Surfaces and Adsorption

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Contents

1 About this book

This book intends to provide a freely available resource on concepts in surface science. You are free to copy this work, redistribute, even print and sell the work, provided you adhere to the terms in the license.

The book is a work in progress and is being used to teach a course titled "Surfaces and adsorption".

1.1 Python

The book uses Python wherever numerical analysis is required. Python is similar in nature to Matlab, but is freely available. We have attempted to introduce the language by examples throughout the book. If you are a new user, you should start at the beginning of the book. If you are experienced with Matlab, the syntax should be easy to read. We recommend the following Python distribution for use with this book.

- Enthought Python Distribution (http://www.enthought.com/products/epd.php)

This package is free for academic use, and available for Windows, Macs and Linux. The package includes all the typical python libraries needed for numerical, scientific and graphics computing.

- An alternative python environment that may be suitable is Python(x,y) (http://code.google.com/p/pythonxy/). This distribution is Windows focused, and there are not Mac or Linux installers available.
- For editing/writing python code, I like the Spyder editor (http://code.google.com/p/spyderlib/). It is also available for Windows, Macs and Linux. You may find the IDLE or SciTE editor that comes with Enthought suitable though.

2 Introduction

2.1 The Importance of Solid Surfaces

- We have never seen anything but the surface of an object.

- Catalysis. Over 90% of all commodity chemical are produced or processed through the use of heterogeneous catalysts. These catalysts are: dispersed metal particles, high surface area zeolites, finely divided oxide powders.
- Corrosion. Destructive oxidation of surfaces or etching for control of surface finishes.
- Brittle fracture. Fracture of solids is often due to segregation of foreign materials to grain boundaries.
- Thermionic emission. Electron emission from heated filaments in TVs (old), electronic tubes etc. Rate of emission depends on surface properties.
- Crystal growth. Growth from solution or from the vapor phase depends on reactions on surfaces and on diffusion on surfaces.
- Semiconductor properties and processing. As the size of devices decreases the surface-to-volume ratio increases and surfaces begin to have an important influence on physical properties.
- Nanophase materials. Solid materials with grains of nanometer dimensions have extremely high grain boundary densities and extraordinary properties.

2.2 Historical Development

- Solids were found to cause reactions. Priestley (1775) CH_3CH_2OH decomposition on Cu. Davy (1817) CO and H_2 oxidation on Pt. Miner's lamp.
- Reactivity increased with porosity. One idea was that the surfaces compress gasses in pores and cause reaction. This was debunked by the fact that porous metal surfaces differ in reactivity.
- Van't Hoff and Sabatier show that surfaces affect the rate but not the equilibrium constant of a reaction. This is a major milestone in the development of chemical thermodynamics. Demonstrates that the equilibrium constant is path independent.
- Several catalytic processes are developed for commerce.
  - Messel (1875) $SO_2 + \frac{1}{2} O_2 \rightarrow SO_3$
  - Mond (1888) $CH_4 + \frac{1}{2} O_2 \rightarrow CO + 2\ H_2$
  - Sabatier (1902) $C_2H_4 + H_2 \rightarrow C_2H_6$
  - Haber (1905) $N_2 + 3\ H_2 \rightarrow 2\ NH_3$
- Langmuir (1915) works on the development of long-life light bulbs for GE and studies the adsorption of gases on hot filaments.

- Davisson and Germer (1927) observe the diffraction of electron from the surface of a Ni crystal and demonstrate that this is due to the wave nature of the electron. Quantum mechanics is proved!
- Modern surface science is born in the 1960's as an outgrowth of space science and the development of instrumentation for achieving ultra-high vacuum (10^{-10} Torr) environments.

2.3 Modern Surface Science

- Atomistic level study of surface imposes extremely stringent demands on experimental methods.
- The total amount of material at the surface of a solid is extremely small. 10^{15} atoms per cm^2 or 10^{-9} moles.
- The surface must be analyzed in the presence of a bulk solid whose contribution to any measurement could swamp that of the surface.

2.4 Surface Sensitivity

- Surface sensitivity must be achieved in order to avoid studying the bulk of a solid rather than the surface of interest.
- Electrons and ions interact very strongly with matter and so they cannot penetrate or escape from the bulk of a solid. In scattering or emission experiments they only sample the surface.

Figure 1: The XPS experiment with electrons coming from the surface only. X-rays penetrate the surface but electrons photemitted from the bulk cannot escape.

$$\hat{C}_4^{(1)} = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \qquad \hat{C}_4^{(1)} \cdot \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \cdot \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} -y \\ x \end{bmatrix}$$

$$\hat{C}_4^{(2)} = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \qquad \hat{C}_4^{(2)} \cdot \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} -x \\ -y \end{bmatrix}$$

$$\hat{C}_4^{(3)} = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}$$

Note also that there is a rigorous mathematical meaning to these matrix operations. Two rotations by 90° about a fourfold axis would be represented by the following.

$$\hat{C}_4^{(1)} \cdot \hat{C}_4^{(1)} = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \cdot \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} = \hat{C}_4^{(2)} = \hat{C}_2^{(1)}$$

This is the basis for a very powerful set of ideas that form the basis of "group theory".[**?**, **?**]

Before continuing, we briefly show how to verify the results above. In python we have three options to describe a matrix, and it is important to know the differences.

```
1:  C41_list = [[0, -1],
2:              [1,  0]]  #(list)
3:
4:  C41_array = np.array([[0, -1],
5:                        [1,  0]])  #(array)
6:
7:  C41_matrix = np.matrix([[0, -1],      #(matrix)
8:                          [1,  0]])
9:
10: C41_matrix = np.matrix([[0, -1],[1,  0]]) #(matrix-alt)
```

In line 2 above, we created a list of lists; that is, there are two lists inside a list. This is not a matrix, and does not act like a matrix.

In line 5 we created a numpy.array. This is closer to a matrix, but most mathematical operations act element-wise.

In line 5 we create a numpy.matrix object. This acts like a matrix for mathematical operations.

In each of the three examples discussed above, the second row of the data was aligned with spaces so you could “see” the intended arrangement of numbers. Since the second row is “inside” a pair of brackets or parentheses, this indentation is meaningless. It is perfectly fine to define the matrix as in line 10, it is just a little harder to read.

Now we consider verifying that two four-fold rotations are equivalent to a two fold rotation.

```
 1:  import numpy as np
 2:
 3:  C21 = np.matrix([[-1, 0], [0, -1]])
 4:
 5:  C41 = np.matrix([[0, -1],      #(matrix)
 6:                   [1,  0]])
 7:
 8:  print(C41 * C41)               #(dot)
 9:
10:  print C41 * C41 == C21         #(equal)
11:  print np.all(C41 * C41 == C21) #(all)
```

```
[[-1  0]
 [ 0 -1]]
[[ True  True]
 [ True  True]]
True
```

In line 5 we define a matrix. This is similar to a matrix in Matlab, except that you have to use a matrix function to create it. The rows are aligned for visual clarity. Because the rows are inside the function parentheses, the indentation of the second row is unimportant. In line 17 we multiply the matrix with itself. This works on a matrix, but not on a list or array.

You can visually see that the product of the two 4-fold matrices is equal to a 2-fold rotation matrix. In line 10 we compare the two quantities. Note the comparison is element-wise, and we get a new matrix of Boolean values. That is inconvenient to examine, we want a single value saying whether the matrices are equal or not. In line 11 we use the numpy.all command to tell us whether all of the elements in the matrix are True or not.

3.1.4 Symmetry in 3D

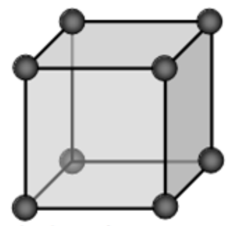
- Real surfaces are formed by slicing planes through 3D object.
- If the 3D solid has some periodicity or is crystalline then the surface that is produced by the cut will also have periodicity and symmetry.
- In 3D there are 14 possible Bravais lattices that will fill space with translational periodicity.

