is made

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

_____ - waves moving in step (in phase)

_____ - waves moving out of phase (one max. & one min. meet up)

interference occurs in waves scattered by atoms in crystal 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

_____ - spectrum of all radiation which travels at the speed of light & includes visible light, x-rays, ultraviolet light, infrared light, radio waves, etc.

$c =$ _____ $= 3.00 \times 10^8$ m/s (through air in a vacuum)

For light $v = f$ $c =$ f

visible part of spectrum consists of many wavelengths of light

longest = _____ = f lowest shortest = _____ = f highest

What type of relationship exists between f & λ ?

-full spectrum not seen when look at a light source

-if look through a diffraction grating, see bright-line spectrum- 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 $E = \text{_____}$

$h = \text{Planck's constant} = 6.6 \times 10^{-34} \text{ Joule/Hertz}$

Example Problems

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

2. Calculate the energy of a photon of radiation with a frequency of $8.5 \times 10^{14} \text{ Hz}$.

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

Slide = array = _____

Diffraction w/LED = _____ = 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 _____.
 $d \sin \theta = n \lambda$ -regions of constructive interference are further separated

_____ - the spacings of spots in the diffraction pattern vary inversely with the feature spacing in the array that produced it
-size of diffraction pattern also depends on _____ of light used to produce it

_____ - 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

_____ - 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

_____ - 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

-_____ forces between electrons & nuclei hold metallic atoms together

-core electrons are bound tightly to nuclei & _____ 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

_____ - 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 _____ energy to _____ 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, electrons 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 _____ 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 sensitive 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. _____ 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. _____ 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. _____

-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 _____

-composed of tungsten or platinum

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

-_____, 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

INVESTIGATION 1

Notes to the Instructor

PURPOSE

To allow students the opportunity to investigate further the use of diffraction patterns to elucidate the arrangement of atoms in materials. It is also intended that the “reciprocal lattice effect” will be discovered.

METHOD

This investigation assumes that students have completed the activity in the guide that accompanies the “Exploring the Nanoworld” kit and are therefore accustomed to using an optical transform slide and seeing the diffraction patterns made by them.

This investigation will elaborate on that activity by using the Discovery slide available from ICE (See supplier information in the Appendix), which includes 8 different arrays of lines and dots. Some development and explanation of Fraunhofer’s equation, either qualitatively or quantitatively, will be necessary. **Note: Throughout this unit we will use “dots” and “arrays” to refer to features on the optical transform slides; and “spots” and “patterns” to refer to diffraction features.**

MATERIALS

Discovery slide and stereoscope or microscope

Materials needed to construct LED circuits*

Rohm super-bright red LEDs, Mouser **592-SLH56-VT3** (See supplier info.)

Molded black battery snaps, Mouser **1236005**

1000 ohm Transohm Carbon Film resistors, Mouser **29SJ250**

*With some precautionary instructions, students could probably assemble their own LED circuits.

Overhead transparencies of the two pages that follow the Answers to the Follow-Up Questions
[Give page numbers for these.](#)

PROCEDURE

- a. Orient the slide provided by the instructor so that the ICE logo is on the right-hand side. Using a stereoscope or microscope, look carefully at the arrays on the slide and make a sketch in the space provided in Table 1 of the Data Sheet.
- b. Connect the battery snap to the red LED and place it at least a meter away from you. View the LED through the different regions of the slide and sketch the diffraction patterns that you see in the appropriate spaces in Table 2.

ANSWERS TO FOLLOW-UP QUESTIONS

1. Consider your sketches of arrays a and c . How are they similar? How are they different?

The arrays on the following page clearly show that a and c both consist of an array of horizontal lines, but the spacing of the lines in c is smaller.

2. Discuss how the difference between arrays a and c affect the diffraction patterns that are produced.

First, note that each array yields a diffraction pattern that consists of a vertical column of spots. The number and intensity of the spots will depend upon the intensity of the LED and the darkness of the room, but the diffraction spots in pattern c are more widely separated than those in pattern a . Secondly, if a question arises as to why a horizontal array produces a vertical diffraction pattern, the following may help. In a horizontal array of lines, the distance between them represents the repeat distance, d . If the incident light is monochromatic, or reasonably so, constructive interference will occur when the product of the sine of the diffraction angle θ times d corresponds to a multiple (n) of the wavelength, according to the Fraunhofer equation developed in the Introduction. Because there is a finite repeat distance in the vertical direction, there will be constructive as well as destructive interference in this direction and therefore, a series of bright spots and dark spaces will be produced. In the horizontal direction the repeat distance is infinite. This, in turn, requires that θ be zero. The same arguments may be made for vertical arrays and the resulting horizontal row of diffraction spots that emerge. As the spacing of the array decreases, the distance between spots in the diffraction pattern increases. This result may be explained by looking at the Fraunhofer equation and noting that as the repeat distance, d , decreases, θ increases, and the regions where constructive interference occurs are further separated.

3. Consider your sketches of arrays b and d . How are they similar? How are they different? How do they both differ from the arrays a and c ?

The similarities are that they both consist of vertical lines. The arrays differ in that the spacing of the lines in array d is smaller. They both differ from a and c in that the arrays comprise vertical, not horizontal lines.

4. Discuss how the differences between arrays a and c , and between b and d , affect the shape of the diffraction patterns that are produced.

The student response should note the obvious difference of the diffraction patterns for a and c being vertical columns of spots and those of b and d being horizontal rows of spots. See the explanation in question 2 above.

5. Discuss how the difference between arrays b and d affects the diffraction patterns that are produced.

As the spacing of the arrays decreases, the distance between spots in the diffraction pattern increases. See the explanation in question 2.

6. Consider the remainder of your sketches in the order e , g , h , and f . What change in the arrays for this sequence do you note?

As you progress through the sequence, the square array of dots becomes smaller. This, of course, is analogous to the arrays of parallel lines considered earlier, and these arrays could be viewed as a series of lines in which segments have been removed, creating an array of dots instead of lines.

7. Discuss how the sequential changes in the arrays e , g , h , and f affect the diffraction patterns that are produced.

The diffraction patterns produced by the square arrays of dots are also squares. As the square formed by the array of dots becomes smaller, the squares formed by the diffraction spots become larger.

Note: The extrapolation from horizontal and vertical lines to a square array of dots may be demonstrated by overlapping arrays c and d using two of the Discovery slides and shining a laser or laser pointer through them. A square diffraction pattern is observed.

8. If we were to call the arrays “lattices”, what is the meaning of the phrase “reciprocal lattice effect” with respect to the diffraction patterns produced by them?

The “reciprocal lattice effect” refers to the observations stated several times above: the spacing of spots in the diffraction pattern varies inversely with feature spacing in the array that produced it. A corollary that was not investigated but which is evident from the Fraunhofer equation is that the size of the diffraction pattern produced is also dependent upon the wavelength of the light used to produce it. This would be a good extension that could be conducted by looking at LEDs of different colors or a point source of white light like a mini-Maglite flashlight.

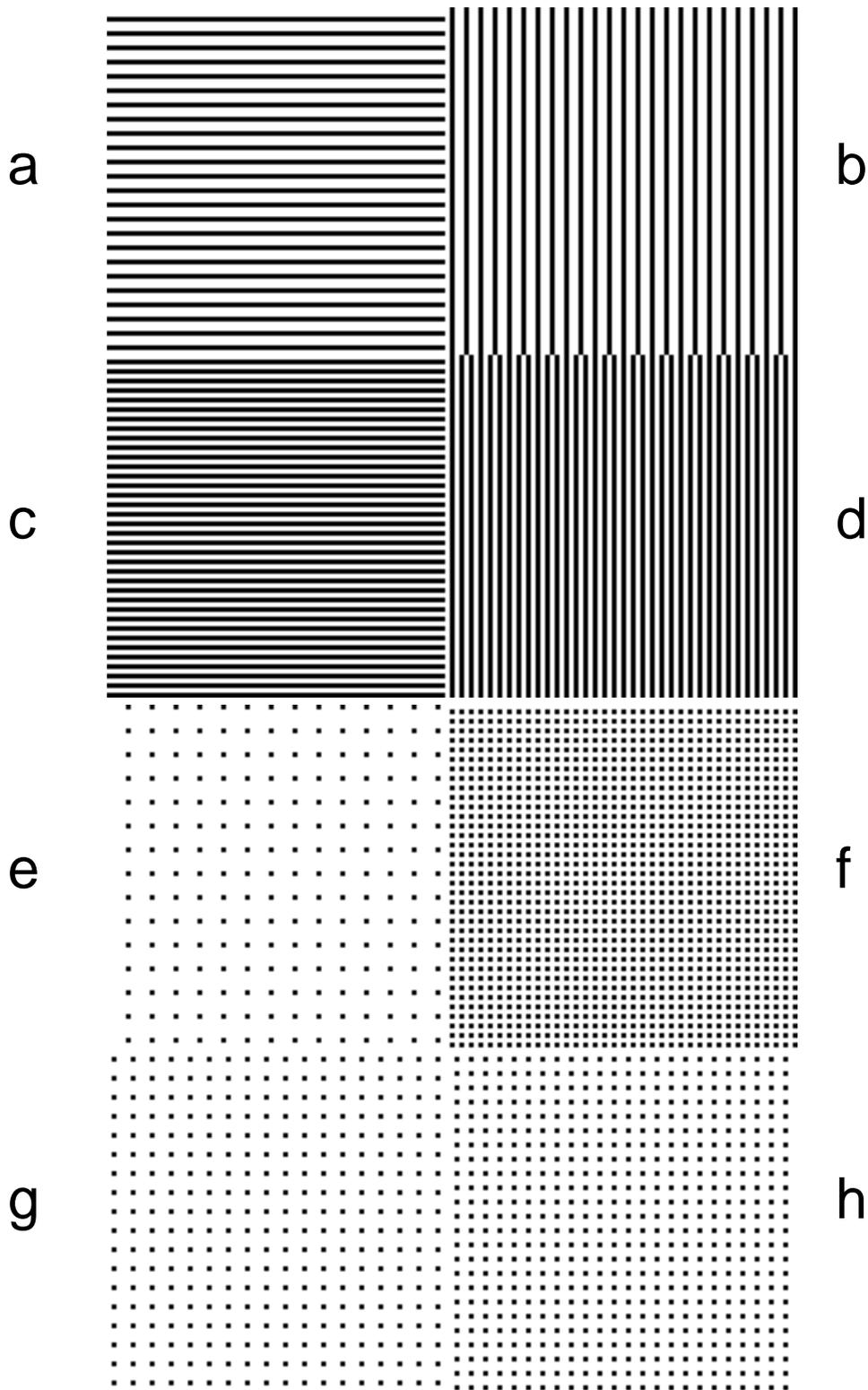


Figure 1. The arrays on the optical transform Discovery slide (Figure 4.4 from [A Materials Science Companion](#)), available from ICE, oriented so that the ICE logo is on the right side as you look through the slide.

