

illustration of this phenomenon has been observed for a Au(111) surface using very high resolution electron microscopy (Fig. 1.3).

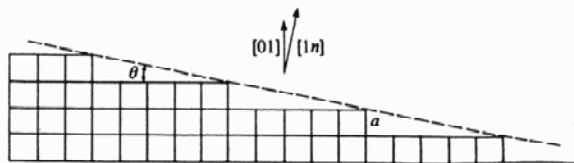
According to (1.5), the surface tension can be regarded as an excess free energy/unit area. This fact suggests a number of experiments that might be used to measure γ directly (Lindford, 1973). For example, in 1857, Faraday noticed that gold foils contracted as they were heated near their melting points. This effect, known as *creep*, occurs because of rapid atomic diffusion under the influence of surface forces. By opposing this creep with known external forces, the surface tension can be determined. These experiments are rather difficult to perform accurately. Nonetheless, we can obtain a crude order-of-magnitude estimate as follows. By definition, γ is the energy cost/unit area to cleave a crystal, i.e., to break surface bonds. Hence, we write $\gamma = E_{\text{coh}} (Z_s/Z) N_s$, where E_{coh} is the bulk cohesive energy, Z_s/Z is the fractional number of bonds broken (per surface atom) when the cleave occurs and N_s is the areal density of surface atoms. Putting in typical numbers ($E_{\text{coh}} \sim 3 \text{ eV}$, $Z_s/Z \sim 0.25$, $N_s \sim 10^{15} \text{ atom/cm}^2$) we get $\gamma \sim 1200 \text{ erg/cm}^2$. The variations in this number across the periodic table can be inferred from measured values of liquid surface tensions (Fig. 1.4) and simply reflect the variations in E_{coh} itself.

Anisotropy of γ

The surface tension of a planar solid surface depends on the crystallographic orientation of the sample. To see this, consider a two-dimensional solid which is very slightly misaligned from the [01] direction (Fig. 1.5). The resulting so-called *vicinal* surface consists of a number of monoatomic steps separated by terraces of width na , where a is the lattice constant. For n large, the small angle between the [01] and [1n] directions is $\theta \cong 1/n$. The surface tension along the [1n] direction, denoted by $\gamma(\theta)$, has a contribution from the surface tension of the (01) face, $\gamma(0)$, and a contribution from each of the individual steps. If β is the energy/step, the total surface tension of the (1n) surface is

$$\gamma(\theta) = \gamma(0) + (\beta/a)|\theta|. \quad (1.16)$$

Fig. 1.5. A vicinal surface.



The change of sign in the second term reflects the fact that it always costs energy to produce steps on a flat surface. Notice that (1.16) implies that $\gamma(\theta)$ is a continuous function near $\theta = 0$ but that it has a *discontinuous* derivative at that point, i.e., there is a cusp. More precisely,

$$\Delta \left(\frac{d\gamma}{d\theta} \right)_{\theta=0} = 2\beta/a. \quad (1.17)$$

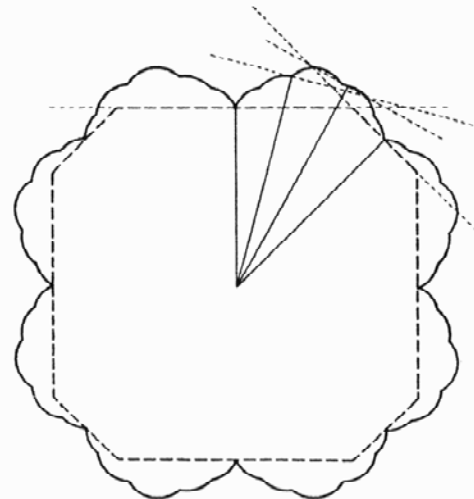
Now take θ to be a large angle. The density of steps will increase and a proper calculation of the surface tension must include the energy of interaction between steps. In this case, Landau (1965) has shown that $\gamma(\theta)$ has a cusp at every angle which corresponds to a rational Miller index! The sharpness of the cusp is a rapidly decreasing function of index:

$$\Delta \left(\frac{d\gamma}{d\theta} \right) \sim \frac{1}{n^4}. \quad (1.18)$$

Hence, a polar plot of the surface tension at $T = 0$ has the form illustrated by the solid curve in Fig. 1.6.