- The symmetry operations that can exist in 3D are :
  - mirror planes
  - rotations
  - inversion
  - rotation translation (screw axes)
- Combination of the Bravais lattices with these symmetry elements

gives *230* possible 3D space groups.

- The only metal with the simple cubic structure is Polonium.

Simple Cubic Lattice - "no-brainer"



primitive lattice - $|a_x| = |a_y| = |a_z|$, and $\alpha = \beta = \gamma = 90^0$

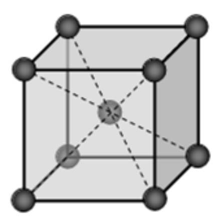
conventional lattice - same

- Most metals have bulk structures that fall into the classes: face

centered cubic, body centered cubic or hexagonal close packed.

- Both fcc and hcp are close packed structures of spheres.

Body Centered Cubic - bcc

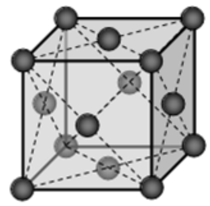


primitive lattice - $|a| = |b| = |c|$, and $\alpha = 90^0$, $\beta = \gamma = 54.7^0$

conventional lattice - $|a'_x| = |a'_y| = |a'_z|$, and $\alpha' = \beta' = \gamma' = 90^0$

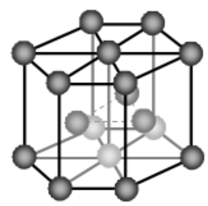
two identical atoms - non-primitive

Face Centered Cubic - fcc



primitive lattice -	$\|a\| = \|b\| = \|c\|$, and $\alpha = 90^0$, $\beta = \gamma = 120^0$
conventional lattice -	$\|a'_x\| = \|a'_y\| = \|a'_z\|$, and $\alpha' = \beta' = \gamma' = 90^0$
	four identical atoms, non-primitive

Hexagonal Close Packed - hcp



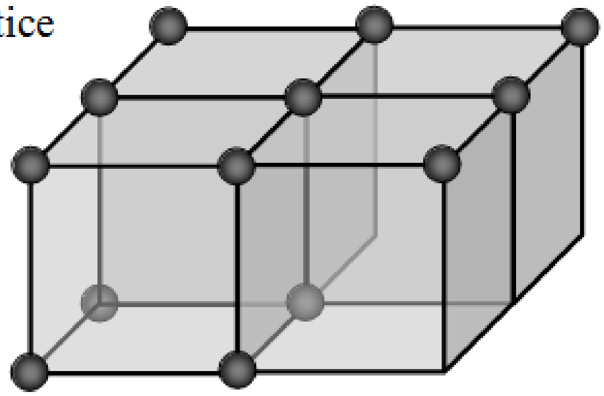
primitive lattice -	hexagonal
	$\|a\| = \|b\| \neq \|c\|$, and $\alpha = 120^0$, $\beta = \gamma = 90^0$
conventional lattice -	same

- Note that the two atoms in the hcp lattice are not identical. They are positioned above triangles of different orientation. As a result the hcp lattice has two atoms per unit cell but is still primitive.

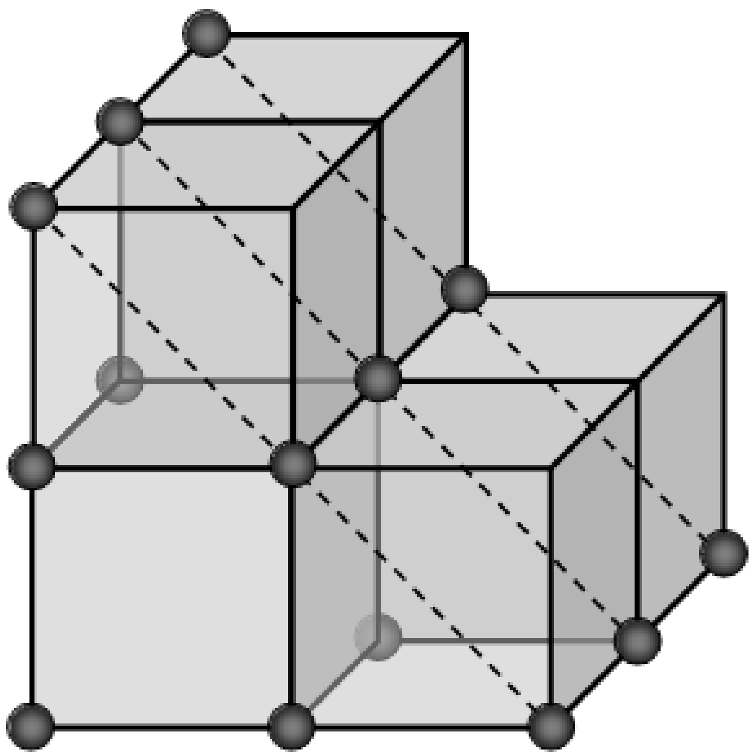
3.2 Surfaces of the Simple Cubic Lattice

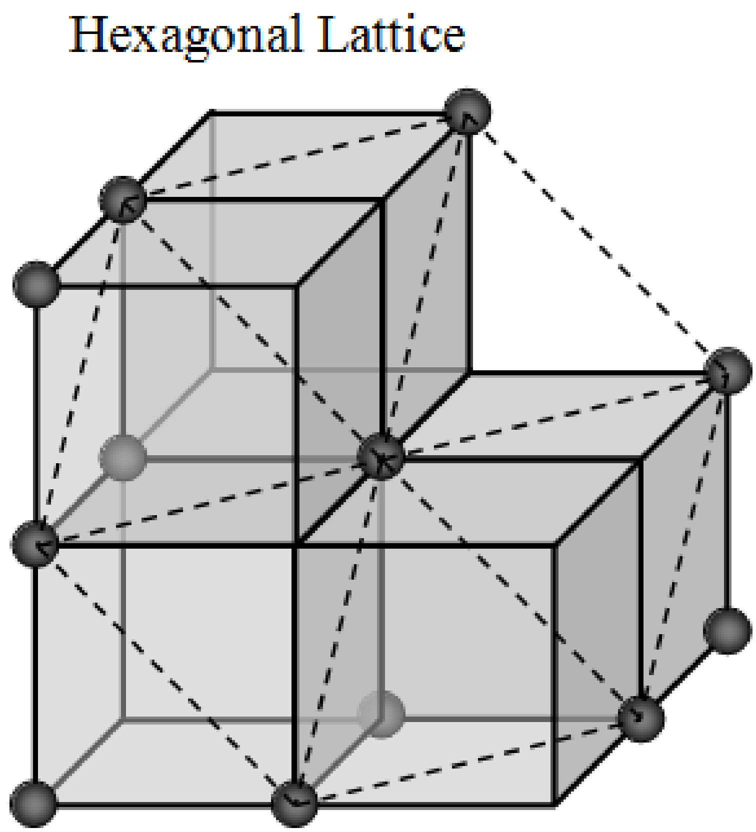
- Start by considering these just to get the idea of taking slices of three dimensional structures. Depending on how you cut the surface, you can get square, rectangular, or even hexagonal arrangements of atoms at the surface.

