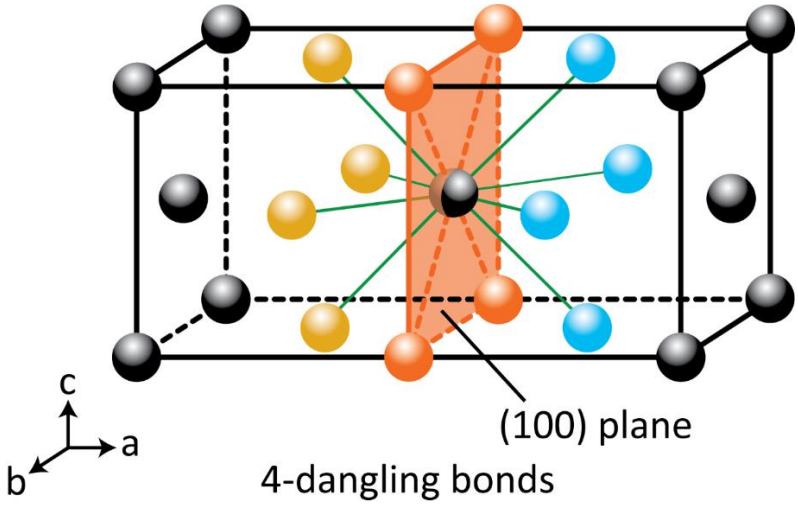
Dangling bonds

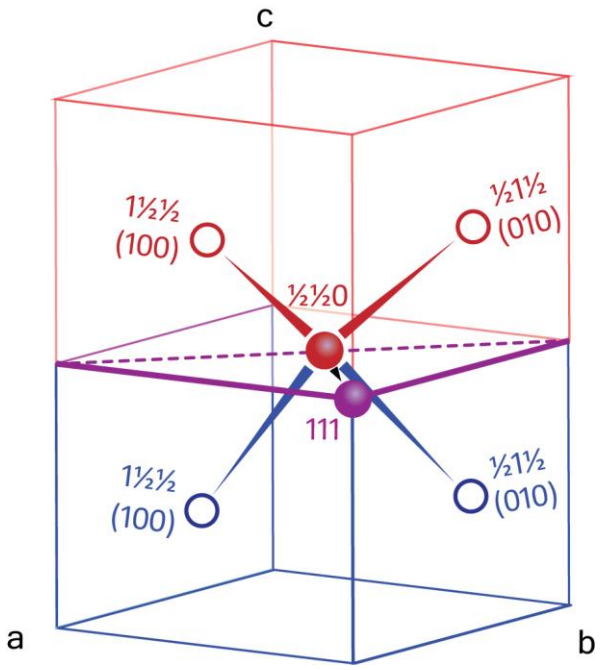
Dangling bonds are the broken bonds yielding undercoordinated atoms. For example, if we draw a simple fcc lattice and slice it along one of the facets, we'll see directly how many bonds are broken.

When we slice along (100) , we are removing 4 nearest neighbors and each atom will have 4 dangling bonds as shown below.



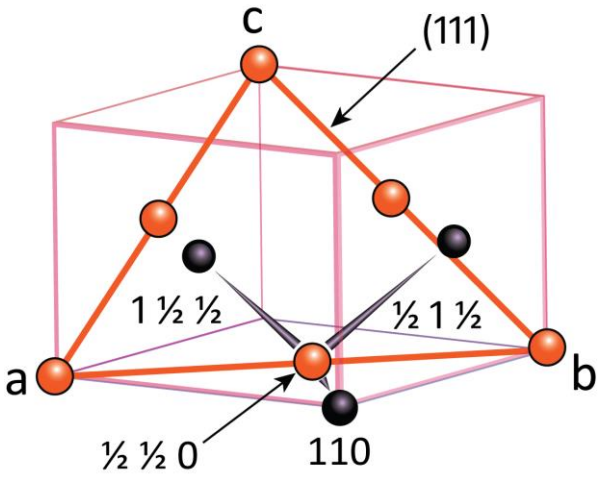
For (100) plane, there are 4 dangling bonds

When we slice along (110) , we are removing 5 nearest neighbors and each atom will have 4 dangling bonds as shown below.



For (110) plane, there are 5 dangling bonds

When we slice along (111) , we are removing 5 nearest neighbors and each atom will have 3 dangling bonds as shown below.



For (111) plane, there are 3 dangling bonds

The number of dangling bonds is a fundamental quantity that is important in deducing surface energy. From the above drawings for metals of fcc structure:

{100} facets would have four broken chemical bonds, {110} surfaces has 5 broken chemical bonds and {111} has 3. Accordingly, in monometallic fcc crystal the {111} family of surfaces have the lowest surface energy, followed by {110} and {100} families of planes.

Surface Energy

The surface properties of a crystal are crucial to the understanding and design of materials for many applications. For instance, technologies such as fuel cells and industrial chemical manufacturing require the use of catalysts to accelerate chemical reactions, which is fundamentally a surface-driven process. Surface effects are especially important in nanomaterials, where relatively large surface area to volume ratios lead to properties that differ significantly from the bulk material. For example, the nanoscale stability of metastable polymorphs is determined from the competition between surface and bulk energy of the nanoparticle.

The stability of a surface is described by its surface energy *γ*, a measure of the excess energy of surface atoms due to a variety of factors, such as the broken bonds yielding undercoordinated atoms. This fundamental quantity is important in understanding surface structure, reconstruction, roughening and the crystal's equilibrium shape.

Each facet has a characteristic surface energy, the value depending of how many broken chemicals bonds you have in the surface.

Calculation of surface energy per unit area *γ*

The surface energy (ɣ)per unit area of different crystal faces can be calculated using the following relation:

$$ɣ = \left(\frac{\text{Dangling bonds}}{\text{Bulk coordination number}}\right) \cdot \frac{U}{N_A} \cdot a_o$$

where:

ɣ = Energy per unit area of a particular crystal plane,

CN = 12

U = lattice energy

N_A = Avogadro's number

a_o = Planar density in atoms/m^2

For (100) of Ca metal possesses a fcc structure of unit cell constant a = 5.6 Å, U = 180 kJ mol^{-1}, dangling bonds = 4, CN in the bulk = 12, the surface density is $2/a^2$ atoms per unit area. i.e.

Planar density = $\frac{2}{(5.6\times10^{-10}\ \text{m})^2}$

= 0.3557×10^{20} atom/m^2

Then,

$\gamma = \frac{4}{12}\cdot\frac{180000\ (\text{J mol}^{-1})}{6.02\times10^{23}\ \text{mol}^{-1}}\cdot0.3557\times10^{20}\ \text{m}^{-2}$

= 0.63 J/m^2

= 630 mJ/m^2

One can proceed with calculations for fcc (111) faces in which: dangling bonds = 3, CN in the bulk = 12, the surface density is $2/\sqrt{3}\ a^2$ atoms per unit area.

For fcc (110) faces, dangling bonds = 5, CN in the bulk = 12, the surface density is $2/\sqrt{2}\ a^2$ atoms per unit area.

It is clear that magnitude of lattice energy reflects the strength of chemical bonding. The surface energy (ɣ)per unit area of the (100) faces of different materials is given as follows.

(100) faces	ɣ mJ/m^2
Diamond	9800

MgO	1200
Ca	630
LiF	480