The anisotropy of the surface tension determines the equilibrium shape of small crystals because a crystal will seek the shape that minimizes the

Fig. 1.6. Polar plot of the surface tension at $T = 0$ (solid curve) and the Wulff construction of the equilibrium crystal shape (dashed curve) (Herring, 1951b).



quantity

$$\oint \gamma(\theta) dA, \tag{1.19}$$

subject to the constraint of fixed volume. This question amounts to a

Fig. 1.7. Electron micrograph of a lead crystal at 473 K (Heyraud & Metois, 1983).

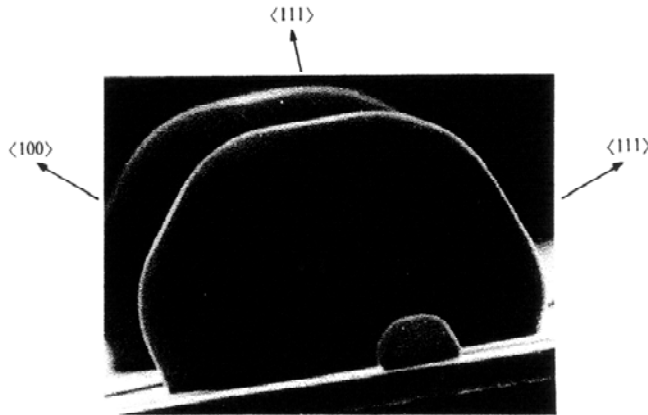
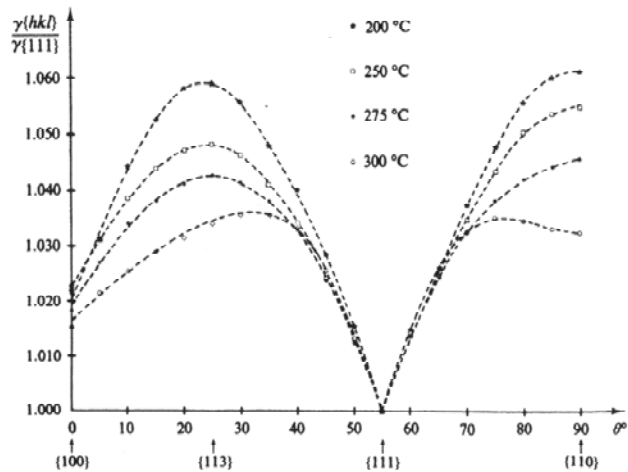


Fig. 1.8. Anisotropy of γ relative to $\langle 111 \rangle$ for lead as a function of temperature (Heyraud & Metois, 1983).



problem in affine geometry which first was solved by Wulff (1901). To find the equilibrium shape, draw a radius vector that intersects the polar plot at one point and makes a fixed angle with the horizontal. Construct the plane that is perpendicular to the vector at the point of intersection. Repeat this procedure for all angles. The interior envelope of the resulting family of planes is a convex figure whose shape is that of the equilibrium crystal (Fig. 1.6). If one tries to cleave a crystal along a direction which does not form part of this equilibrium boundary the crystal will spontaneously facet along those directions that do. It must be borne in mind that this construction is relevant only when the crystal is in true thermodynamic equilibrium. Unfortunately, crystal growth generally occurs under highly non-equilibrium conditions so that the equilibrium shape rarely is achieved; kinetic constraints restrict the necessary transport of mass along the surface. Nonetheless, some reliable data are available.

Electron microscopy has been used to study the shape of very small (diameter $\cong 10$ microns) lead crystallites. The equilibrium shape (Fig. 1.7) is found to be a cubo-octahedron with a number of well-developed facets. The Wulff theorem then can be run in reverse to determine the anisotropy of the surface tension (Fig. 1.8). Note the 'blunting' of the cusp near $[111]$ as the temperature is raised.

The roughening transition

At finite temperatures, the discussion of the previous section must be supplemented to include entropy effects. At very low temperature any given facet is microscopically flat with only a few thermally excited surface vacancies or defects (Fig. 1.9a). However, at higher temperature more and more energetic fluctuations in the local height of the surface can occur

Fig. 1.9. Surface morphology: (a) $T < T_r$; (b) $T > T_r$ (Muller-Krumbhaar, 1978).