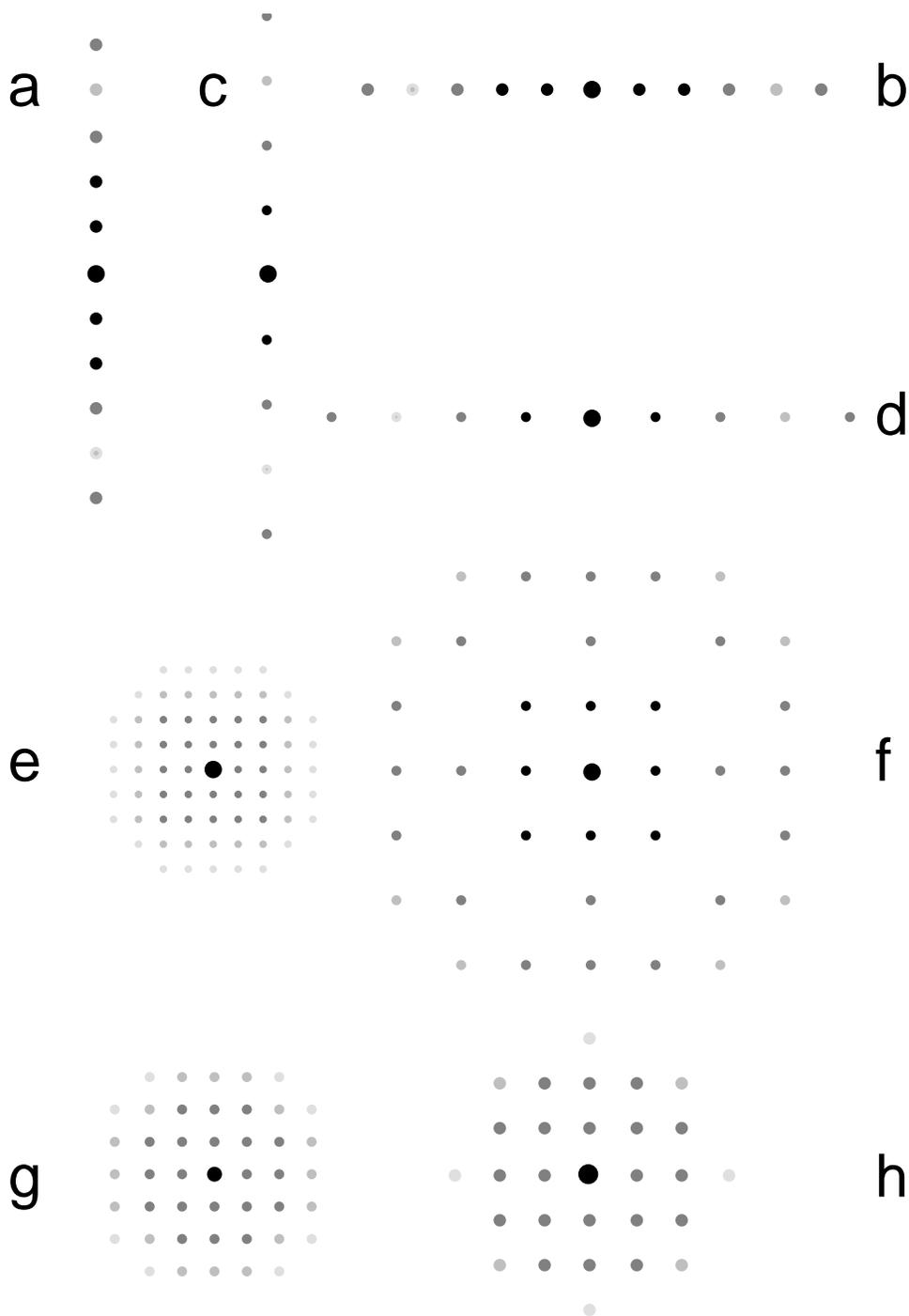


Figure 2. A simulation of the diffraction patterns obtained from the Discovery slide, with the indicated letter corresponding to the array (Figure 4.5 from A Materials Science Companion) from which the diffraction pattern is produced. (The number and intensity of spots observed will vary with the intensity of light used and the darkness of the room in which the patterns are observed.)

INVESTIGATION 1

PURPOSE

To investigate the use of diffraction patterns as an indirect method of determining the arrangement of atoms in materials.

PROCEDURE

- a. Orient the slide provided by the instructor so that the ICE logo is on the right-hand side. Using a stereoscope or microscope, look carefully at the arrays on the slide and make a sketch in the space provided in Table 1 of the Data Sheet.
- b. Connect the battery snap to the red LED and place it at least a meter away from you. View the LED through the different regions of the slide and sketch the diffraction patterns that you see in the appropriate spaces in Table 2.

FOLLOW-UP QUESTIONS

1. Consider your sketches of arrays a and c . How are they similar? How are they different?
2. Discuss how the difference between arrays a and c affect the diffraction patterns that are produced.
3. Consider your sketches of arrays b and d . How are they similar? How are they different? How do they both differ from the arrays a and c ?
4. Discuss how the differences between arrays a and c , and between b and d , affect the shape of the diffraction patterns that are produced.
5. Discuss how the difference between arrays b and d affects the diffraction patterns that are produced.
6. Consider the remainder of your sketches in the order e , g , h , and f . What change in the arrays for this sequence do you note?

7. Discuss how the sequential changes in the arrays e , g , h , and f affect the diffraction patterns that are produced.

8. If we were to call the arrays “lattices”, what is the meaning of the phrase “reciprocal lattice effect” with respect to the diffraction patterns produced by them?

Name _____
Date _____ Period _____

**INVESTIGATION 1
DATA SHEET**

Table 1

a	b
c	d
e	f
g	h

Table 2

a	b
c	d
e	f
g	h

PURPOSE

To extend student understanding of how arrays produce diffraction patterns by using optical transforms that resemble various unit cells assumed by metals, ionic solids, and molecular solids. Molecular solids can be connected to predictions of molecular structure using VSEPR theory.

METHOD

To give the results obtained in Investigation 1 some chemical significance, the rows of horizontal and vertical lines could be viewed as long, highly oriented polymer chains. The square arrays of dots could be seen as several cubic structural arrangements. This investigation should build from these views and allow students to see that changing the structure from simple cubic to a body centered or a closest packed arrangement has a dramatic affect on the diffraction pattern produced. This provides a deeper understanding of the relationship between diffraction patterns and structures. The first part of this investigation uses optical transforms of different unit cells of extended solids. The second part explores optical transforms of common molecular geometries.

MATERIALS

Unit Cell and VSEPR optical transform slides (Available from ICE. See supplier information in the Appendix).

LEDs from Investigation 1

overhead transparencies of the following **four pages -- ADD PG #s**

stereoscope or microscope

PROCEDURE

- a. Orient the Unit Cell slide provided by the instructor so that the ICE logo is on the right-hand side. With the stereoscope, look carefully at the arrays on the slide and make a sketch in the space provided in Table 1 of the Data Sheet.
- b. Connect the battery snap to the red LED and place it at least a meter away from you. View the LED through the different regions of the slide and sketch the diffraction patterns that you see in the appropriate spaces in Table 2.
- c. Repeat steps a and b above using the VSEPR slide provided by the instructor and record your observations in Table 3 and Table 4.

ANSWERS TO FOLLOW-UP QUESTIONS

Note: For comparison, it may be necessary to show the overheads of the following 4 pages to the class after they have completed their sketches.

1. Look at your sketches of arrays *a* and *b* on the Unit Cell slide. Array *a* is the two-dimensional projection of a body-centered cubic structure and *b* of a simple cubic arrangement. Now look in Table 2 at the diffraction patterns produced by each. What is the effect on the diffraction pattern of placing an identical atom at the center of each simple square in the array?

Every other diffraction spot is eliminated. These are referred to as systematic absences.

2. Look at your sketches of arrays *c* and *d* in Table 1. Array *c* represents two different kinds of atoms, each surrounded by four atoms of the other type. Array *d* is like that of array *b* above. Now look in Table 2 at the diffraction patterns produced by these arrays. What is the effect on the pattern of placing a different sized atom at the center of each simple cube?

Every other diffraction spot has changed in intensity.

3. Look at your sketches of arrays *e* and *f* in Table 1. Array *e* represents a structure in which all angles are 90° , but the sides are of unequal length (rectangle); and *f* one in which the angles are not 90° (inclined parallelograms). Now look in Table 2 at the diffraction patterns that are produced and describe what you see.

