

# 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,  $\lambda$ , and a frequency,  $\nu$ , such that the relationship  $c = \lambda \nu$  is satisfied.

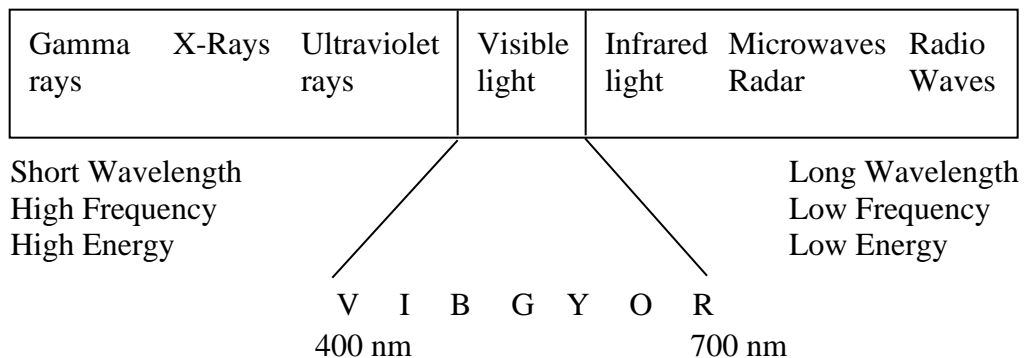


Figure 1. Electromagnetic spectrum. The colors of the visible range of the spectrum are abbreviated violet (V), indigo (I), blue (B), green (G), yellow (Y), orange (O), and red (R).

## 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.

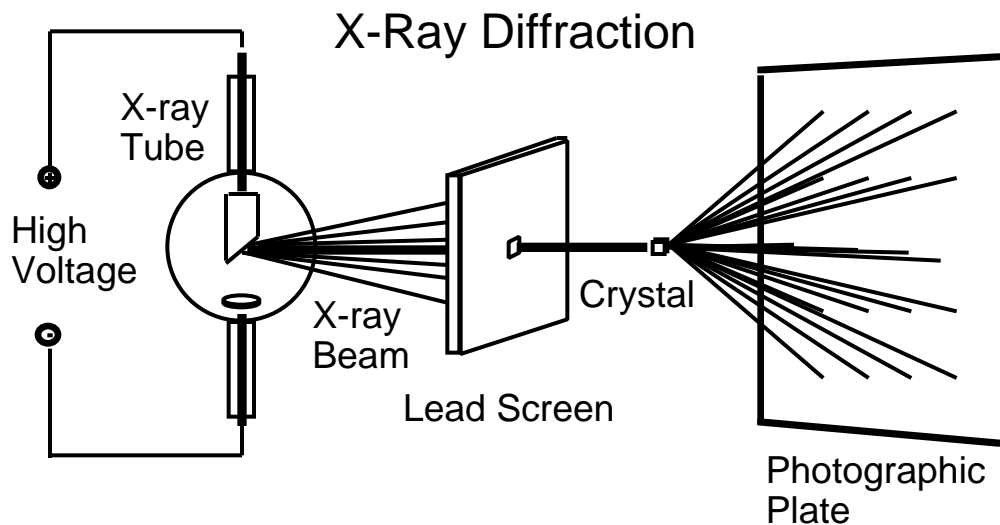


Figure 2. A schematic of X-ray diffraction.

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.

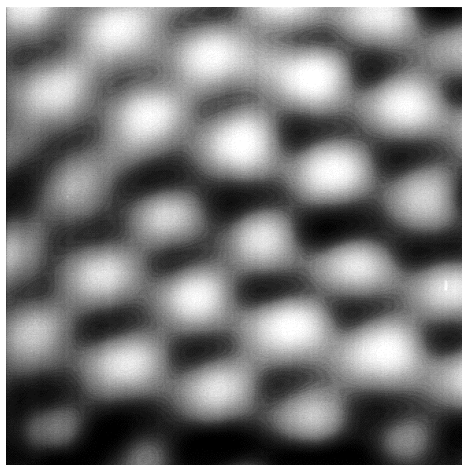


Figure 3. The STM image of a close-packed layer of Ag atoms. (Photograph courtesy of Robert Hamers.)

