3.091 – Introduction to Solid State Chemistry

Lecture Notes No. 6a

BONDING AND SURFACES

1.   INTRODUCTION

Surfaces have increasing importance in technology today. Surfaces become more important as the size scale of devices gets smaller and smaller. We have discussed the properties of solids depend on the type of bonding and structure that exits on the molecular scale. The average atom or molecule in a crystal is saturated by the bonding between it and its nearest neighbors. The atoms or molecules near the surface of a solid are, however, different. They cannot be fully saturated by bonding. Thus, in a sense, the surface must have different properties than the bulk of the solid. As the volume of the solid decreases, the proportion of the solid that is near the surface increases. *This means properties of the solid are a function of size*. Nanoscale powder, for example, has different properties than the same material has if the particles of solid are much larger. In this chapter, we will learn about the properties of surfaces and how a surface is affected by the bonding and crystal structure of the solid.

2.   THE THERMODYNAMICS OF SURFACES

A fundamental law of nature is that it tries to reach a compromise between adopting the lowest energy and adopting an energy state that is more *probable*. The probability of a given state is related to its *entropy, S*. The compromise that nature makes is based on the comparison between the internal energy change, often called an enthalpy change, to the change in entropy. A spontaneous change in a system somehow balances lowering its internal energy ($\Delta H < 0$) with changing to a state that is more probable ($\Delta S > 0$). This balance is achieved by lowering the Free energy (see Chapter 6), or as we will call it, the Gibbs energy. The change in Gibbs energy change, $\Delta G,$ reflects the compromise between the enthalpy change and the entropy change and is given by

$$\Delta G = \Delta H - T\Delta S$$

A reaction can only proceed if the Gibbs energy change is negative. The right-hand side of the Gibbs equation contains the enthalpy change as the first term. The second term is the temperature, T (in Kelvin), weighted entropy change. Thus, nature's compromise depends on temperature.

A system undergoes a change in Gibbs energy when it experiences a change in temperature, pressure, or when it performs any type of work. When the change in state is carried out reversibly (very slowly and never far from equilibrium), the exact relationship between these factors is

$$\partial G_{rev} = V\partial P - S\partial T - \partial W_{non-PV}$$

where ∂G_{rev} is the reversible Gibbs energy change, V is the volume of the system, ∂P is the change in pressure, S is the entropy of the system, ∂T is the change in temperature, and ∂W_{non-PV} is the non pressure-volume work done by the system. Each of the terms represents different types of energy that must be accounted for. The first term is PV-work or the kind of work performed when the system changes its volume or pressure. The second term represents the change in energy of the system due to a temperature change. The last term is associated with any other type of work. We call this non-PV work because it is all work except the PV-work portion. This non-PV work can be of any type, such as electrical or magnetic and, as we will see includes work performed to change the surface area of the system.

The equation above reveals the maximum non-PV work derivable from a system at constant T and P. Another way of saying this is that maximum work is associated with a reversible process. Conversely, ∂G_{rev} equals the minimum non-PV work extended by the surroundings to cause a change in the system at constant T and P. This later statement will be the basis for identifying the work needed to form a surface. Specifically, let's consider a change in a system that results in a small change in the system's surface area, ∂A. Secondly, we cause this change to occur at constant T and

P, and that the change is carried reversibly. The work involved to form this surface is equal to the Gibbs energy changes:

$$\partial G = \left(\frac{\partial G}{\partial A}\right)_{T,P} \partial A$$

No terms in *T* and *P* are involved since the process is carried out at constant *T* and *P*. The partial derivative in equation the equation above is the non-PV work per unit area done to create a surface. Indeed, it is the minimum work required since the equality with Gibbs energy is only when the change in area is carried out reversibly. Implied in this discussion is that the surroundings must perform work to create surface area. This is equivalent to saying that $\left(\frac{\partial G}{\partial A}\right)_{T,P}$ is always positive. We shall see that this is the case for equilibrium systems.