The diffraction patterns appear rotated. In *e*, the long direction of the rectangular array is vertical; in diffraction, the rectangle's long direction is horizontal. Note that this is a reciprocal relationship: long distances in the array become short distances in the diffraction pattern. In the array *f*, the diffraction pattern is rotated by 60° relative to the array.

4. Look at your sketches in Table 3. Each array simulates a molecule that consists of three atoms. What shape molecule is represented by array *a*? If the entire array was rotated 90° , describe what the new diffraction pattern would look like.

Array *a* comprises linear "molecules". If the array were rotated 90° , the spots in the diffraction pattern would rotate by 90° , also.

5. The sequence of arrays (*b*, *d*, and *c*) represents an array of angular molecules. What happens to the angle as you proceed through this sequence? Why is the diffraction pattern produced by *c* similar to that produced by *a*?

The angle increases in size. The diffraction pattern produced by *c* is similar to that produced by *a* because pattern *c* is almost linear.

6. A close look at your sketches for diffraction from arrays *e* and *f* in Table 4 reveals that these diffraction patterns are mirror images of each other. Explain why this is not surprising.

Because the arrays are also mirror images of one another.

7. What molecular shapes are simulated by arrays *g* and *h* in Table 3?

Array *g* is T-shaped, while *h* is arranged to simulate a trigonal planar arrangement.

EXTENSIONS

For more information on this experiment there are a number of interesting web sites:

www.yorvic.york.ac.uk/~cowtan/sfapplet/sfintro.html

- This is an Interactive Structure Factor Tutorial.

There are many other websites linked to these.

[The following figures are from A Material Science Companion, figures 4.6-4.9](#) |

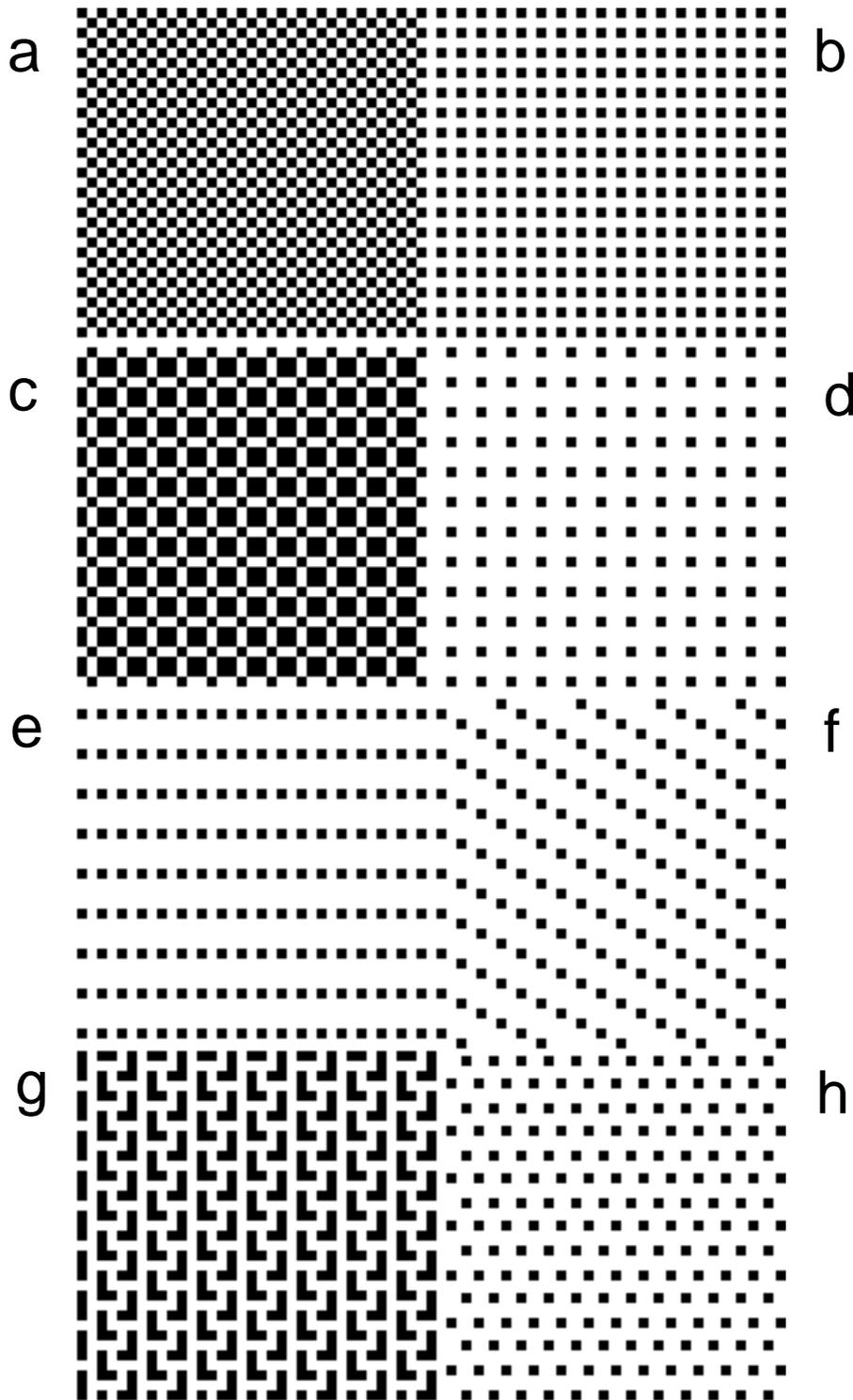


Figure 3. The arrays on the optical transform Unit Cell slide, available from ICE (oriented so that the ICE logo is on the right side as you look through the slide).

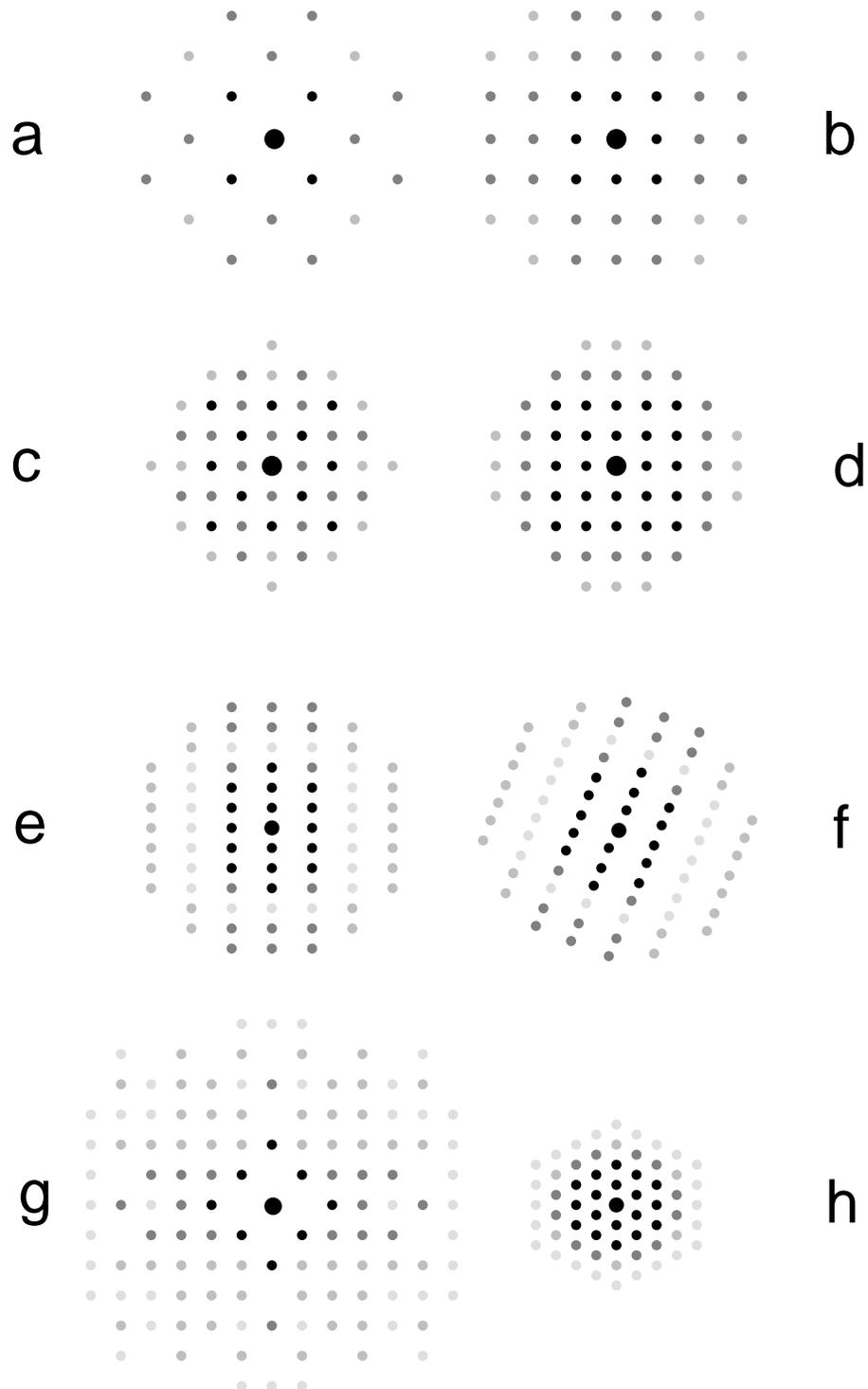


Figure 4. A simulation of the diffraction patterns from Figure 3. The letter by each pattern corresponds to the array from which the diffraction pattern is derived.