### **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

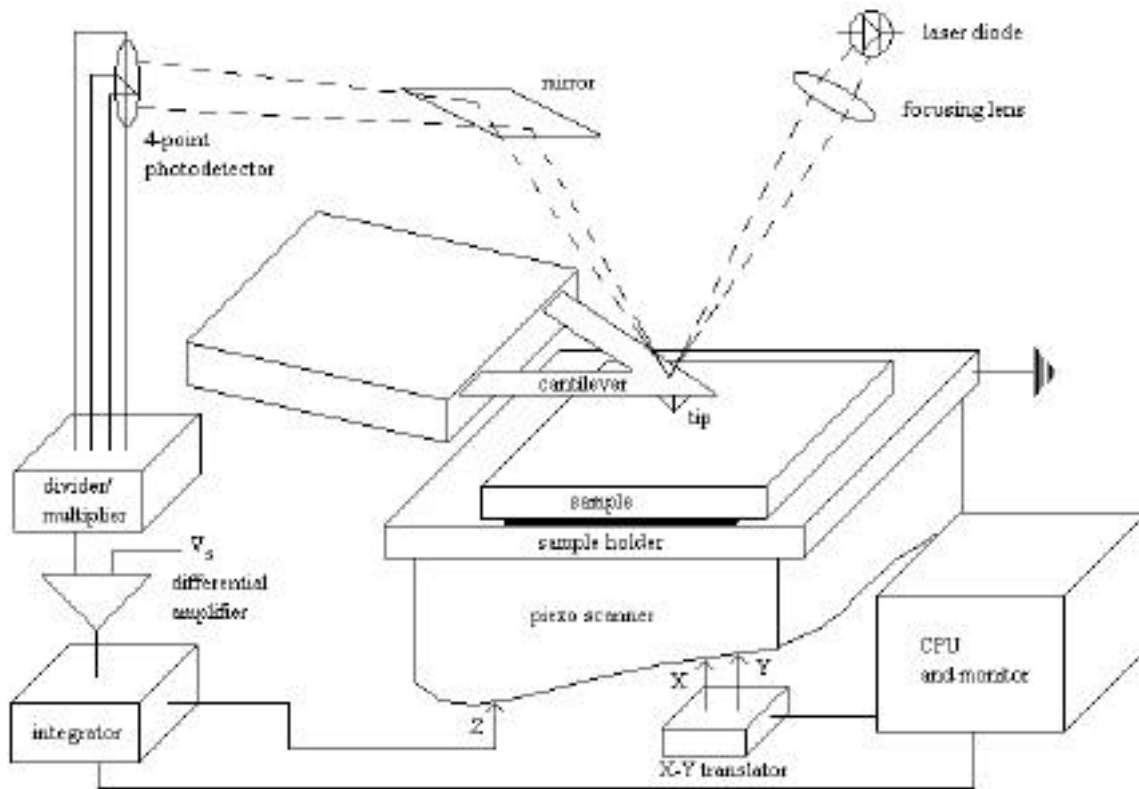


Figure 4. In AFM, small forces are measured between the tip and the sample during scanning. These forces cause vertical movement of the cantilever, which is monitored by a laser beam that is reflected from the top cantilever surface.

