X-Ray Diffraction and Scanning Probe Microscopy *Student Materials*

X-Ray Diffraction and Scanning Probe Microscopy

x-ray diffraction provides ______________________________________

<u>How it works</u>
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

<u>Light</u>
Controversy: Newton = __________________ **Modern View** = ______________________
others = ____________________

light consists of <u>quanta</u>- ___________________________________
-amount of energy dependent on color of light

Picture of a wave –crest/trough/wavelength identified

__________________- distance between 2 neighboring peaks or troughs (λ)

__________________- 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
$v = f\lambda$ 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 (λ = angstrom) = distance between atoms in a crystal

visible light = spacing on 35 mm slide = diffraction grating

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

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 $\rightarrow$ diffraction pattern

Purpose: provide info. about structures of crystalline solids
data used to determine molecular structures b/c relative atomic positions determined therefore, evidence & indirect proof of atoms-periodic repeating atomic arrangement in crystals

symmetry of pattern = symmetry of atomic packing

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

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

c = ____________________ = 3.00×10^8 m/s (through air in a vacuum)

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

visible part of spectrum consists of many wavelengths of light

longest λ = _____ = f lowest shortest λ = ___________ = 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 = ______

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.

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

$d\sin\varphi = n\lambda$ -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

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**

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**

Name ______________________
Date___________Period______

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

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 ?

Name______________________
Date____________Period______

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

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.

   XXXXXXXXX
   XXXXXXXXX
   OOOOOOOOO cross-sectional view of solid **A**
   OOOOOOOOO **X = Cu; O = Au**
   XXXXXXXXX
   XXXXXXXXX
   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:

   XXXXXXXXX
   OOOOOOOOO cross-sectional view of solid **B**
   XXXXXXXXX **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 8000Å and to ultraviolet (UV) light with a wavelength of 3000Å, using Fraunhofer's diffraction equation $\lambda = d \sin\varphi$ with d equal to the spacing between the lines in the diffraction grating (in this case 1.0×10^6Å), find the values for φ and compare them.

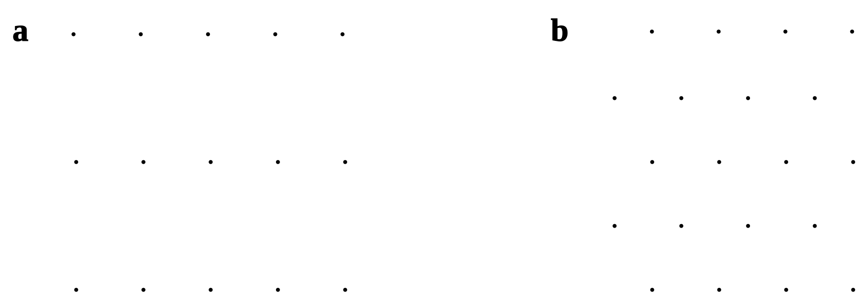
b. What difference would you see in the diffraction patterns produced by these two types of light?

3. The diffraction equation for the slides you used in lab can be written as d x = λ L, 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?

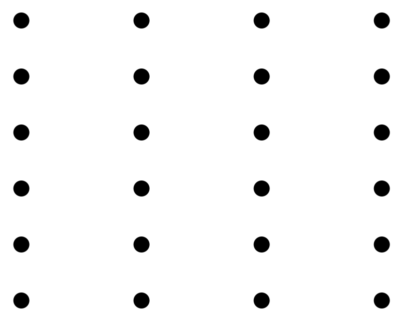
b. If you use a given array with a white light source, what is the relative size of the diffraction pattern for red vs. violet light.

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**.

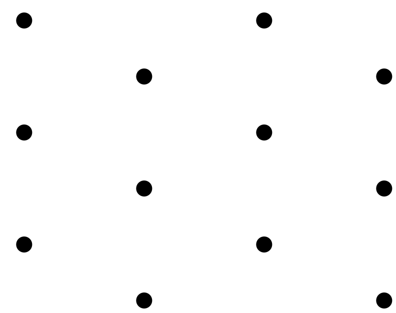


Using the same experimental conditions (same wavelength and distance from the array to the screen where diffraction is observed), the diffraction patterns for the two arrays are found to be identical, except that every other diffraction spot is missing from one of the patterns, as shown below. Call the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

X



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**?

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 $dx/L = \lambda$, 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.

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

   b. 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

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!**

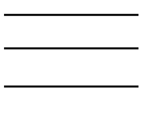
17. How far (in meters) does an STM tip traverse in scanning a row of 400 nickel atoms? The radius of a nickel atom is 1.24 angstroms. **SHOW WORK!**

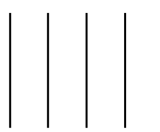
18. a.) What is the frequency of an X-ray with a wavelength of 1.54 angstroms, the wavelength produced by an X-ray tube with a copper target? (The speed of light is 2.998 x 10^8 m/s.)

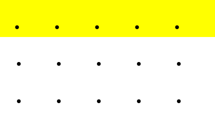
b.) What is the frequency of an X-ray with a wavelength of 0.7107 angstroms, the wavelength produced by an X-ray tube with a molybdenum target?

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

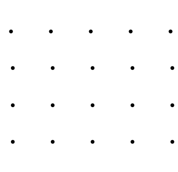
20. Sketch a qualitative representation of the diffraction pattern produced by the following two-dimensional arrays.

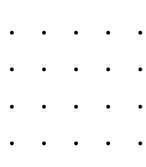
a 

b 

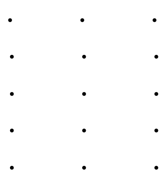
c 

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

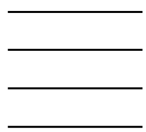
a. 

b. 

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.