The partial derivative $\left(\frac{\partial G}{\partial A}\right)_{T,P}$ has units of energy per unit area and is a property of the system. We call this term the surface energy, γ:

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P}$$

Again, all this equation means is that the surface energy is just the worked required to change the surface energy of a system. We can use this concept to apply a bonding model to estimate the surface energies of solids.
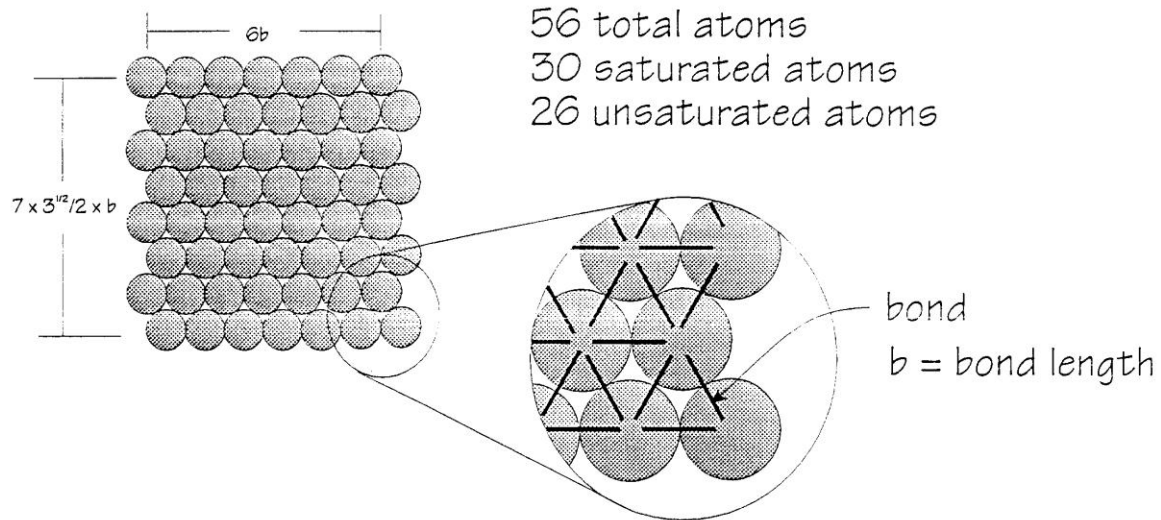
3. MICROSCOPIC ORIGIN OF SURFACE ENERGY

Now let's try and get a physical picture of what surface energy means. We will do this by considering the example of a small crystal formed from a small number of atoms. The figure below depicts the situation in two dimensions. It represents a very long crystal with a very small cross section. The section contains only 56 total atoms and they are arranged in a close-packed configuration. All the interior atoms are surrounded by six nearest neighbors, each with a corresponding bond. The atoms on the perimeter, however, do not have a full complement of neighbors and, therefore, do not have six bonds. We say these later atoms are unsaturated with respect to bonding. Counting

reveals that of the 56 atoms in the figure, 30 are saturated with respect to bonding and 26 are unsaturated. The total number of bonds is found to be 138.
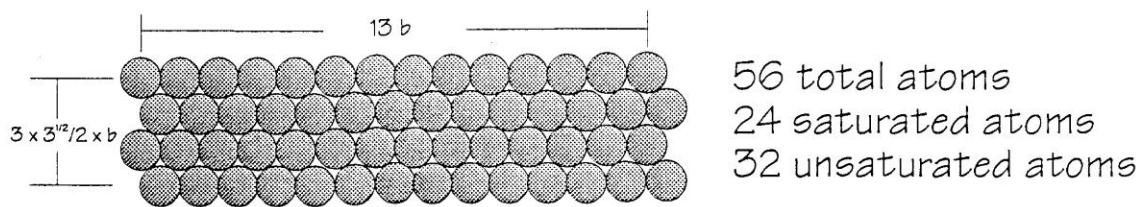
The surface area of this crystal can be estimated in terms of bond lengths. First, one must recognize that the crystal is very long in the dimension perpendicular to the page. Thus, we will define a surface per unit depth which is just the perimeter of the cross section shown in the figure. There are seven atoms across the top of the crystal. Thus, the length of the top is just the sum of the bond lengths associated with the six bonds formed between the seven atoms, $6b$, where b is the individual bond length. The situation of the vertical sides is more complicated since the bonds are not parallel to vertical. Instead, the bonds are at an angle of 30° with respect to the side. The contribution of each bond to the perimeter is, therefore,