### 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.

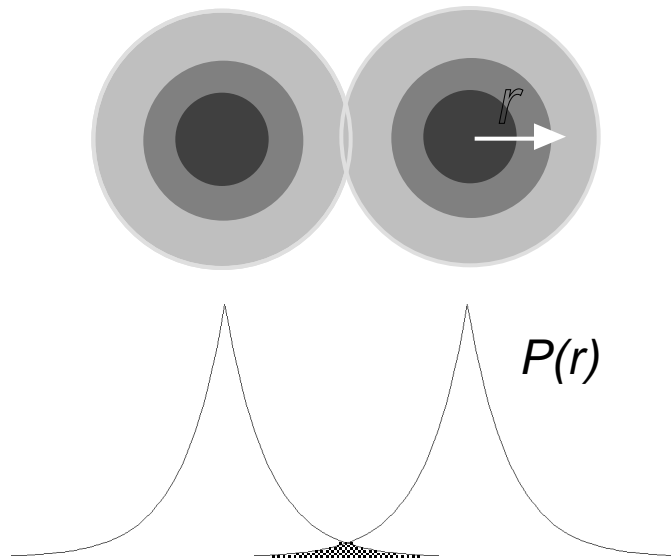


Figure 5. Two atoms with their electron probability clouds slightly overlapping. In the top part of the figure, the atoms are represented as spheres with overlapping volumes. In the bottom part of the figure, the graphical representations of the electron probabilities (as a function of distance from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

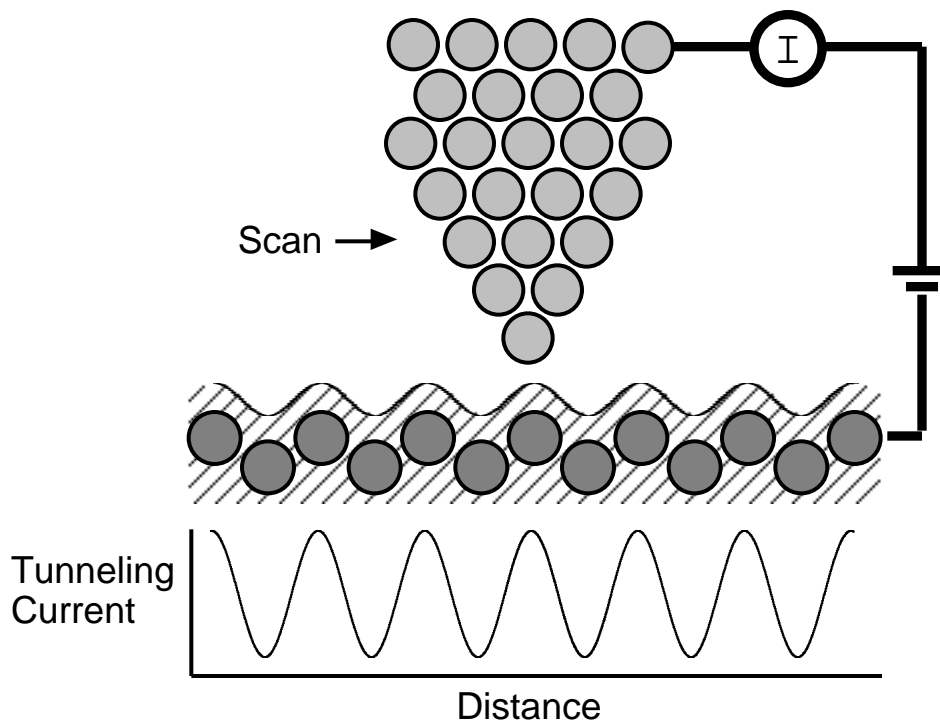


Figure 6. A plot of tunneling current as a function of horizontal probe tip position. The absolute vertical position is held constant. When the tip is nearest the surface atoms, the current is highest. The wavy line above the shaded circles represents the contour of the surface.