Square Lattice



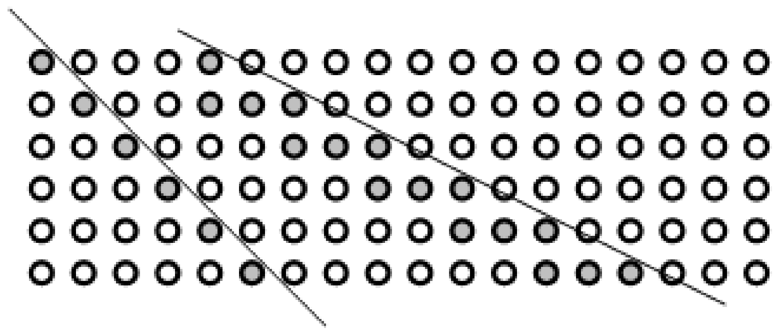
Rectangular Lattice



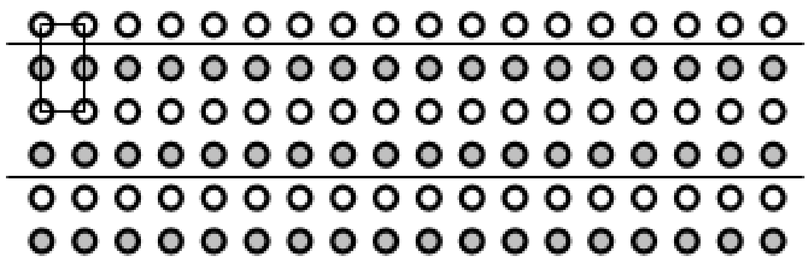


3.3 Miller Indices

- There are an infinite number of planes that can be cut through a 3D lattice. We need a way to name the planes.
- For every vector direction that one defines in the lattice there is a set of planes perpendicular to that vector.
- In a lattice that has some symmetry to it there will be equivalent directions that expose identical faces.
- For atomic lattices or even molecular lattices one does not usually think of cutting "through" atoms or molecules. Cuts pass between atoms and expose those whose centers lie to one side of the cutting plane.



- If one considers just the lattice then it doesn't matter at what position along a given direction that the cut is made. However, if one considered the contents of the unit cell then it does matter.



3.3.1 Miller Index Formulation

- For a plane cut through a lattice:

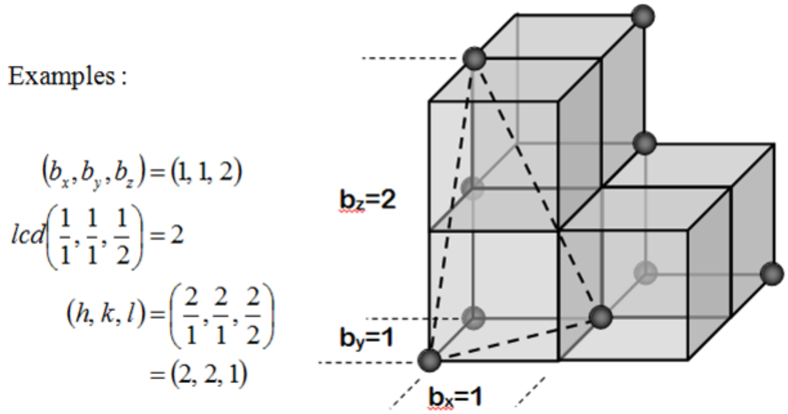
  1. Find the intersections (b_x, b_y, b_z) with b_i ¿ 1 along each of the three lattice vectors (in units of the vector length).
  2. Find the lowest common denominator of the three lengths.

$n = lcd \, \frac{1}{b_x}, \frac{1}{b_y}, \frac{1}{b_z}$

1. Define the Miller indices of the plane as:

$(h, k, l) = \left(\frac{n}{b_x}, \frac{n}{b_y}, \frac{n}{b_z} \right).$

1. If $b_x = \infty$ then $h = 0$



That example is pretty easy to work out in your head. Here is how to compute the lowest common denominator in Python. Note that the lowest common denominator is the same as the lowest common multiple of the numbers in the divisor, and is related to the greatest common divisor. [3] Also, the lowest common denominator of three numbers is the same as the lowest common denominator of one number with the lowest common denominator of the other two numbers.

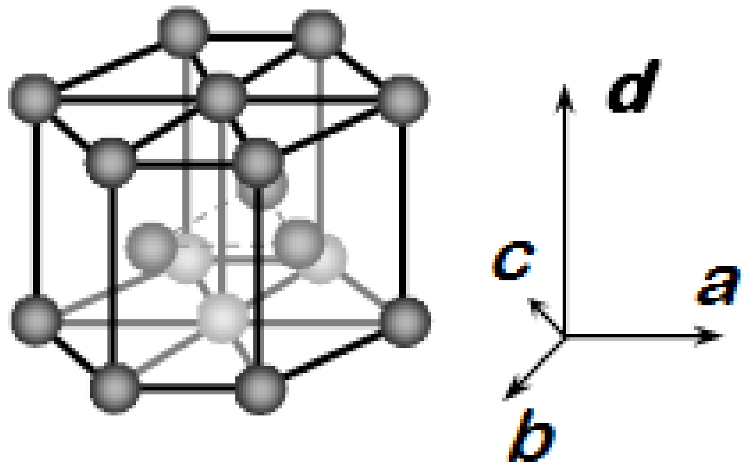
```
1:  from fractions import gcd
2:
3:  def LCM(a, b):
4:      'returns the least common multiple of a and b'
5:      return a * b / gcd(a, b)
6:
7:  print(LCM(1, LCM(1, 2)))
```

```
2
```

In line 1 we import the `gcd` function from the fractions module. Line 3 illustrates a new python concept: the definition of a function. The function is called `LCM` and it takes two arguments. Line 4 is simply a documentation string that tells us what the function does. Note that the body of the function *must* be indented! This is a critical difference between python and Matlab. The standard indentation is 4 spaces. Finally, in line 7, we use the functional form of the print command to output the result.

- Note that for the hexagonal lattice it is quite common to use four indices (h, k, l, m) as though there were four vectors needed to define the unit cell. This is illustrated below.

[3] http://en.wikipedia.org/wiki/Least$_{\text{common multiple}}$#Computing$_{\text{the least common multiple}}$



- In this case the four indices are not unique and the relationship between them is that

  $h + k = -l.$

3.4 Common Low Miller Index Surface Structures

- The most common and important crystal structures for metals are the fcc, bcc, and hcp.
- The most common and important structures for the semiconductors are the diamond and zincblende structures.
- Of these, the most important surfaces are usually the low Miller index surfaces. These tend to be closely packed arrays that are thermodynamically stable.
- Metal crystallites in catalysts usually expose low Miller index surfaces.

3.4.1 The most common fcc surfaces

3.4.2 The most common bcc surfaces

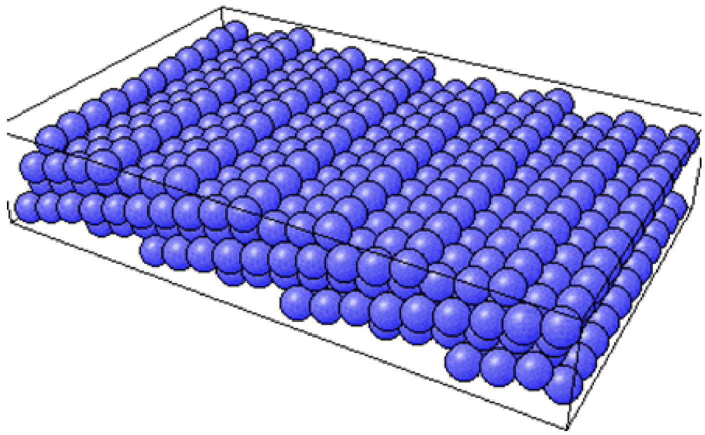
3.4.3 hcp surfaces

3.5 High Miller Index Surfaces

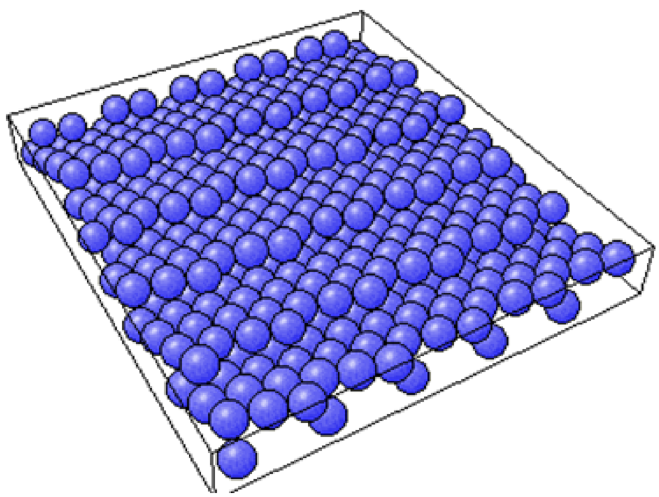
- Surfaces cut along planes that are not low Miller index planes can have very complex structures and are certainly not close packed.