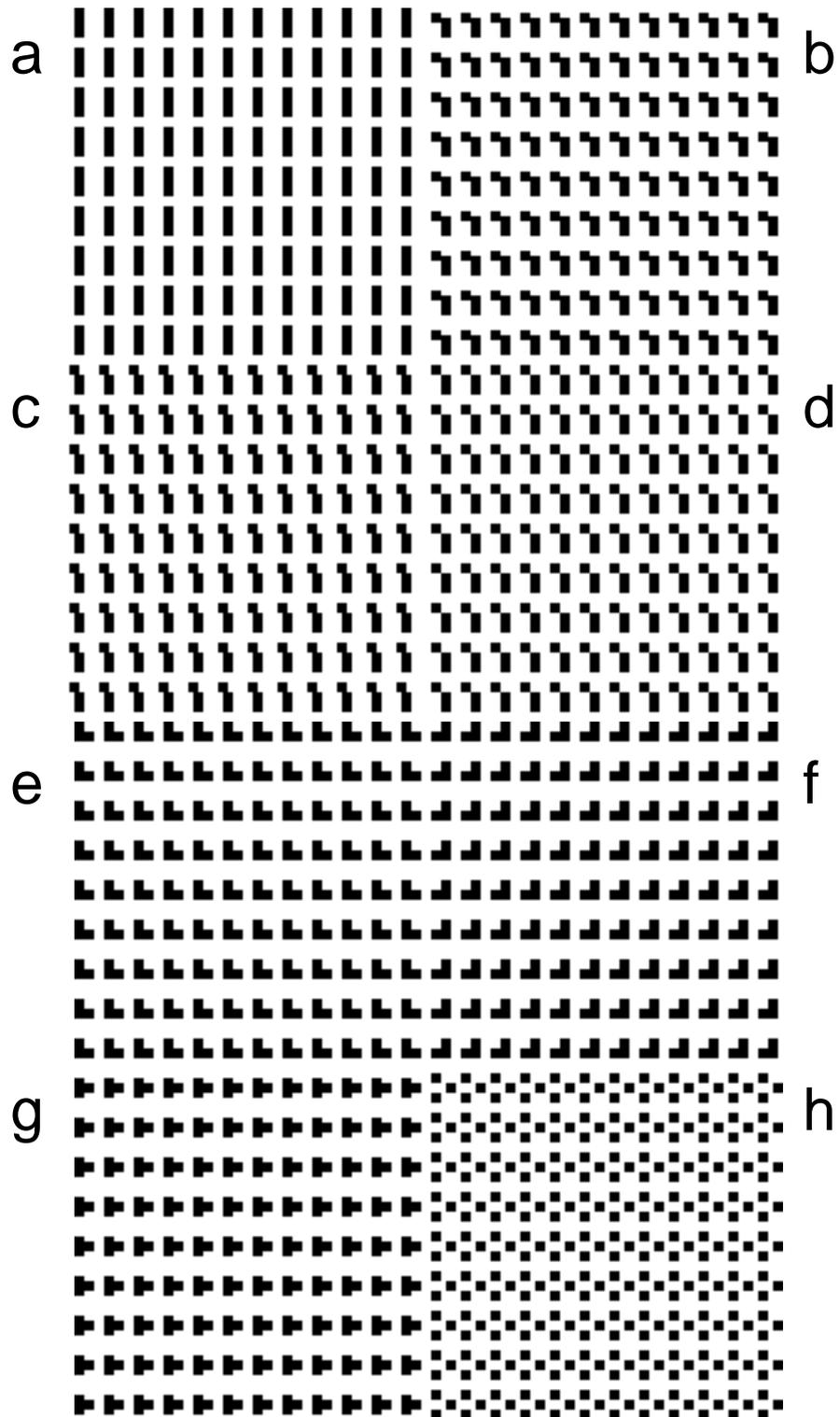


Figure 5. The arrays on the optical transform VSEPR slide, available from ICE (oriented so that the ICE logo is on the right side as you look through the slide).

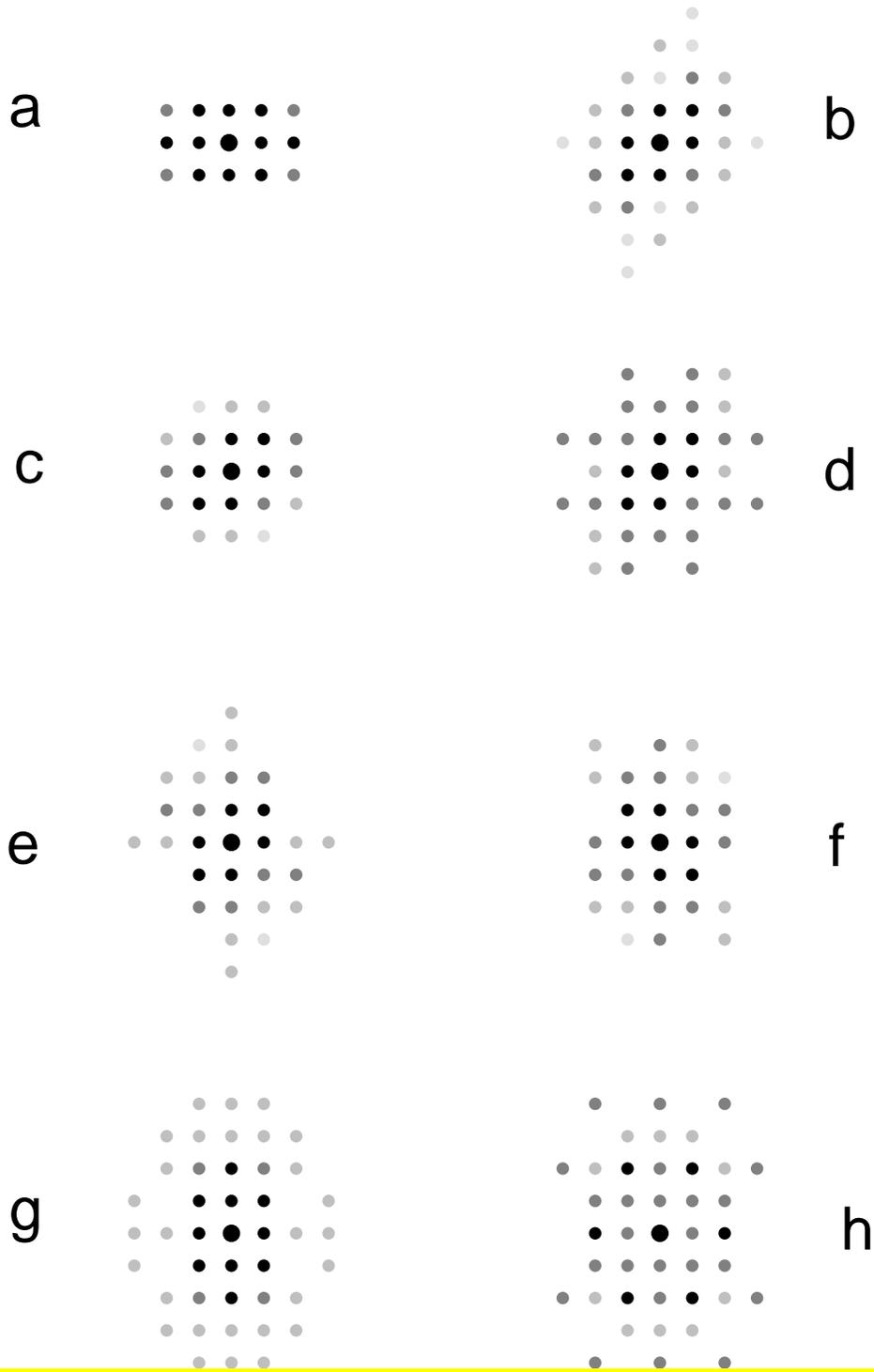


Figure 6. A simulation of the diffraction patterns from Figure 5. The indicated letter corresponds to the array from which the diffraction pattern is produced.

INVESTIGATION 2

PURPOSE

To relate diffraction patterns to real arrays of atoms, ions and molecules.

PROCEDURE

- a. Orient the Unit Cell slide provided by the instructor so that the ICE logo is on the right-hand side. With the stereoscope, look carefully at the arrays on the slide and make a sketch in the space provided in Table 1 of the Data Sheet.
- b. Connect the battery snap to the red LED and place it at least a meter away from you. View the LED through the different regions of the slide and sketch the diffraction patterns that you see in the appropriate spaces in Table 2.
- c. Repeat steps a and b above using the VSEPR slide provided by the instructor and record your observations in Table 3 and Table 4.

FOLLOW-UP QUESTIONS

1. Look at your sketches of arrays *a* and *b* on the Unit Cell slide. Array *a* is the two-dimensional projection of a body-centered cubic structure and *b* of a simple cubic arrangement. Now look in Table 2 at the diffraction patterns produced by each. What is the effect on the diffraction pattern of placing an identical atom at the center of each square in the array?
2. Look at your sketches of arrays *c* and *d* in Table 1. Array *c* represents two different kinds of atoms, each surrounded by four atoms of the other type. Array *d* is like that of array *b* above. Now look in Table 2 at the diffraction patterns produced by these arrays. What is the effect on the pattern of placing a different sized atom at the center of each square in the array?
3. Look at your sketches of arrays *e* and *f* in Table 1. Array *e* represents a structure in which all angles are 90° , but the sides are of unequal length (rectangle); and *f* one in which the angles are not 90° (inclined parallelograms). Now look in Table 2 at the diffraction patterns that are produced and describe what you see.
4. Look at your sketches in Table 3. Each array simulates a molecule that consists of three atoms. What shape molecule is represented by array *a*? If the entire array was rotated 90° , describe what the new diffraction pattern would look like.