### 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.

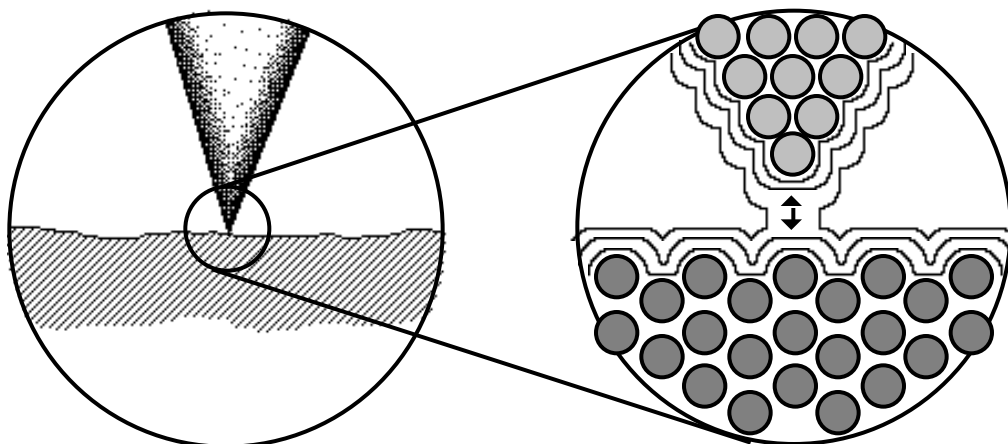


Figure 7. A sketch of an atomically sharp tip near a surface (left-hand picture) and a blow-up (right-hand picture) of the atoms of the tip (grey circles) and the surface (black circles).

### 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.

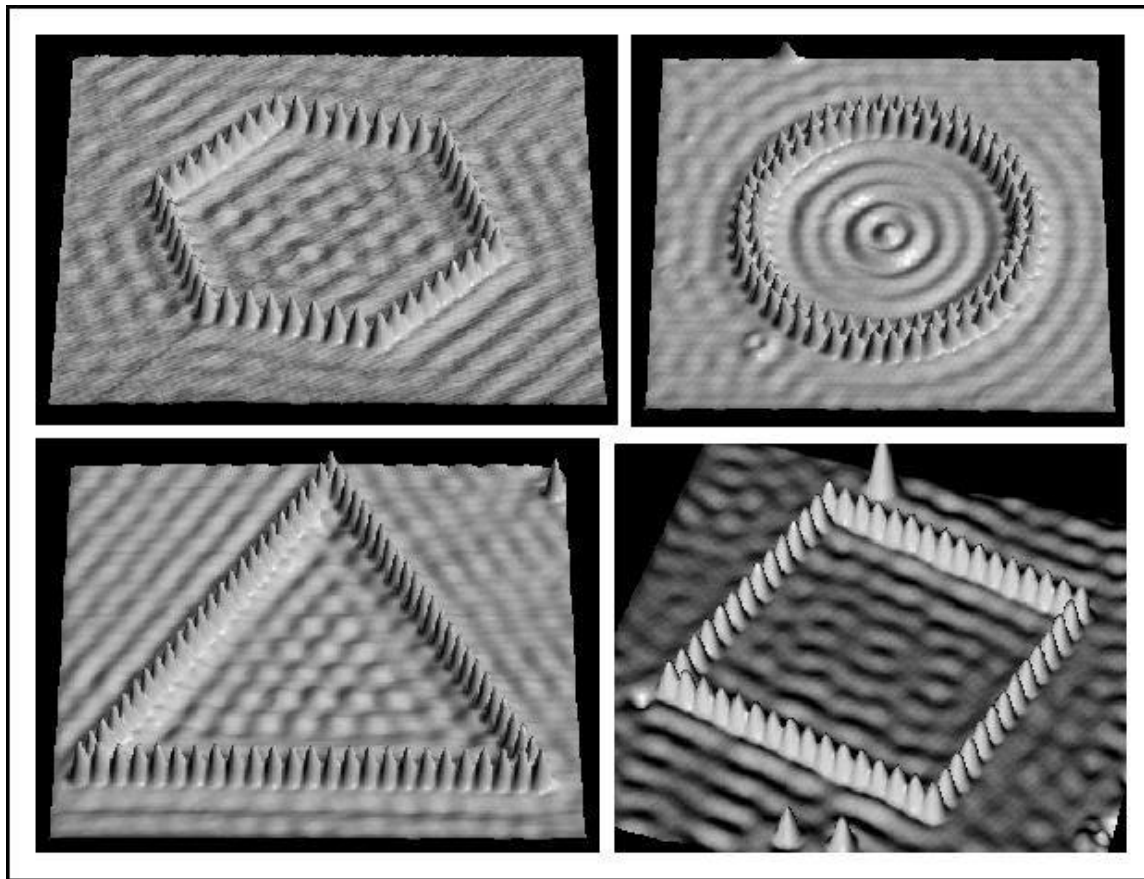


Figure 8. An example of the images that can be made with atoms using Scanning Tunneling Microscopy. The images shown are of iron atoms on copper.