- The structures that are exposed by high Miller index cuts are :
  - monoatomic steps, and
  - kinked steps.

fcc(511)



fcc(643)



- All possible structure can be viewed on the web at the site:

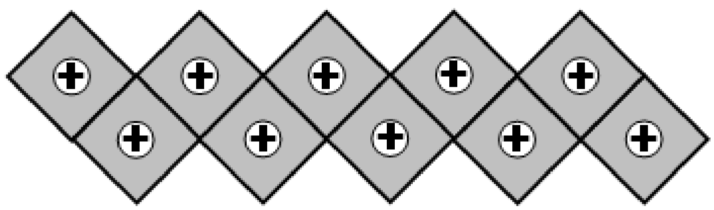
http://surfexp.fhi-berlin.mpg.de/

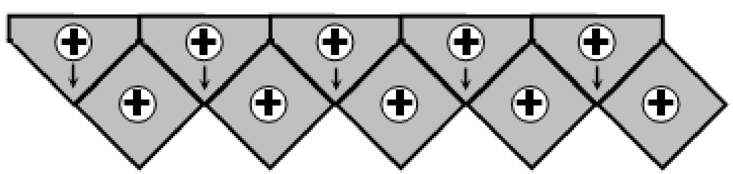
- It is important to realize that the steps have certain structure to them also and that they can be thought of as planes that project up through the surface.

- The fcc(511) surface can be thought of as (111) steps combined with the (100) terraces.
- When thinking about the step structure it is important to remember the atoms within the original unit cell.

3.6 Surface Relaxation

- Cleavage of a 3D solid removes one degree of translational periodicity. The semi-infinite solid is now only periodic in the plane parallel to the cut.
- Clearly this must have some effect on the positions of atoms at the surface. They are now only bonded to atoms on one side and must react to minimize total energy.
- The universally observed effect is that there is a contraction of the layers at the surface.
- The contraction is due to the contraction of electron density into the bulk of the solid.



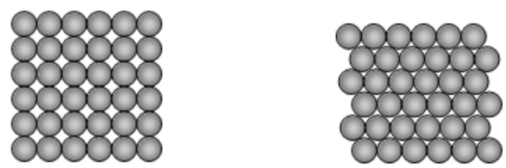


- For the close packed surfaces the contraction is minimal; 1-3% of the plane spacing.
- For non-close packed low Miller index surfaces the contraction can be 5-10% of the plane spacing.
- For rough surfaces the contraction is greater as a percentage of the surface plane spacing because the surface plane spacing is lower. The absolute contraction is not necessarily much different from that of a low Miller index surface.
- Relaxation preserves the 2D translational periodicity of the bulk.

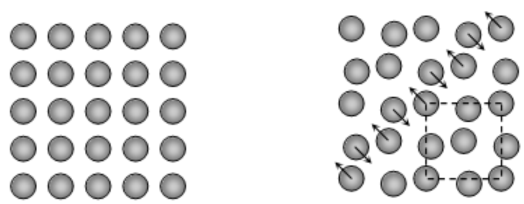
3.7 Reconstruction

- The need to minimize the total energy of the surface can drive the surface to much more drastic rearrangements than relaxation.
- Reconstruction involves an atomic rearrangement that changes the 2D translational periodicity of the surface.

Pt(100) - hex



W(100) - c(2x2)



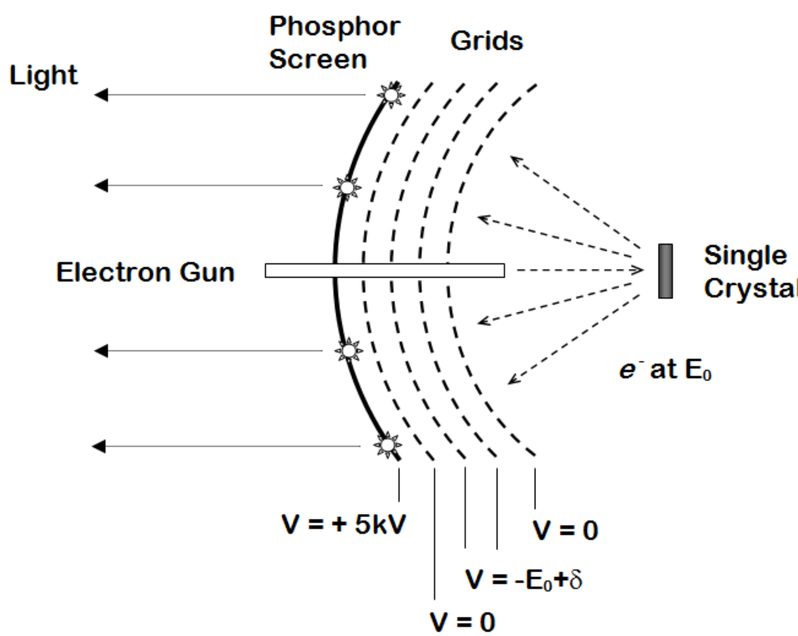
Au(110) - (2x1)

- The tendency is that the close packed or low Miller index surfaces of metals are thermodynamically stable.
- A number of the reconstructions that have been observed can be rationalize in terms of a surface taking on close packed structures. The Au(110)-(2 $\times$ 1) forms facets of (111) surfaces.
- One of the types of reconstruction that should be obvious is the coalescence of steps. Steps are high energy features but are prevented from coalescence by dipole repulsion.
- At high enough step density, however, these become unstable and do coalesce into polyatomic steps.

4 Low Energy Electron Diffraction (LEED)

- As mentioned the structures of surface are not just what they would appear to be from cleaving of the bulk crystal. Reconstructions can occur that change the periodicity of the surface lattice. Relaxations cause changes in the layer spacings at solid surfaces. Furthermore, adsorbed atoms and molecules can create new surface lattices, induce reconstructions or even remove the reconstructions of the clean surfaces.

- There are several types of structural experiments that have been developed. The most common are Low Energy Electron Diffraction (LEED) and Scanning Tunneling Microscopy (STM).
- LEED is the primary way in which the structures of surfaces and the adsorbed layers have been determined quantitatively and is quite commonly done by most research groups in the field of surface science.
- LEED can be used in one of two modes :
  - determination of unit cells of surfaces and adsorbed overlayers, and
  - true quantitative structure determination.
- The quantitative determination of structure is very difficult and highly computationally intensive.



- The phosphorus screen allows easy and cheap visualization of the LEED pattern. Usually a photograph is taken of the back side of the screen. This projects the diffraction pattern onto a plane.
- More complex methods of detection allow measurement of the diffraction spot profiles and the intensities.