Microscopic origin of surface energy

56 total atoms
30 saturated atoms
26 unsaturated atoms

bond
b = bond length

138 bonds in particle

Area per unit depth = perimeter = $2(6b) + 2(7 \times 3^{1/2}/2 \times b)$

$$= 24.1\ b$$

56 total atoms
24 saturated atoms
32 unsaturated atoms

133 bonds in particle

Area per unit depth = $2(13b) + 2(3 \times 3^{1/2}/2 \times b)$

$$= 31.2\ b$$

$\frac{\sqrt{3}}{2}b$. There are seven such bonds on the vertical side, so its length is $7 \cdot \frac{\sqrt{3}}{2}b$. The perimeter of the crystal's cross-section is, therefore,

$$\text{Area per unit depth = perimeter} = 2(6b) + 2\left(7 \cdot \frac{\sqrt{3}}{2}b\right)$$

$$\text{Area per unit depth} = 24.1b$$

Now, let's deform the crystal in such a way that we maintain the close-packed structure. The resulting deformed crystal is shown in the figure below. The same 56 total atoms are shown, but now the numbers of saturated and unsaturated atoms have changed. There are 24 saturated atoms and 32 unsaturated, with a total of 133 bonds in the section. Clearly, there has been a reduction of the total number of bonds. How much has the surface area changed? There are 13 number of bonds across the top and 3 on the vertical side. The area per unit depth is, therefore,

$$\text{Area per unit depth = perimeter} = 2(13b) + 2\left(3 \cdot \frac{\sqrt{3}}{2}b\right)$$

$$\text{Area per unit depth} = 31.2b$$

Thus, the area has increased from $24.1b$ to $31.2b$. The increase in area occurred with the breaking of five bonds (138-133). The bond energy required to break these bonds is associated with the increase in area. That is, the surface energy is

$$\gamma[\text{per unit depth}] = \frac{5 \cdot E_b}{(31.2 - 24.1)b}$$

where E_b is the bond energy. Clearly, the quantity γ will always be positive since it takes energy to break bonds. Secondly, we see that the origin of surface energy is the fact that surfaces of materials are inherently unsaturated with respect to bonding. Thus, increasing the surface area means increasing the number of unsaturated atoms and breaking bonds.

4.   THE SURFACE ENERGY OF ICE (DUE TO OVERBEEK)

We now take a simple approach to estimating the surface energy of a solid. The surface is viewed as an array of atoms or molecules that are unsaturated with respect to bonding. The surface energy is related to the energy required to break all those bonds.

The approach is illustrated by an example; the surface energy of ice. The calculation strategy is simply to imagine that an ice cube is broken in half, creating two new surfaces. The number of intermolecular bonds broken is calculated and multiplied by the energy per bond. The result is then divided by the total surface area created to give the surface energy.

Ice is a molecular crystal where the individual water molecules are arranged on a lattice held together by intermolecular bonding. The nature of this bonding is complicated and involves hydrogen bonding between hydrogen on one molecule and oxygen on another. Ice occurs in several polymorphs but the structure below is illustrative. Note that each water molecule has four nearest neighbors that are tetrahedrally arranged.
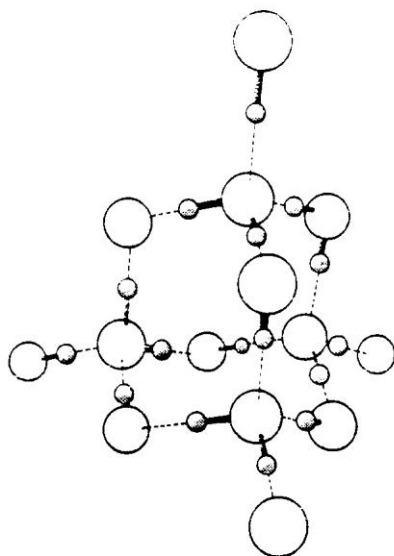
Fig. 22.19. The crystal structure of one form of ice (notice the underlying diamond structure).