5. The sequence of arrays (b , d , and c) represents an array of angular molecules. What happens to the angle as you proceed through this sequence? Why is the diffraction pattern produced by c similar to that produced by a ?

6. A close look at your sketches for diffraction from arrays e and f in Table 4 reveals that these diffraction patterns are mirror images of each other. Explain why this is not surprising.

7. What molecular shapes are simulated by arrays g and h in Table 3?

Name _____

Date _____ Period _____

INVESTIGATION 2 DATA SHEET

Table 1

a	b
c	d
e	f
g	h

Table 2

a	b
c	d
e	f
g	h

**INVESTIGATION 2
DATA SHEET (continued)**

Table 3

a	b
c	d
e	f
g	h

Table 4

a	b
c	d
e	f
g	h

INVESTIGATION 3

Notes for the Instructor

PURPOSE

To give students a better feeling for how a STM, AFM, or related SPM instruments operate and how they provide direct evidence for the existence of atoms.

METHOD

All of the SPM devices are based on the underlying principle of being able to detect changes in either a current or force of some kind, as a probe is moved across the surface of a material in atomic-scale increments. Recall the activity with a refrigerator magnet described on pages 14-16 in the “Exploring the Nanoworld” guide. This investigation will simulate the operation of a STM by using a multimeter to measure the resistance at various locations on a six-inch square metal plate onto which a simple pattern made from masking tape has been placed. Fit a piece of counted cross stitch needlepoint fabric over the metal to hide the pattern. A cartesian co-ordinate grid may also be marked on the fabric, if you wish students to include the quadrant or specific points covered by the tape. The alligator clip from one of the leads of the multimeter may be attached to the plate under the fabric at one of the corners while the other lead ends in a probe tip. The uncovered regions of the plate will show a relatively low resistance while those covered by the tape will show a high resistance. The students are then instructed to probe the plate through the spaces in the fabric. This will allow students to “map” the plate and discern the shape from their resistance data. This investigation may be conducted as either a “known” or “unknown” activity, depending on your focus. The procedure as outlined in the investigation itself is only a suggestion and may be modified in many ways.

MATERIALS

metal plate (any clean metal like aluminum cut into six-inch squares will work)

multimeter and leads (should be available from the physics department)

needlepoint fabric (counted cross stitch type)

ANSWERS TO FOLLOW-UP QUESTIONS

1. Student responses will vary.
2. The analogy is a good one in that it illustrates how the systematic recording of resistance data can be used to identify surface features on a material. It does not however have atomic resolution.

INVESTIGATION 3

PURPOSE

In this experiment you will simulate the operation of a Scanning Probe Microscope to determine the surface “structure” of a material.

INTRODUCTION

You will be given a metal plate onto which a piece of masking tape cut into a simple pattern has been placed. The plate has been covered with needlepoint fabric to provide you with some reference points as you “raster” the surface with the probe from the multimeter. Regions of low resistance indicate that you are probing the plate and those of high resistance are regions where the tape has been placed.

PROCEDURE

- a. Obtain a metal plate from your instructor. **Do not** remove the needlepoint fabric that masks the shape hidden beneath.
- b. Obtain a multimeter and leads. Connect the leads to the meter so as to read the resistance in a circuit. Set the meter to read ohms and turn the power switch to the “on” position.
- c. Touch the leads to a metal surface and observe that the resistance reading diminishes significantly since metals are far better electrical conductors than air. Touch the leads to a piece of masking tape to determine its electrical conductivity. Which is more electrically conductive?
- d. Attach the alligator clip from the black lead to one of the corners of the plate. Be careful not to detach the fabric from the plate
- e. Now, in a systematic way begin to move the red probe back and forth across the fabric. The probe is sharp and must be carefully pushed through the fabric in order to make contact with the plate below.
- f. Using the axes and scale provided on the fabric, record the points on the paper where high resistance was measured.

FOLLOW-UP QUESTIONS

1. From your data, describe or draw the shape that is hidden below the paper.
2. a. In what ways has this been a useful analogy to SPM? In what ways does it fail ?

ACTIVITY 1

Notes to the Instructor

This activity was designed to encourage students to use various library resources and/or the Internet to obtain some more information about the topics being studied in this section. It could also be used at the end of all of these sections to encompass a wider variety of different topics that could then be assigned to students. It may be necessary to modify the questions on the hand out for certain topics. **There should also be a discussion with the students concerning the validity of the information that can be found on the web. Caution them to not rely on a single source, but to try to verify their findings at other sites.**

Some possible topics to assign within this section include, but are not limited to

- SPM
- STM
- AFM
- MFM (Magnetic Force Microscopy)
- X-ray diffraction
- Crystalline structures/solids
- Amorphous solids
- Visible light
- Electromagnetic radiation
- Optical transform experiments
- Tungsten
- Platinum
- Platinum-Iridium alloys
- Electrostatic forces
- Piezoelectric materials

If the activity is done after all the sections are completed, some possible topics to include are those listed above as well as:

- Memory metal
- Nitinol
- Alloy
- Austenite
- Martensite
- LEDs, including white LEDs
- CDs
- Semiconductors
- Blue light emitting diodes and lasers
- Ferrofluids

ACTIVITY 1**INTRODUCTION**

The intent of this activity is to allow you to see the extent to which the topics of this unit have permeated both the scientific world and the everyday world around you. Your specific topic will be assigned to you by your instructor.

1. List some possible search terms.

2. Explain what your topic is.

3. List two web sites that would be useful in teaching you more about _____.

a. _____

b. _____

Search Engine _____

4. Find references that contain directions for laboratory applications of _____.
List some uses of your topic. If it is not usable in the laboratory, explain its use(s) and/or why you would want to know about it.

Applications/Uses:

a. _____

b. _____

Sources:

a. _____

b. _____

5. If you have an actual “thing” as opposed to a concept, name two firms that manufacture or sell _____(name topic here).

a. _____

b. _____

Source _____

6. The price/cost of _____ is approximately _____.
(buying/selling)

Source _____

[This question is not applicable to all topics.]

7. See if your topic can be found in a popular publication, such as *Time*, *Newsweek*, *Popular Science*, *Discovery*, *National Geographic*, etc.

Publication _____

Title _____

8. Find a “good” article on your topic and print it.

Briefly defend why you believe it is good.

How is this topic relevant to what we have been studying in class?

Summarize the article and explain what information you can learn from it.

X-Ray Diffraction Review Questions

Instructor's Guide

1. It is now possible to grow certain solids virtually an atomic layer at a time. Consider solid **A**, formed exclusively from copper and gold atoms, in which two atomic layers of gold atoms are put down, followed by two atomic layers of copper atoms, followed by two atomic layers of gold atoms, etc. The cycle is repeated until the desired thickness is reached, say, 100 atomic layers of each kind of atom; this is shown schematically below with X's and O's being Cu and Au, respectively.

```

XXXXXXXXXX
XXXXXXXXXX
OOOOOOOOO  cross-sectional view of solid A
OOOOOOOOO  X = Cu; O = Au
XXXXXXXXXX
XXXXXXXXXX
OOOOOOOOO
OOOOOOOOO etc.
    
```

In preparing solid **B**, in contrast, the growth is changed after each layer: an atomic layer of Cu is grown, then an atomic layer of Au, then another atomic layer of Cu, etc:

```

XXXXXXXXXX
OOOOOOOOO  cross-sectional view of solid B
XXXXXXXXXX  X = Cu; O = Au
OOOOOOOOO etc.
    
```

Why can diffraction be used to tell the two solids apart?

The different structures create unit cells of different sizes, which, in turn, cause different diffraction patterns.

2. a. Infrared light and ultraviolet light can be used to generate a diffraction pattern from an array like those you worked with in lab. If your eyes were sensitive to infrared (IR) light with a wavelength of 8000\AA and to ultraviolet (UV) light with a wavelength of 3000\AA , using Fraunhofer's diffraction equation $\lambda = d \sin \phi$ with d equal to the spacing between the lines in the diffraction grating (in this case $1.0 \times 10^6\text{\AA}$), find the values for ϕ and compare them.

IR	UV
$\lambda = d \sin \phi$	$\lambda = d \sin \phi$
$8000 = 1.0 \times 10^6 \text{\AA} (\sin \phi)$	$3000 = 1.0 \times 10^6 \text{\AA} (\sin \phi)$
$\sin \phi = 8.0 \times 10^{-3}$	$\sin \phi = 3.0 \times 10^{-3}$
$\phi = 0.46^\circ$	$\phi = 0.17^\circ$

The IR light, which has a longer wavelength, has a larger angle, and UV has a shorter wavelength and a smaller angle.

- b. What difference would you see in the diffraction patterns produced by these two types of light?

(Students may have a hard time answering this.)

The angle and therefore the size of the diffraction pattern increases with the wavelength of light used. You can see this, if you look back at *Appendix A* which shows Fraunhofer diffraction. Mathematically, students should understand that the side opposite the larger angle will be larger in size. Therefore, as shown in the diagram the side opposite the angle, ϕ , is calculated by $d \sin\phi$. The distance between dots in a diffraction pattern is also calculated by $d \sin\phi$. Therefore, UV radiation would lead to a small diffraction pattern, and IR radiation would yield a large diffraction pattern.

3. The diffraction equation for the slides you used in lab can be written as $d \sin\theta = m\lambda$, where d is the spacing between dots on the slide; x is the spacing between spots in the resulting diffraction pattern; L is the distance from the slide to the screen (onto which the diffraction pattern is projected); and λ is the wavelength of light used. Using this equation, note which of the variables d , x , λ , and L are constant and which are changing as you answer the questions.