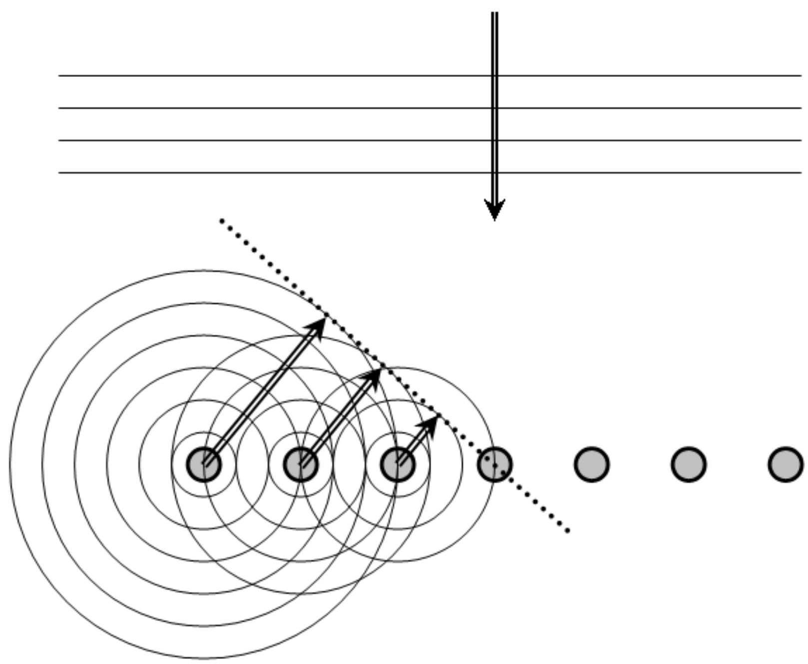
4.1 Diffraction

- Diffraction requires wavelike behavior of the electron. This was postulated by de Broglie.

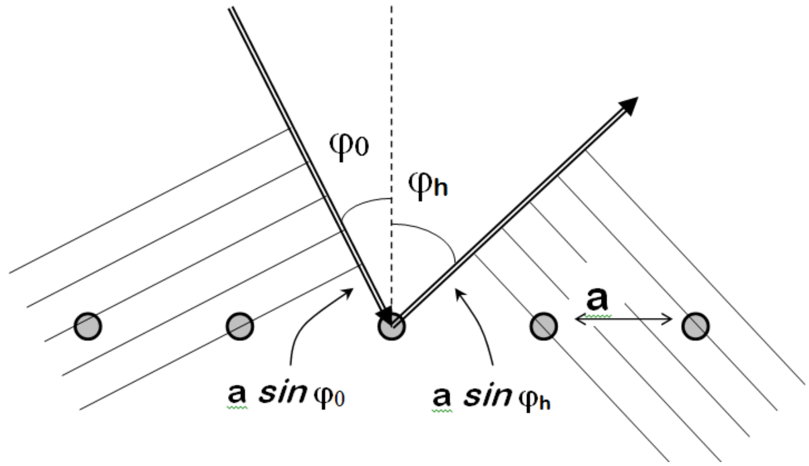
$$\lambda = \frac{h}{p} = \sqrt{\frac{150}{E_{kin}}}$$

This gives the wavelength in Å for kinetic energy in eV.

- Let us review the rules of diffraction from a lattice in 1-D. Basically diffraction is a process in which a wave is incident on an array of atoms. To first order the waves scattered by each atom are spherical waves propagating with the same wavelength as the incident wave. At long distances from the array the scattered waves can be considered to be planes waves from each source atom.



• Diffraction occurs when the distances traveled by the scattered plane waves all differ by some integral multiple of the wavelength. A wave with wavelength λ is incident on a 1D lattice with spacing a at an angle ϕ_0.



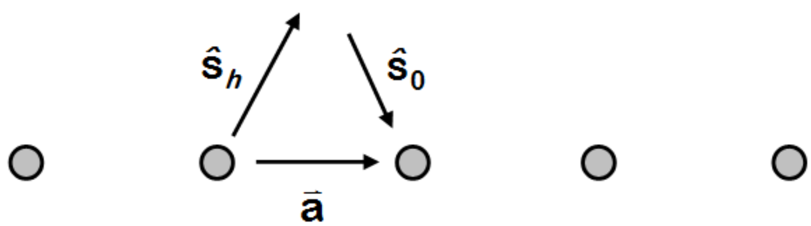
• In order to have constructive interference and obtain a diffracted beam the waves scattering off adjacent lattice points must travel distances which differ by integral multiples of the wavelength.

• The diffraction condition must be that

$$a(\sin\phi_h - \sin\phi_0) = h\lambda$$

for $h \in I$. For a given incident angle ϕ_0 this determines the angles ϕ_h at which diffracted beams appear.

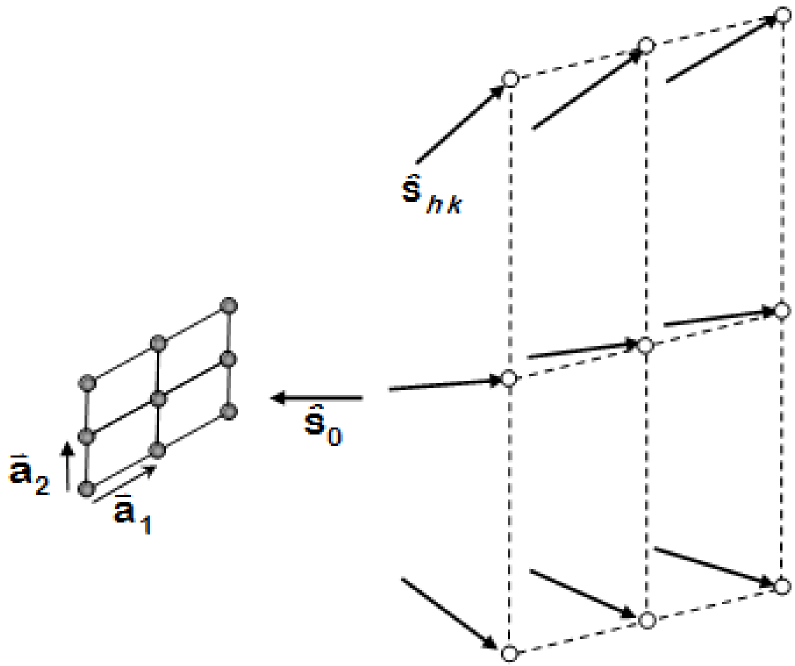
• Another way of writing this equation is to think of the lattice spacing as a vector $\overrightarrow{a}$ and the incident and scattered waves as traveling along directions given by the unit vectors ${}_0 and\hat{s}_h$.



• Then the diffraction condition can be written as

$$\overrightarrow{a} \cdot (\hat{s}_h - \hat{s}_0) = h\lambda$$

Consider the 2D diffraction problem from a lattice with vectors $arrow a_1$ and $\overrightarrow{a}_2$. The beam is incident along a vector ${}_0 anddiffractinginadirection\hat{s}_{\{hk\}}$.



- Now the diffraction conditions are given by

$$\overrightarrow{a}_1 \cdot (\hat{s}_{hk} - \hat{s}_0) = h\lambda$$

and

$$\overrightarrow{a}_2 \cdot (\hat{s}_{hk} - \hat{s}_0) = k\lambda$$

.

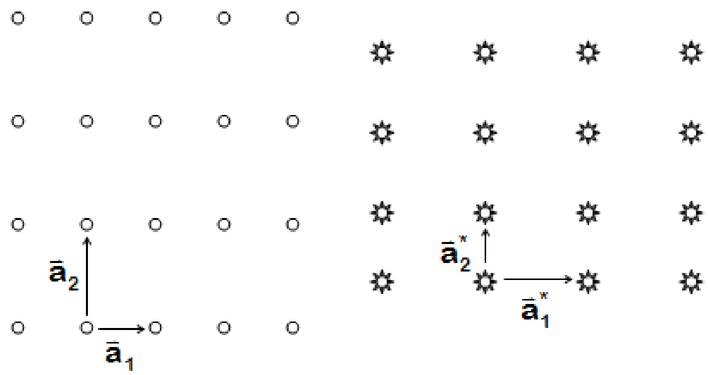
Both must be satisfied in order to get diffraction

4.2 The reciprocal lattice

For any lattice vectors, ($\overrightarrow{a}_1, \overrightarrow{a}_2$), we can define a new set of vectors, which we call the reciprocal lattice ($\overrightarrow{a}^*_1, \overrightarrow{a}^*_2$) based on these definitions:

$$\bar{a}_1 \cdot \bar{a}_1^* = 1 \qquad \bar{a}_1 \cdot \bar{a}_2^* = 0$$

$$\bar{a}_2 \cdot \bar{a}_1^* = 0 \qquad \bar{a}_2 \cdot \bar{a}_2^* = 1$$



• Note that the reciprocal lattice is periodic and has symmetry just like the real space lattice.