When an ice cube is cleaved, a surface is exposed that is composed of molecules that are missing one of their nearest neighbors. The number of such molecules per unit area can be obtained from the molecular density, $\hat{\rho}$, or number of molecules per unit volume. This can be obtained from

$$\hat{\rho} = \frac{(6.02 \times 10^{23} \text{ molecules/mol})(0.9 \text{ gm/cm}^3)}{18 \text{ gm/mol}} = 3.0 \times 10^{22} \text{ molecules/ cm}^3$$

The number of molecules per unit area of surface, Γ, is obtained directly from $\hat{\rho}$. The simplest way to explain this is to first ask how many molecules are on one edge of one cubic centimeter of ice? The answer is just $(\hat{\rho})^{1/3}$. The number on one square centimeter of ice is simply $\left[(\hat{\rho})^{1/3}\right]^2$ or

$$\Gamma = (\hat{\rho})^{2/3} = 0.97 \times 10^{15}$$

This number is good to remember since the surface molecular density of many simple crystals is of the order of 1×10^{15}. The energy per bond can be estimated from the heat of sublimation. The structure of ice demands that four bonds be broken for each water molecule that is sublimed. Thus, the heat of sublimation per molecule must equal four times the bond energy. Heats of sublimation are frequently tabulated in units of energy per mass. This means we first have to convert units of energy per volume and then divide by the molecular density to get the heat of sublimation per molecule:

$$\frac{\Delta H_{sub}[\text{energy/mass}] \cdot \rho}{\hat{\rho}} = 4E_b$$

where E_b is the intermolecular bond energy. Substitution gives

$$E_b = \frac{(677 \text{ cal/gm})(0.9 \text{ gm/cm}^3)}{4(3.0 \times 10^{22} \text{ molecules/cm}^3)} \cdot (4.2 \text{ J/cal})$$

$$E_b = 2.1 \times 10^{-20} \text{J/bond}$$

Consider breaking 1 cm^3 cube of ice in half. Two 1 cm^2 surfaces are created and 1 cm^2 of bonds are broken. Thus,

$$\gamma \cong \frac{(1 \text{ cm}^2 \text{ of bonds})(\Gamma \text{ bonds per unit area}) \cdot E_b}{2 \text{ cm}^2 \text{ of new surface}}$$

$$\gamma \cong \frac{(1 \text{ cm}^2 \text{ of bonds})(0.97 \times 10^{15} \text{bonds per unit area}) \cdot 2.1 \times 10^{-20} \text{ergs}}{2 \text{ cm}^2 \text{ of new surface}}$$

$$\gamma \cong 1.0 \times 10^{-5} \text{ J/cm}^2$$

The experimental value[*] is 1.09×10^{-5} J/cm^2, which is amazingly close given how simple this model is.

5.   SURFACE TENSION AND SURFACE ENERGY

There is often confusion about the relationship between surface energy and surface tension. You often see the terms used interchangeably. This is legitimate for surfaces of liquids but can be seriously flawed when considering solids.

First, let's get a working knowledge of surface tension. The classic description of surface tension is in terms of an experiment performed on a soap film. The film is retained in a wire hoop like that shown in the figure below:
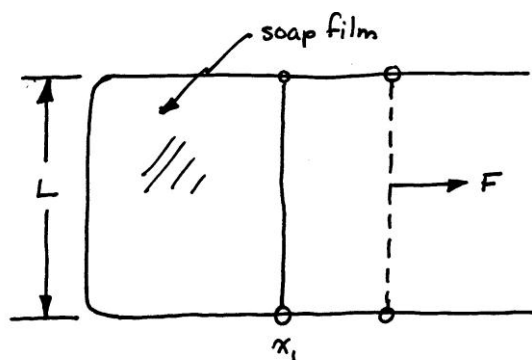
One edge of the hoop is adjustable and can be pulled to increase the surface area of the film. A force is required to do this. Scientists learned hundreds of years ago that the force imposed by the film on the wire is proportional to the length of the wire. The force in moving the sliding edge is proportional to its length, *L*. Thus,

$$F = 2\tau L$$

[*] W.M. Ketcham, P.V. Hobbs, "An experimental determination of surface energy of ice," *Phil. Mag. A.*, 19, No. 162, 1161 (1969).

where 2τ is the proportionality constant. The factor of two is included to reflect the fact that the soap film actually consists of two identical surfaces, front and back. This equation, therefore, provides the definition of the surface tension, τ.