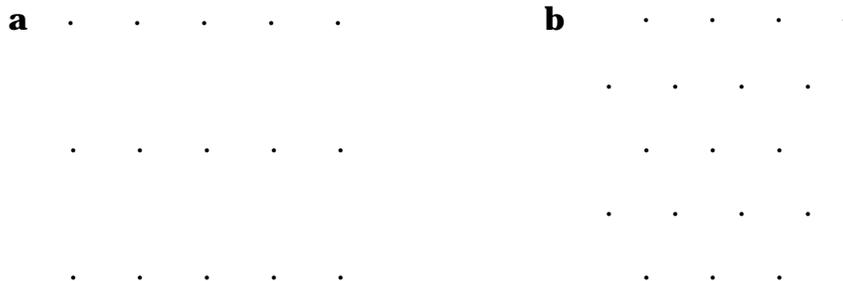
- a. If you have a given array with a laser light source, what happens to the size of the diffraction pattern if you move the slide farther from the screen?

L is increasing. λ and d are held constant, so the equation predicts that x (the spacing between the diffraction spots) will increase. Therefore, the diffraction pattern should get larger as the length between the slide and the screen increases.

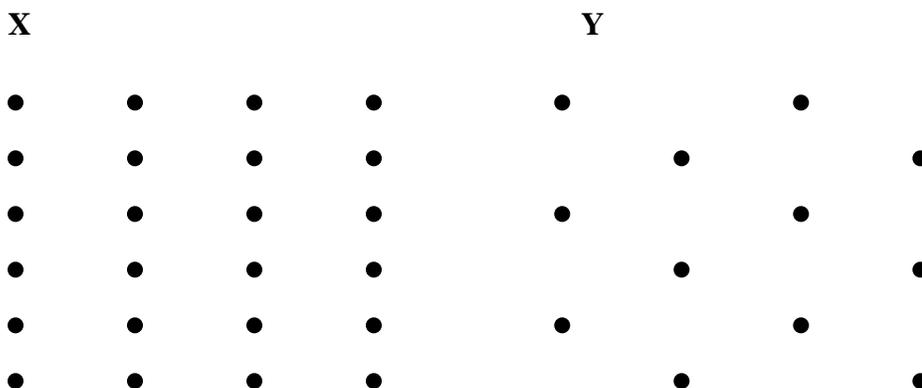
- b. If you use a given array with a white light source, what is the relative size of the diffraction pattern for red vs. violet light.

For any array, the diffraction spots have a rainbow appearance with the red portion of the spots defining the largest diffraction pattern and the violet portion of the spots defining the smallest diffraction pattern. In terms of the equation, d and L are constants so that $x = a$ constant times λ . The wavelength, λ , is larger for red light than for violet light, so x should be larger for red light than for violet light. Therefore, a larger diffraction pattern is expected for red compared to violet light.

4. The two arrays of dots, **a** and **b**, are identical except that in array **b** there is an extra dot in the middle of each rectangle formed by four neighboring dots in array **a**.



Using the same experimental conditions (same wavelength and distance from the array to the screen where diffraction is observed), the diffraction patterns for the two arrays are found to be identical, except that every other diffraction spot is missing from one of the patterns, as shown below. Call the diffraction pattern on the left **X** and that on the right **Y**.



- a. Based on your laboratory observations, which of the two diffraction patterns **X** and **Y** corresponds to array **a** and which to array **b**?

Diffraction pattern X corresponds to array a and diffraction pattern Y corresponds to array b: what was seen in lab with square arrays was that adding an extra dot to the middle of the array caused every other diffraction spot to disappear.

- b. Explain why having additional dots in the centers of the array of rectangles (array **b** relative to array **a**) has the effect you describe in part *a* on the diffraction pattern.

The extra dots in the middle of the array cause destructive interference.

- c. Compare the relative sizes of unit cells for arrays **a** and **b**. What happens to the relative sizes of their diffraction patterns?

Array a has a larger unit cell than array b (see Figure). However, the diffraction pattern of a would be smaller than that of b because there is an inverse relationship that exists between the spacing between the dots in the array and spots projected in the diffraction pattern (reciprocal lattice effect).

5. It has been predicted that if we could put the element hydrogen, normally an invisible gas of diatomic molecules at room temperature and pressure, under sufficiently high pressure – millions of atmospheres - it would become a metal!

If you could conduct a diffraction experiment on the hydrogen sample while it was being squeezed, what do you predict would happen to the spacing between diffraction spots as the atoms are placed under increasing pressure and why?

An increase in pressure should cause the atoms to become closer together, and the spacing between spots of the diffraction pattern would consequently increase: Recall that $dx = \text{constant}$, i.e., atomic spacing and their diffraction spot spacing are inversely related.

6. As mentioned in class, relative atomic positions in crystals are generally determined by diffraction experiments. The optical transform slide was used to investigate diffraction effects: the photographically-reduced dot arrays on your slide represent arrays of atoms in a crystal. The diffraction equation for the slide you used can be written as $dx/L = \lambda \sin \theta$, where d is

the distance between the dots on the slide; x is the distance between the spots of the resulting diffraction pattern; L is the distance between the slide and the surface where the diffraction pattern is observed; and λ is the wavelength of light used for the experiment. For your experiment, you can observe a distant point source of white light through your slide (a street lamp, e.g.); and/or a point source of colored light, like your LED from lab or a traffic light.

- a. Design and interpret an experiment using the Discovery slide to show that d and x are inversely related.

In array "b" there is a smaller spacing (value of d) than in array "d." If we keep the viewing arrangement of a light source constant (L and λ constant), then $dx = \text{constant}$, predicting that the size of the diffraction pattern, x , and the dot spacing on the slide, d , are inversely related. You should see that array "d" gives a smaller diffraction pattern than array "b."

- b. Design and interpret an experiment to show that x and λ are directly related.

If you look at any single array from a fixed distance, you are keeping d and L constant, so that $x/\lambda = \text{constant}$, meaning they are directly related. You should see by looking at a white light source, e.g., that the longer wavelength red light gives a larger diffraction pattern (value of x), than shorter wavelengths of light that occur toward the violet part of the spectrum.

7. A sample of Fe, like many materials, expands as it is warmed. What will happen to the size of the diffraction pattern as the sample is warmed why?

There is an inverse relationship between atom spacing and diffraction spot spacing, if the wavelength and spot-to-screen separation remain constant during an experiment. Thus, the diffraction pattern should contract as the material expands with heating.

X-Ray Diffraction Review Questions

Name _____

Date _____ Period _____

1. It is now possible to grow certain solids virtually an atomic layer at a time. Consider solid **A**, formed exclusively from copper and gold atoms, in which two atomic layers of gold atoms are put down, followed by two atomic layers of copper atoms, followed by two atomic layers of gold atoms, etc. The cycle is repeated until the desired thickness is reached, say, 100 atomic layers of each kind of atom; this is shown schematically below with X's and O's being Cu and Au, respectively.

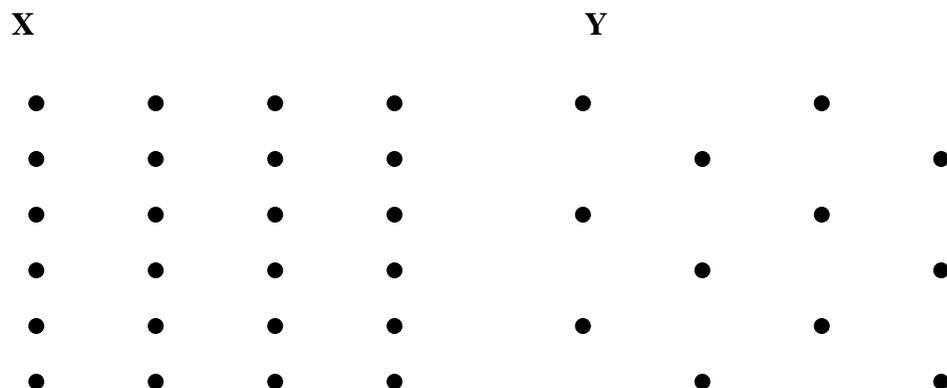
```
XXXXXXXXXX
XXXXXXXXXX
OOOOOOOOO cross-sectional view of solid A
OOOOOOOOO X = Cu; O = Au
XXXXXXXXXX
XXXXXXXXXX
OOOOOOOOO
OOOOOOOOO etc.
```

In preparing solid **B**, in contrast, the growth is changed after each layer: an atomic layer of Cu is grown, then an atomic layer of Au, then another atomic layer of Cu, etc:

```
XXXXXXXXXX
OOOOOOOOO cross-sectional view of solid B
XXXXXXXXXX X = Cu; O = Au
OOOOOOOOO etc.
```

Why can diffraction be used to tell the two solids apart?

2. a. Infrared light and ultraviolet light can be used to generate a diffraction pattern from an array like those you worked with in lab. If your eyes were sensitive to infrared (IR) light with a wavelength of 8000\AA and to ultraviolet (UV) light with a wavelength of 3000\AA , using Fraunhofer's diffraction equation $m\lambda = d \sin \theta$ with d equal to the spacing between the lines in the diffraction grating (in this case $1.0 \times 10^6\text{\AA}$), find the values for θ and compare them.



- a. Based on your laboratory observations, which of the two diffraction patterns **X** and **Y** corresponds to array **a** and which to array **b**?
- b. Explain why having additional dots in the centers of the array of rectangles (array **b** relative to array **a**) has the effect you describe in part *a* on the diffraction pattern.
- c. Compare the relative sizes of unit cells for arrays **a** and **b**. What happens to the relative sizes of their diffraction patterns?
5. It has been predicted that if we could put the element hydrogen, normally an invisible gas of diatomic molecules at room temperature and pressure, under sufficiently high pressure – millions of atmospheres - it would become a metal!