• The power of this construction is that it provides us with the solutions to the diffraction problem. The directions in which diffraction occurs are given by

$$\hat{s} - \hat{s}_0 = h\lambda \overrightarrow{a}_1^* - k\lambda \overrightarrow{a}_2^*$$

.

Let us consider a general approach to computing the reciprocal lattice. First, we consider how to represent the vectors in the form of a matrix. For the two lattice vectors $\overrightarrow{a}_1$ and $\overrightarrow{a}_2$, we express them in a matrix as: $A = [\overrightarrow{a}_1 \overrightarrow{a}_2]$. We next consider the reciprocal lattice vectors, \$A$^* = \left[\begin{array}{c} \overrightarrow{a}_1^* \\ \overrightarrow{a}_2^* \end{array}\right]$.\$$Now, wehavethefollowingequation$:A $\cdot A^* = I$, where I is the identity matrix. We can readily solve for the reciprocal lattice vectors as $A^* = I \cdot A^{-1} = A^{-1}$.

Let us consider a specific example where $a_1 = 1x + 0y$ and $a_2 = 0x + 2y$.

```
import numpy as np

a1 = [1, 0]               #(a1)
a2 = [0, 2]

A = np.vstack([a1, a2])   #(vstack)
print('A = \n{0}'.format(A))

Astar = np.linalg.inv(A)     #(inv)

a1star= Astar[0]             #(ref:a1*)
a2star = Astar[1]
print 'a1* = {0}'.format(a1star)
print 'a1* = {0}'.format(a2star)
```

```
15  15:
16  16:  # Verify the requirements.
17  17:  print np.dot(a1, a1star)    #(dot)
18  18:  print np.dot(a1, a2star)
19  19:  print np.dot(a2, a1star)
20  20:  print np.dot(a2, a2star)
```

```
A =
[[1 0]
 [0 2]]
a1* = [ 1.  0.]
a1* = [ 0.   0.5]
1.0
0.0
0.0
1.0
```

This method works generally for 2 and 3 dimensional lattices. Some notes about the code above:

1. In line 3 we represent the components of the vector as a *list*.

2. In line 6 we create an array by using numpy.vstack. This makes the columns of the array the components of the vector. An array is not the same as a matrix!

3. In line (inv) we calculate the inverse of the array. Note that now the components of the reciprocal lattice vectors are in the *rows* of the resulting array.

4. In line nil we use indexing to extract the first row. In Python, indexing starts at 0.

5. In line 17 we must use the numpy.dot function to get the matrix multiplication, or dot product of the two vectors. The * operator will perform element-wise multiplication.

5 References

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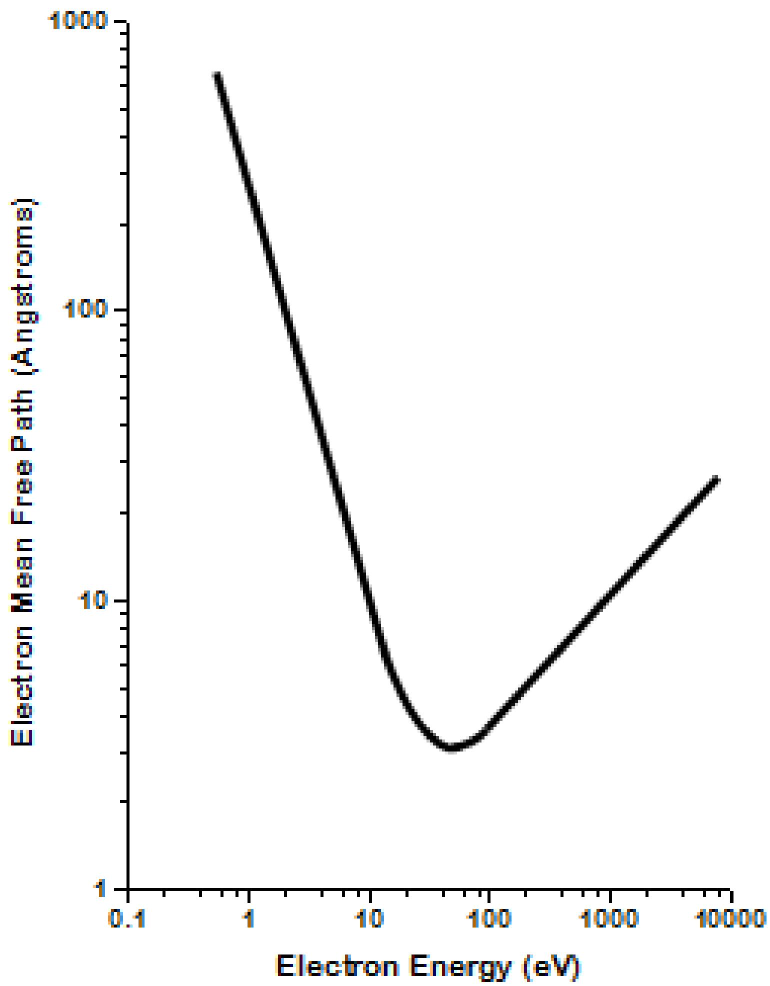

Figure 2: The universal curve of electron mean free paths in solids. The mean free path is the mean distance traveled before an electron is scattered by an atom. This curve has been obtained from measurements made with many materials.

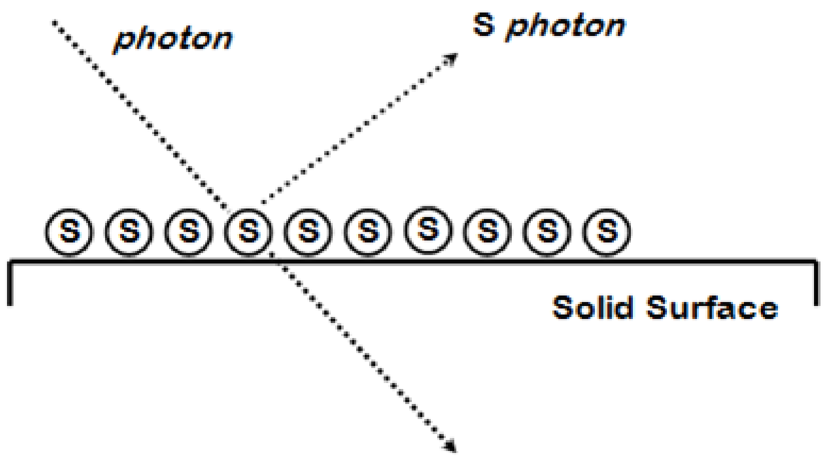

Figure 3: Photon in → photon out only detecting sulfur atoms on a surface. If there were high concentrations of sulfur in the bulk then the bulk signal would swamp the signal from the surface atoms.

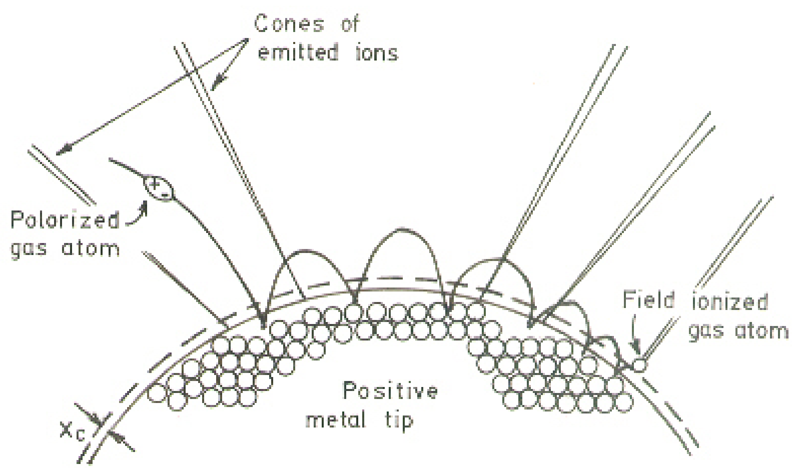

Figure 4: Field ion emission microscope. The metal tips has a high applied potential ($\approx$ 25 kV). He atoms are ionized at the points of high field gradient (atoms at step edges and then accelerated away from the tip along the field lines. They are imaged on a phosphorus screen.