The work performed in moving the adjustable edge from position x_1 to x_2 is just

$$\text{work} = F(x_2 - x_1) = F\Delta x$$

$$\text{work} = 2\tau L\Delta x$$

The total area of film, A_1, before moving the edge is $2Lx_1$. Note that we have included both the front and back surfaces of the film. Similarly, the total area, A_2, after moving the edge to x_2 is $2Lx_2$. Thus,

$$A_2 - A_1 = 2Lx_2 - 2Lx_1$$

$$A_2 - A_1 = 2L\Delta x$$

Substituting this into the equation above gives

$$\text{work} = \tau(A_2 - A_1)$$

Now, let's consider what the surface energy, γ, tells us about the work done when moving the edge. The Gibb's energy before moving is $(\gamma A)_1$, and after is $(\gamma A)_2$, , assuming both states are at the same temperature and pressure. This means that if the edge is moved in a reversible manner, then the work performed is

$$\text{work} = (\gamma A)_2 - (\gamma A)_1$$

Note that I have been careful not to assume that the surface energy is the same in both states. Rather, we have left open the possibility that the surface energy can be a function of area.

Equating the two expressions for work gives:

$$\tau(A_2 - A_1) = (\gamma A)_2 - (\gamma A)_1$$

which for small displacements can be written

$$\tau = \left.\frac{\partial(\gamma A)}{\partial A}\right|_{T,P}$$

Carrying out the derivative gives

$$\tau = \gamma + A\left.\frac{\partial \gamma}{\partial A}\right|_{T,P}$$

This equation tells us several things. First, if the surface energy is truly a constant, then the second term on the right is zero and surface tension and surface energy are identical. If, however, the surface energy changes as the surface area is changed, then the surface tension and surface energy differ.

The nature of the material determines which case is appropriate. For example, as we deform a liquid droplet the surface arrangement of molecules is essentially unchanged since the molecules are rapidly moving and are free to adjust their relative positions. This means that a unit area of the liquid's surface looks the same before and after the deformation. Thus, a liquid's surface area is really constant. An elastic solid is, however, quite different. Atoms and molecules are not mobile in this case. They preserve their relative positions with small deformations, but simple elastic strains require that the bond lengths change. Bond energy varies with bond length and, often times, quite strongly. Thus, the surface energy of an elastic solid will vary as the solid is strained. This means that we expect the surface energy of a solid to be a function of area.

6. BROKEN BOND MODELS AND CRYSTAL STRUCTURE

Let's now consider how surface energy might vary with crystalline face. The broken bond approximation considered in the last lecture can be used to help us understand how surface energy might vary with various possible crystalline faces. The FCC crystal will be used as an example and the expected surface energy for the (100), (110), and (111) surfaces will be estimated. More precisely, we will estimate the relative surface

energies of these faces by comparing the number of broken bonds per unit area on each face.

A single FCC unit cell is shown in the diagram below. The atoms rendered in heavy lines will form the new (100) surface created by removing the other atoms of the cell. Note atom *A* in particular. Atoms labeled *D*, are all nearest neighbors to atom *A*. These are the atoms that occupy the centers of the four perpendicular faces to the new surface. The bonds between atom *A* and all four atoms. *D*, will be broken when the new surface is formed. Thus, for each atom on the new (100) surface, four bonds must be broken. The two dimensional unit cell of the (100) surface is also shown in the figure. There is one atom in the center of each cell and four atoms that are each shared between four cells. This means that the number of atoms per unit cell on the (100) surface of an FCC crystal is

$$\frac{atoms}{2D-unitcell} = 1 + 4\left(\frac{1}{4}\right) = 2$$

Each 2*D* unit cell has an area of a^2 where a is the lattice parameter Thus, the number of bonds broken per unit area is

$$\frac{bonds\,broken\,on\,(100)\,surface}{unit\,area} = \frac{\left(4\dfrac{bonds}{atom}\right)\left(\dfrac{2\,atom}{U.C.}\right)}{a^2} = \frac{8}{a^2}$$