If you could conduct a diffraction experiment on the hydrogen sample while it was being squeezed, what do you predict would happen to the spacing between diffraction spots as the atoms are placed under increasing pressure and why?

6. As mentioned in class, relative atomic positions in crystals are generally determined by diffraction experiments. The optical transform slide was used to investigate diffraction effects: the photographically-reduced dot arrays on your slide represent arrays of atoms in a crystal. The diffraction equation for the slide you used can be written as $d\sin\theta = \lambda$, where d is the distance between the dots on the slide; x is the distance between the spots of the resulting diffraction pattern; L is the distance between the slide and the surface where the diffraction pattern is observed; and λ is the wavelength of light used for the experiment. For your experiment, you can observe a distant point source of white light through your slide (a street lamp, e.g.); and/or a point source of colored light, like your LED from lab or a traffic light.
- Design and interpret an experiment using the Discovery slide to show that d and x are inversely related.
 - Design and interpret an experiment to show that x and λ are directly related.
7. A sample of Fe, like many materials, expands as it is warmed. What will happen to the size of the diffraction pattern as the sample is warmed why?

X-Ray Diffraction & Scanning Probe Microscopy Assessment

Instructor's Guide

Matching

Match the word with the best definition.

- | | | |
|-----------------|----------------------------------|---|
| <u>D</u> | 1. diffraction | a. an instrument that can image atoms and operates by sensing the force between the surface atoms of a sample and a probe tip |
| <u>H</u> | 2. atom | b. an instrument that can image atoms by the quantum mechanical tunneling of tunneling effect electrons between an electrically conducting atomic tip and a substrate |
| <u>K</u> | 3. rastering | c. energy of the most weakly bound electrons in a metal |
| <u>G</u> | 4. tunneling effect | d. the scattering of light from a regular array, producing constructive and destructive interference |
| <u>L</u> | 5. X-ray | e. opposition to the flow of electric current |
| <u>J</u> | 6. piezoelectric material | f. visible light-based method of investigating atomic arrangements at a macroscopic level |
| <u>A</u> | 7. AFM | g. the movement of an electron due to its wave nature through a classical barrier |
| <u>B</u> | 8. STM | h. the smallest unit of a chemical element |
| <u>E</u> | 9. electrical resistance | i. radiant energy that exhibits wavelike behavior and travels through space at the speed of light in a vacuum |
| <u>I</u> | 10. electromagnetic radiation | j. material that distorts when a voltage is applied to it |
| <u>F</u> | 11. optical transform experiment | k. scanning back and forth across the surface of a material |
| <u>C</u> | 12. Fermi Energy | l. electromagnetic radiation with a wavelength of about the size of an atom |

18. a.) What is the frequency of an X-ray with a wavelength of 1.54 angstroms, the wavelength produced by an X-ray tube with a copper target? (The speed of light is 2.998×10^8 m/s.)

$$c = \lambda\nu$$

$$(2.998 \times 10^8 \text{ m/s}) = (\nu)(1.54 \text{ angstroms})(1 \times 10^{-10} \text{ m/ angstrom})$$

$$\nu = 1.95 \times 10^{18} \text{ s}^{-1}$$

- b.) What is the frequency of an X-ray with a wavelength of 0.7107 angstroms, the wavelength produced by an X-ray tube with a molybdenum target?

$$c = \lambda\nu$$

$$(2.998 \times 10^8 \text{ m/s}) = (\nu)(0.7107 \text{ angstroms})(1 \times 10^{-10} \text{ m/ angstrom})$$

$$\nu = 4.218 \times 10^{18} \text{ s}^{-1}$$

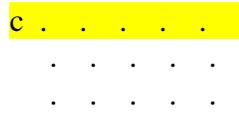
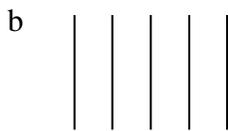
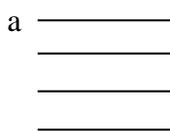
19. What is the frequency of a 670 nm red laser?

$$c = \lambda\nu$$

$$(2.998 \times 10^8 \text{ m/s}) = (\nu)(670 \text{ nm})(1 \times 10^{-9} \text{ m/nm})$$

$$\nu = 4.47 \times 10^{14} \text{ s}^{-1}$$

20. Sketch a qualitative representation of the diffraction pattern produced by the following two-dimensional arrays.



Vertical spots

Horizontal spots

Square pattern of spots

21. Sketch a qualitative representation that shows the difference in the diffraction pattern produced by the following pairs of two-dimensional arrays.



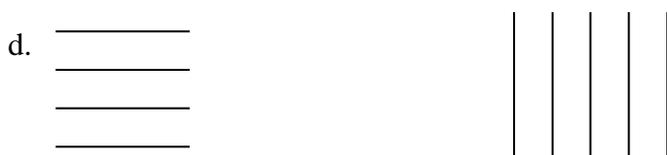
The smaller square array gives the larger square diffraction pattern.



The pattern on the left gives a square diffraction pattern; the array on the right gives a rectangular diffraction pattern with the long distance between spots in the horizontal direction.



Both arrays give rectangular diffraction patterns. The array on the left will give a diffraction pattern with the longer edge of the rectangle in the vertical direction. The array on the right will produce a diffraction pattern with the longer edge of the rectangle in the horizontal direction.



An array of lines gives a series of dots in the diffraction pattern. The horizontal pattern of lines will give a diffraction pattern consisting of a set of spots running in the vertical direction, and the vertical array of lines gives a diffraction pattern consisting of a set of spots in the horizontal direction.

22. Why must X-rays be used in crystal-structure determinations rather than visible light?

In order for diffraction to occur, the wavelength of incident radiation must be approximately the same as the spacing of the atoms. Atomic separations are typically a few angstroms. X-rays, with wavelengths of about one angstrom, are a far better match to interatomic spacings than visible light ($\lambda \sim 4,000$ angstroms to 7,000 angstroms).

23. Why does X-ray diffraction give more information about the three-dimensional structure of a crystalline solid than does scanning tunneling microscopy?

The STM can only collect two-dimensional information. The penetrating nature of X-rays and subsequent diffraction of various planes of atoms adds information in the third dimension.

24. Use the Bragg equation to explain the observation that as the spacing between the atoms decreases, the spacings in the resulting diffraction pattern increase.

For a given order of diffraction (n value), as d becomes smaller, $\sin \theta$ must become larger to satisfy the Bragg equation: $2d(\sin \theta) = n\lambda$. Thus, as $\sin \theta$ and θ increase, the observed spacing of the spots in a diffraction pattern increases.

25. Briefly explain how the STM works.

The STM is an instrument that moves a probe tip terminating in a single atom over a surface that is within Angstroms of it. It maps out the contours of the features of the surface, using differences in height at constant current or in electrical current at constant height. Electrostatic forces hold the electrons on the surface of any material, and this acts as a barrier for preventing the electrons from escaping. However, if another material, such as the probe tip is brought close enough to the surface, the electron can escape from the surface into the tip (or vice versa, depending on the direction of the applied voltage) through the quantum mechanical phenomenon of tunneling. A computer typically sends instructions to the tip, and the tip rasters over the surface and creates a complete image of the surface with atomic resolution.

X-Ray Diffraction & Scanning Probe Microscopy Assessment

Name _____

Date _____ Period _____

Matching

Match the word with the best definition.

- | | | |
|-------|----------------------------------|---|
| _____ | 1. diffraction | a. an instrument that can image atoms and operates by sensing the force between the surface atoms of a sample and a probe tip |
| _____ | 2. atom | b. an instrument that can image atoms by the quantum mechanical tunneling of tunneling effect electrons between an electrically conducting atomic tip and a substrate |
| _____ | 3. rastering | c. energy of the most weakly bound electrons in a metal |
| _____ | 4. tunneling effect | d. the scattering of light from a regular array, producing constructive and destructive interference |
| _____ | 5. X-ray | e. opposition to the flow of electric current |
| _____ | 6. piezoelectric material | f. visible light-based method of investigating atomic arrangements at a macroscopic level |
| _____ | 7. AFM | g. the movement of an electron due to its wave nature through a classical barrier |
| _____ | 8. STM | h. the smallest unit of a chemical element |
| _____ | 9. electrical resistance | i. radiant energy that exhibits wavelike behavior and travels through space at the speed of light in a vacuum |
| _____ | 10. electromagnetic radiation | j. material that distorts when a voltage is applied to it |
| _____ | 11. optical transform experiment | k. scanning back and forth across the surface of a material |
| _____ | 12. Fermi Energy | l. electromagnetic radiation with a wavelength of about the size of an atom |

Multiple Choice

Choose the best answer.

- _____ 13. _____ forces act between the electrons and the nuclei of atoms to hold the atoms of a metal together.
- a. Magnetic
 - b. Covalent
 - c. Intermolecular
 - d. Electrostatic
- _____ 14. The STM uses differences in height or _____ to “map out” the atomic surface.
- a. spatial orientation
 - b. electrical current
 - c. resolution
 - d. light
- _____ 15. Challenges that must be overcome in order to have scanning probe microscopy work effectively include all of the following **EXCEPT**
- a. vibrations
 - b. probe sharpness
 - c. position control
 - d. substance is nonconductor of electricity

Problems

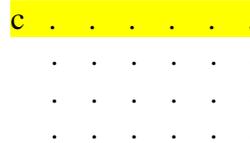
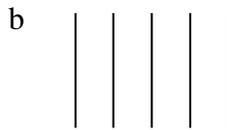
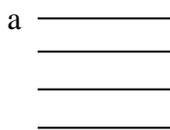
16. The radius of a tungsten atom is estimated to be 137 pm. What is the diameter in meters, centimeters, and angstrom units of a perfect STM tip that terminates in a single atom of tungsten? **SHOW WORK!**
17. How far (in meters) does an STM tip traverse in scanning a row of 400 nickel atoms? The radius of a nickel atom is 1.24 angstroms. **SHOW WORK!**

18. a.) What is the frequency of an X-ray with a wavelength of 1.54 angstroms, the wavelength produced by an X-ray tube with a copper target? (The speed of light is 2.998×10^8 m/s.)