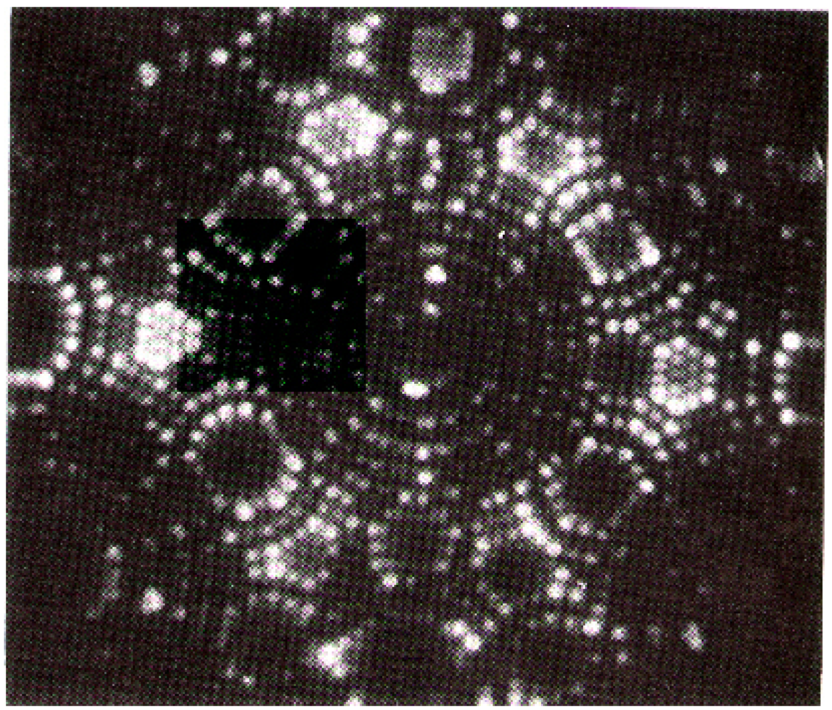

Figure 5: Field ion micrograph of a tungsten tip. The atomic structures of various planes are easily observable.

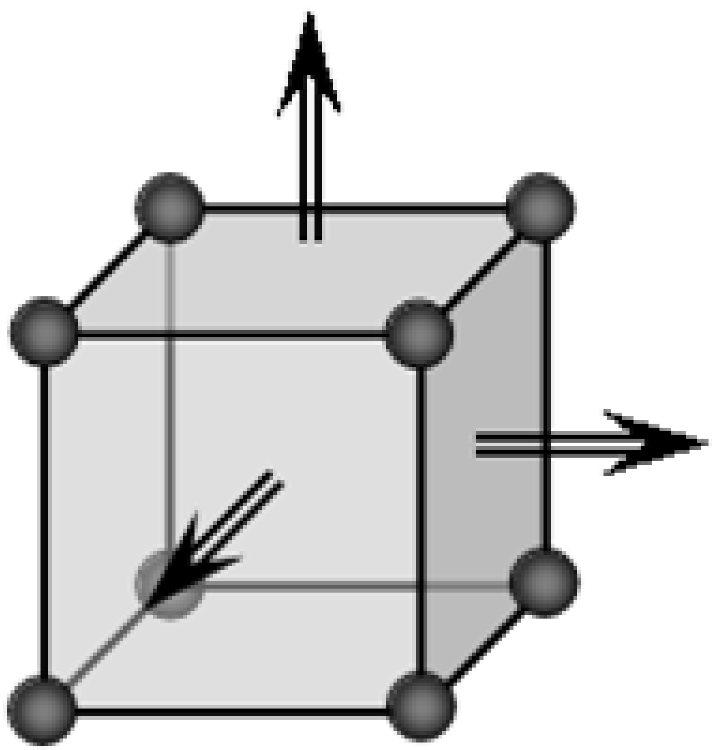

Figure 6: The arrows indicate symmetrically equivalent surfaces.

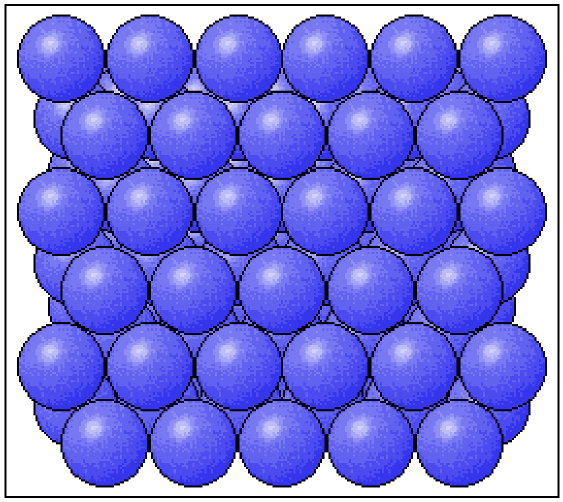

Figure 7: fcc(111)

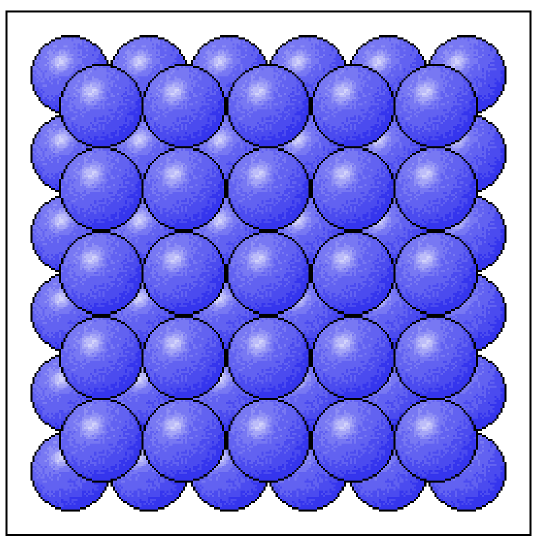

Figure 8: fcc(100)

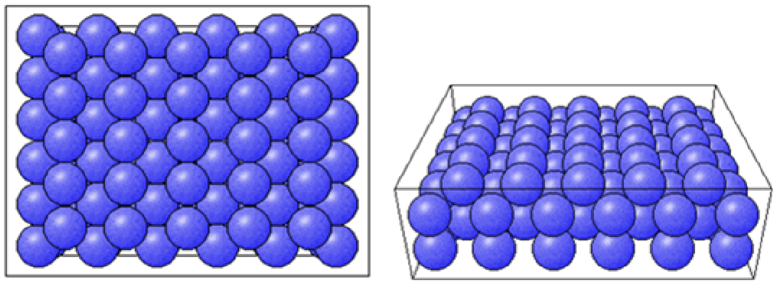

Figure 9: fcc(110)