Two dimensional (100) surface
of the FCC crystal
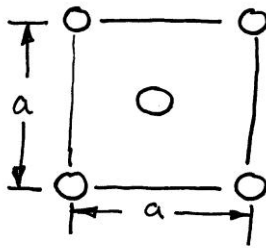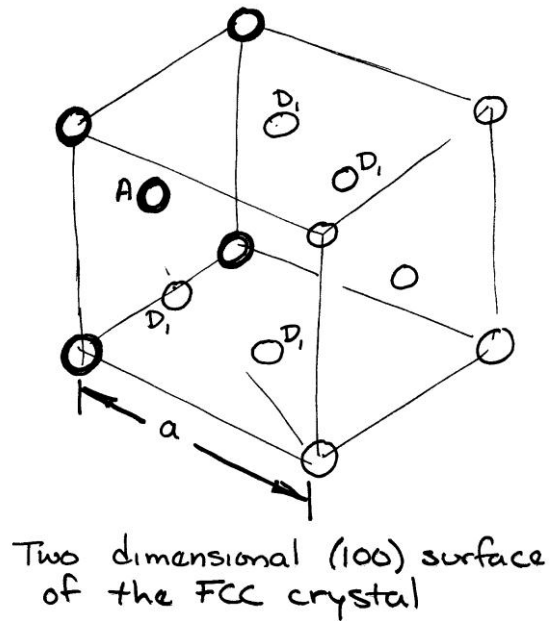
Now let's consider the (110) surface. The easiest way to visualize this situation is to consider two FCC unit cells stacked on top of one another, as shown in the figure below. Atom *A* is on the (110) surface that will form the new surface created by removing the atoms to the right in the figure. Close examination shows that the five atoms marked *D*, are all equidistant from atom *A*. Each atom lies $\dfrac{\sqrt{2}}{2}a$ away. Thus, for each atom *A* on the new (110) surface, five nearest neighbors will be removed and five bonds will be broken. The 2*D* unit cell of the (110) surface is also shown in the figure. The four corner atoms are shared between four 2*D* unit cells, while the two atoms on the center of two sides are shared between two unit cells. This means the number of atoms per unit cell on the (110) surface is

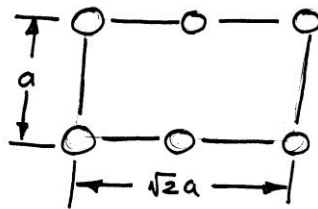$$\frac{atoms}{2D-unit\ cell}=4\left(\frac{1}{4}\right)+2\left(\frac{1}{2}\right)=2$$

The unit cell area on the surface is $a \bullet \sqrt{2}\,a = \sqrt{2}\,a^2$. Thus, the number of bonds broken per unit area on the (110) surface is

$$\frac{bonds\ broken\ on\ (110)\ surface}{unit\ area} = \frac{\left(5\dfrac{bonds}{atom}\right)\left(2\dfrac{atoms}{U.C.}\right)}{\sqrt{2}a^2}$$

$$= \frac{7.07}{a^2}$$
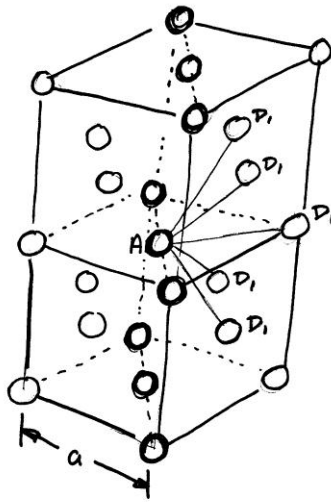


Two dimensional (110) surface of the FCC crystal

The atoms that make up the (111) surface in an FCC crystal are a close-packed array. The nearest neighbor atoms that are removed to form the (111) surface are in another close-packed layer. Three nearest neighbors are removed for each atom in the new surface or three bonds are broken per atom on the final (111) surface, as shown in the

figure below. A surface unit cell is also shown in the figure that is superimposed on the six atoms that make up new (111) surface created from the $3D$ unit cell in the top of the figure. The repeat unit is a parallelogram with angles 60° and 120° and sides with length $\dfrac{\sqrt{2}}{2}a$ and area $\dfrac{\sqrt{3}}{4}a^2$. Each of the corner atoms is shared between four surface unit cells. Thus, there is