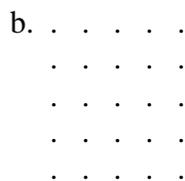
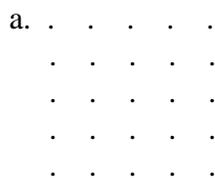
b.) What is the frequency of an X-ray with a wavelength of 0.7107 angstroms, the wavelength produced by an X-ray tube with a molybdenum target?

19. What is the frequency of a 670 nm red laser?

20. Sketch a qualitative representation of the diffraction pattern produced by the following two-dimensional arrays.



21. Sketch a qualitative representation that shows the difference in the diffraction pattern produced by the following pairs of two-dimensional arrays.



c. . . .
. . . .
. . . .
. . . .
. . . .

d. _____

22. Why must X-rays be used in crystal-structure determinations rather than visible light?

23. Why does X-ray diffraction give more information about the three-dimensional structure of a crystalline solid than does scanning tunneling microscopy?

24. Use the Bragg equation to explain the observation that as the spacing between the atoms decreases, the spacings in the resulting diffraction pattern increase.

25. Briefly explain how the STM works.

APPENDIX A

A More Detailed Look at Diffraction

Reflection of X-rays from parallel planes of atoms creates constructive interference, referred to as the Bragg diffraction condition. As a result of the angle of incidence equaling the angle of reflection, if the atomic planes are separated by a distance, d , then X-rays reflected at a given angle, θ , relative to the plane will arrive at a detector in phase, provided the additional distance traveled by the lower light ray relative to the upper light ray is an integral number of wavelengths, n ($n = 1, 2, 3, \dots$). Using trigonometry, this extra path length that the lower light ray travels is $2(d \sin \theta)$, leading to Bragg's law, $2(d \sin \theta) = n \lambda$.

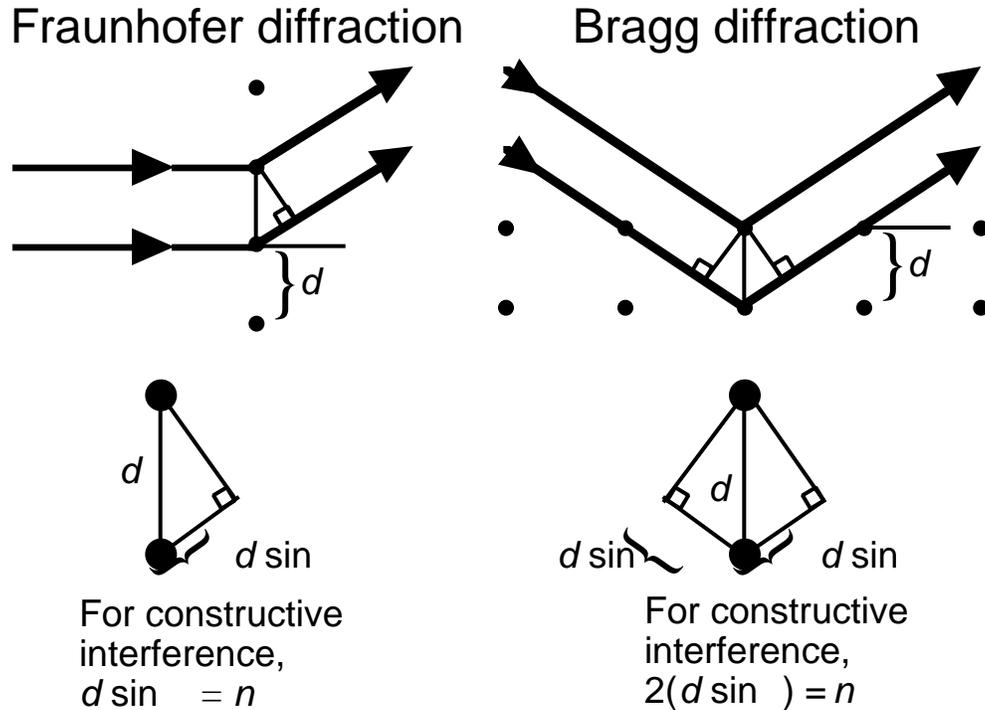


Figure 1. A comparison of Fraunhofer and Bragg diffraction.

The optical transform experiment, based on visible light, is an example of Fraunhofer diffraction. If the light transmitted through an array of scattering centers is viewed at what is effectively infinite distance, the condition for constructive interference is $d \sin \theta = n \lambda$, where the spacing, d , between the atoms and the scattering angle, θ , are shown in the figure. The scattered rays are in phase if the lower ray travels an additional distance ($d \sin \theta$) that is an integral number of wavelengths, $n \lambda$.

APPENDIX B

More on Tunneling

If a metal probe tip terminating in a single atom is placed sufficiently close to an electrically conductive sample and a small voltage is applied between the probe and sample, then electron tunneling may occur between the tip and substrate. The net flow of electrons can be measured as a tunneling current, which is proportional to the transmission probability. When the probe above the sample is moved horizontally, any bumps on the surface will change the tip-to-surface separation, because of changes in the overlap between the tip atom and the surface atoms. Changes in the separation distance of as small as 0.01 nm result in measurable changes in the tunneling current, because of the exponential relationship between the separation and the transmission probability. Thus, when the tip is directly over a surface atom, the tunneling current will be higher than when the tip is between two atoms. Higher currents mean that the substance being investigated has a higher surface height at that position and shorter tunneling distance. Measurement of the tunneling current obtained from scanning (rastering) consequently generates the topographic map of the surface with atomic resolution.

APPENDIX C

How the Challenges are Solved

To circumvent the problem of vibrations, the STM is usually operated in constant-current mode, which makes use of a feedback controller. The feedback controller measures the actual tunneling current and compares it to a desired value that the operator can control. The tip is connected to a positioner that is in turn connected to the feedback controller. Voltages from the feedback controller change the length of the positioner. The tip will be pulled away from the surface if the current is higher than desired or lowered toward the surface if the current value is lower than desired. In this way the desired current value is maintained as the probe scans over the surface. The change in the positioner's length is directly proportional to the applied voltage. Thus, changes in voltage produced by the feedback controller are directly proportional to the changes in surface height.

At each location on the surface, the computer measures the surface height based on the voltage applied to maintain constant tunneling current. This two-dimensional array of numbers, representing heights at different positions in the area surveyed, is often represented by gray-scale imaging. With gray-scale imaging, the height at each point is represented by the intensity of color with white used for showing the highest points and black for the lowest points. As a result, the image created shows a striking resemblance to the atomic model. The deep holes correspond to the positions of missing atoms in the model. The bright spots correspond to the atoms that protrude above the surface plane. The STM does not actually give the physical positions of the atoms, but it senses their electrons and bonds. As a result, the current detected is dependent upon both the tip-to-atom distance as well as the chemical identity of the surface atoms.

APPENDIX D

More about the STM Tip

An electrochemical process is used to make the tips. For tungsten, a fine wire is held vertically and partially immersed in an aqueous solution of base. The tungsten surface is oxidized to a dense, soluble oxide when a 5-V potential is applied to the wire. The tungsten oxide flows down past the tip and prevents further electrolysis except where the wire enters the solution. A different method, an alternating current etching procedure, is used with Pt and Pt-Ir alloys. In both cases localized etching creates a “neck” in the wire, and the wire will be etched through at this thin part, as the bottom part falls off. The tip usually terminates in a small cluster of atoms or the desired single atom.

Piezoelectric materials that expand or contract when a voltage is applied to them are used to make a scanner that controls the tip's position. The most common way of using piezoelectric materials for the tip positioning is to take a single tube of piezoelectric material, typically a ceramic, and to place four metal electrodes on the outside of the tube and a single electrode inside. The tube will extend or contract along its length and/or bend in any direction, if appropriate combinations of voltages are applied to the electrodes. The tip is mounted along the axis of the tube, at its end. The surface-to-tube separation increases or decreases with changes in the level of expansion or contraction. The tip moves mainly sideways, because it has been made so that the amount that it bends is small compared to its length. A typical piezoelectric scanner requires voltages that are around 100V, and the tip can move inside a square scan area with 0.004 mm sides. Levers, gears, and other piezoelectric translators allow the tip to come within a few micrometers of the sample without crashing into it. It needs to be less than 10 angstroms from the surface to detect the tunneling current between the sample and the tip. At this distance the electron orbitals of the sample and the tip nearly overlap. Hence, a small voltage can be applied, and current is produced from the quantum mechanical tunneling that occurs.

APPENDIX E

Imaging

For any molecule to be imaged by the STM, it must be attached to a rigid, flat, conducting material. However, this anchoring must not damage the molecule or change it in any way. Hence, large molecules have been imaged by attaching them to substrates such as graphite and gold, or they may be absorbed from electrolyte solutions. Variations of STM have been developed that are capable of imaging samples that are not electrical conductors (atomic force microscopy). Magnetic properties have also been used to image surfaces.

Moving Atoms

To move an atom, the tip is placed above the atom and lowered to a closer distance than is normally used for scanning. The tip is then moved across the surface, dragging the atom with it. The interaction of van der Waals forces is thought to be the most likely explanation of this phenomenon.