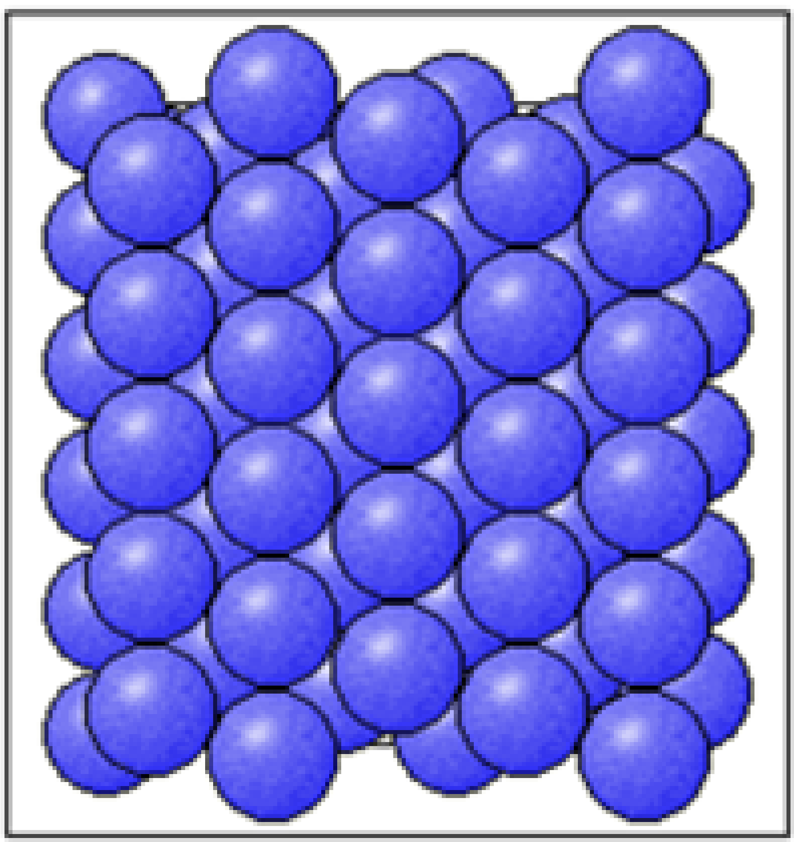

Figure 10: bcc(110)

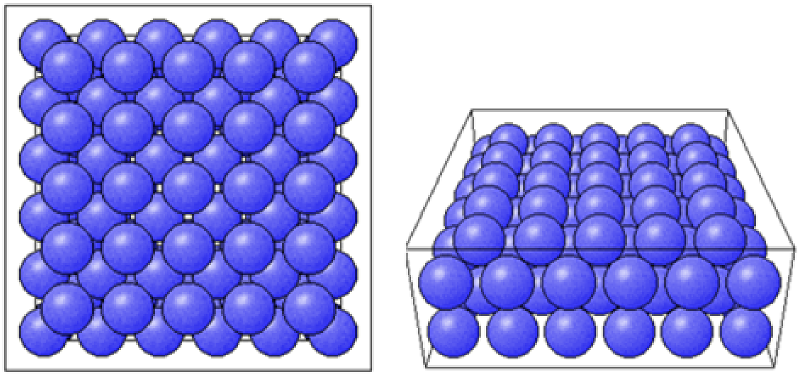

Figure 11: bcc(100)

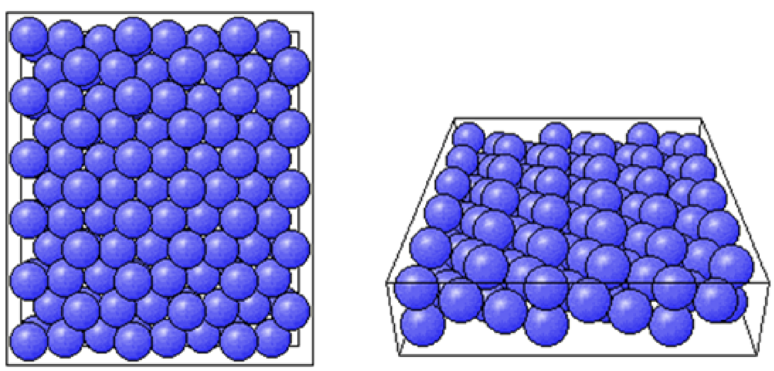

Figure 12: bcc(111)

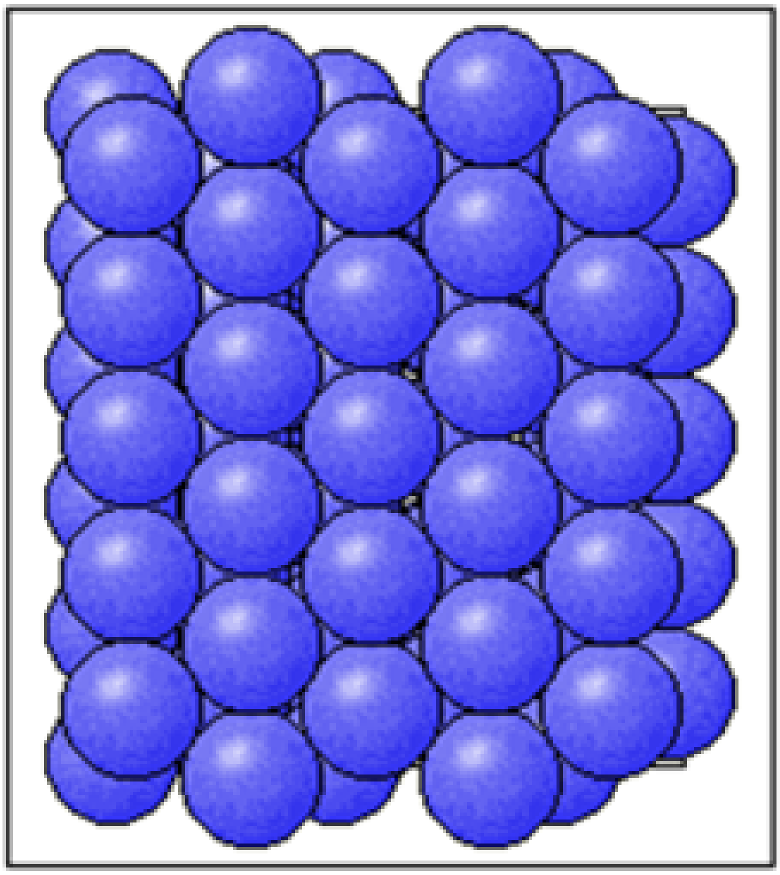

Figure 13: hcp(001)

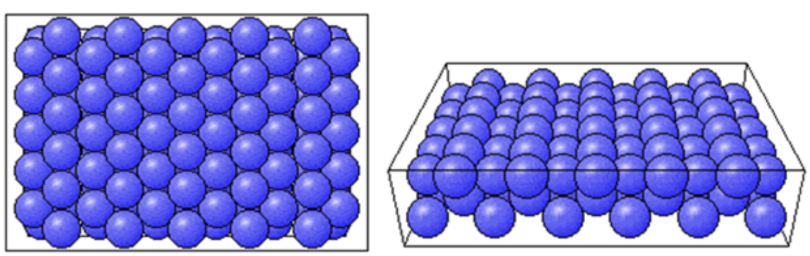

Figure 14: hcp(100)

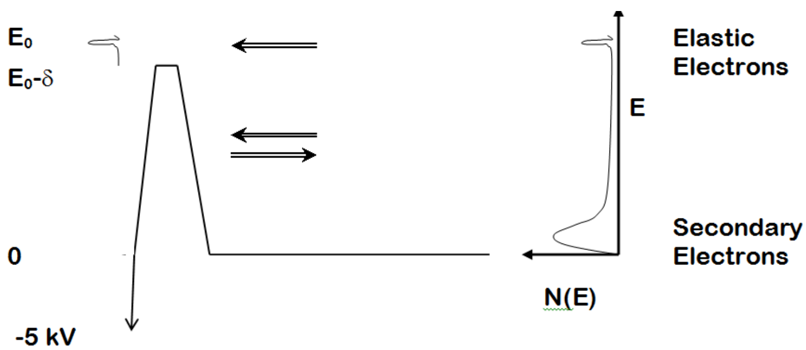

Figure 15: Potential energy profile seen by the electron beam.