$$\frac{atoms}{2D-unitcell} = 4\left(\frac{1}{4}\right) = 1\frac{atom}{U.C.}$$

three neighbors removed

2D unit cell of the (111) surface of an FCC crystal.
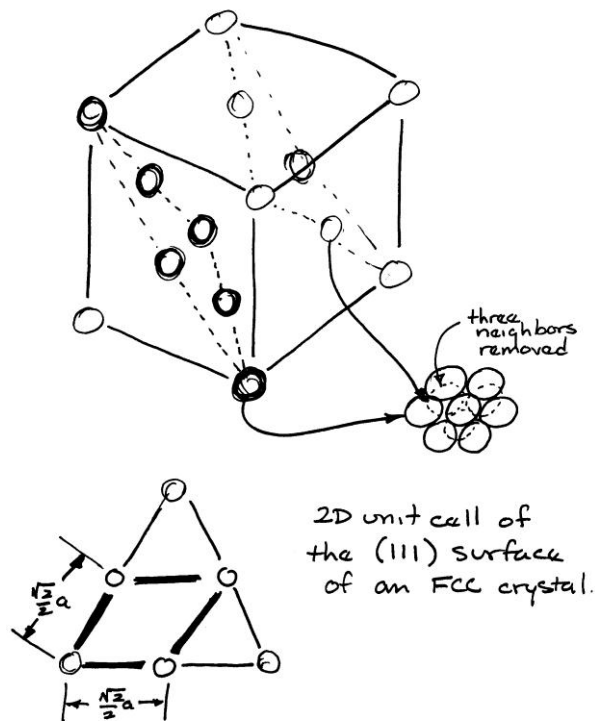
Thus, the number of bonds broken per unit area to form a (111) surface in an FCC crystal is

$$\frac{bonds\ broken\ on\ (111)\ surface}{unit\ cell} = \frac{\left(3\dfrac{bonds}{atom}\right)\left(1\dfrac{atoms}{U.C.}\right)}{\sqrt{3}a^2}$$

$$= \frac{6.92}{a^2}$$

That is, the lowest surface energy of the three surfaces considered will be the (111) surface.

Obviously the surface energies of the (100), (110), and (111) surfaces will vary as the number of bonds per unit required to form the respective surfaces. The bond energy will be the same in all cases for a given crystal and will depend on the heat of vaporization. Shown below are the various surface energies of rare gas crystals as well as the expected ratios based on the discussion above. Rare gas crystals adopt the FCC crystal structure and the dimensions of the unit cell are indicated in the table below as $2a$ in Angstoms.

			$\gamma(\times 10^{-7}\ J/cm^2)$		
Rare gas	$2a$(A)	E_{vap}(J/atom)	(100)	(110)	(111)
Ne	4.52	4.08x10^{-21}	21.3	20.3	19.7
Ar	5.43	13.89x10^{-21}	46.8	44.6	43.2
Kr	5.59	19.23x10^{-21}	57.2	54.5	52.8
Xe	6.18	26.87x10^{-21}	67.3	64.1	62.1
Expected ratio			8	7.07	6.92

Also in the table above is the energy required to take an atom in each of the crystals and put in in the vapor, E_{vap}. One can use the broken bond model to estimate the surface energy of each of these surfaces and compare to the table above. The estimated bond energy (per atom) and surface energies for Ne are

$$E_b = \frac{1}{2} \cdot \times \frac{4.08 \times 10^{-21}}{12} = 1.7 \times 10^{-22}\ J/atom$$

$$\gamma_{100} = \frac{8 \cdot (1.7 \times 10^{-22})}{\left(\frac{0.452}{2} \times 10^{-7}\right)^2} = 26.6 \times 10^{-7} \text{ J/cm}^2$$

$$\gamma_{110} = \frac{7.07 \cdot (1.7 \times 10^{-22})}{\left(\frac{0.452}{2} \times 10^{-7}\right)^2} = 23.5 \times 10^{-7} \text{ J/cm}^2$$

$$\gamma_{111} = \frac{6.92 \cdot (1.7 \times 10^{-22})}{\left(\frac{0.452}{2} \times 10^{-7}\right)^2} = 23.0 \times 10^{-7} \text{ J/cm}^2$$

While the relative order between the surface energy of each face is correct, the absolute magnitude is slightly over estimated by the broken bond model. The reason for this is that the broken bond model for surface energy neglects the slight relaxation in positions of the atoms near the surface of a crystal. That is, surface atoms will recover some of their lost bond energy by slightly moving from their expected positions based on the bulk atomic positions. This surface relaxation energy can amount to a significant portion of the total surface energy.

7.   THE BROKEN BOND MODEL AND CRYSTAL FACETS

High index surface planes will have steps as shown in the figure below. Here, the nominal surface is at an angle, θ, with respect to a low index plane of the crystal. Clearly, each of the edges has an increased number of unsaturated bonds relative to the flat portion of the step. The edges are much more similar to the edges of cubes discussed earlier.
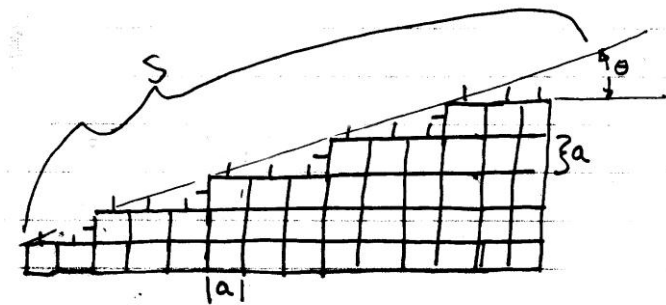
A simple broken bond model can explain how the surface energy might vary with angle from a low index plane. Note that the steps are assumed to be only one unit cell high. Thus, the number of unit cells in the horizontal direction on an average flat portion of the step

$$N_{Flat} = \frac{S\cos\theta}{a}$$

where S is a length of the macroscopic surface. The average number of vertical edges on that same length is

$$N_{edges} = \frac{S\sin\theta}{a}$$

Note that the absolute value of the angle is required to account for cases where the surface slopes the other direction. If each edge contributes only one extra broken bond and each flat surface unit cell has only one broken bond, then the number of broken bonds per unit cell depth in length S is

$$\frac{brokenbonds}{unitcellde\,pth} = \frac{S \bullet \cos\theta}{a} + \frac{S \bullet \theta}{a}$$

Now, if we consider a macroscopic depth of say, d. Then, the broken bonds I the macroscopic area $S \bullet d$ are

$$\frac{broken\,bonds}{} = \left(\frac{S \bullet \cos\theta}{a} + \frac{S \bullet \sin\theta}{a} \right) \frac{d}{a}$$

or the broken bonds per unit area is

$$\Gamma = \frac{broken\,bonds}{unit\ area} = (\cos\theta + \sin\theta) \frac{1}{a^2}$$

Our calculation of surface energy is the same as before. Each bond broken requires E_b of energy. Thus, the energy required to break the bonds in a unit area of surface is $E_b\Gamma$. Two surfaces of equal area are created, however, so the surface energy is this number divided by two, or

$$\gamma = (\cos\theta + \sin\theta)\frac{E_b}{2a^2}$$

A plot of this function looks like this
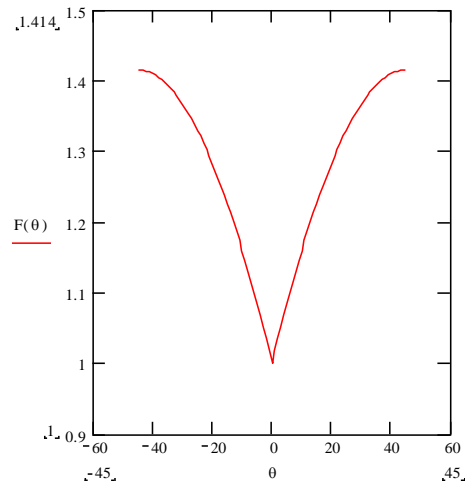
This strange looking function says that there is a sharp minimum energy around low index surface planes ($\theta = 0$). That is, the surface of crystals have a minimum energy when all the surfaces are composed of low index planes. This is the reason why many crystals naturally form facets. These crystals are the low index planes.