



TMT4320 Nanomaterials, fall 2015

EXERCISE 2 - SOLUTION

PROBLEM 1

a) (100) surface: The surface is represented by one of the surfaces of the cube:

Area: a^2

Number of atoms at the surface: $1 + \frac{1}{4} \times 4 = 2$

Surface atomic density: $2/a^2 = 2 a^{-2}$

(110) surface: The surface is represented by a plane, which is parallel to the diagonal in a face of the cube and which cut the cube in two (not shown in the figure in the exercise). The area of the rectangular is calculated by using Pythagoras' theorem.

Area: $a \times (a^2 + a^2)^{1/2} = \sqrt{2} a^2$

Number of atoms at the surface: $\frac{1}{2} \times 2 + \frac{1}{4} \times 4 = 2$

Surface atomic density: $2/(\sqrt{2} a^2) = \sqrt{2}/a^2 = 1.414 a^{-2}$

(111) surface: The surface is shown in the figure in the exercise and we need to calculate the area of the equilateral triangle shown in the figure using Pythagoras' theorem. The triangle has sides of $\sqrt{2} a$. If we call the line from one corner to the middle of the opposite side h , we get:

$$h^2 + \left(\frac{\sqrt{2}a}{2}\right)^2 = (\sqrt{2}a)^2$$

$$h = \left(2a^2 - \frac{a^2}{2}\right)^{\frac{1}{2}} = \frac{\sqrt{3}}{\sqrt{2}} a$$

$$\text{Area} = \frac{1}{2} \times \sqrt{2}a \times \frac{\sqrt{3}}{\sqrt{2}} a = \frac{\sqrt{3}}{2} a^2$$

Number of atoms at the surface: $\frac{1}{2} \times 3 + \frac{1}{6} \times 3 = 2$

Surface atomic density: $2/(\sqrt{3}/2 a^2) = (4/\sqrt{3}) a^{-2} = 2.309 a^{-2}$

Surfaces by increasing surface atomic density: (110) < (100) < (111)

b) (111): 3 broken bonds per atom

(110): 5 broken bonds per atom

(100): 4 broken bonds per atom

c) The surface energy of the crystal surfaces:

$$\gamma_{100} = \frac{1}{2} 4 \frac{2}{a^2} \varepsilon = 4 \frac{\varepsilon}{a^2}$$

$$\gamma_{110} = \frac{1}{2} 5 \frac{\sqrt{2}}{a^2} \epsilon = \frac{5}{\sqrt{2}} \frac{\epsilon}{a^2} = 3.54 \frac{\epsilon}{a^2}$$

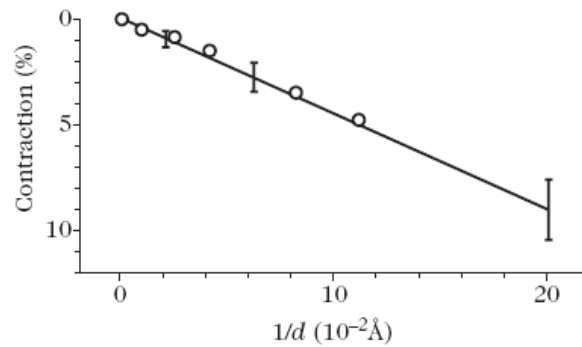
$$\gamma_{111} = \frac{1}{2} 3 \frac{4\sqrt{3}}{a^2} \epsilon = 2\sqrt{3} \frac{\epsilon}{a^2} = 3.46 \frac{\epsilon}{a^2}$$

$$\gamma_{111} < \gamma_{110} < \gamma_{100}$$

PROBLEM 2

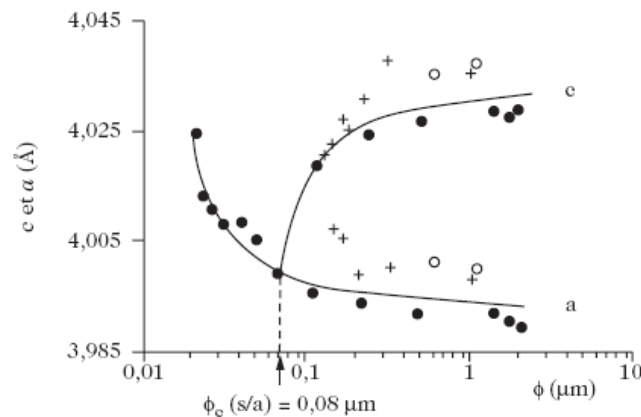
- a) The lattice parameter of an fcc metal nanoparticle will decrease with decreasing nanoparticle size.

Figure 1.2. (p. 6) in “Nanomaterials and Nanochemistry” shows the contraction of the lattice parameter of copper clusters as a function of the reciprocal of their diameter:



- b) The lattice parameter of a BaTiO₃ nanoparticle in the cubic phase will increase with decreasing nanoparticle size.

Figure 2.4. (p. 38) in “Nanomaterials and Nanochemistry” shows the size dependence of the crystallographic lattice parameters a and c for BaTiO₃ in the cubic and tetragonal state, at 25 °C and standard atmospheric pressure in the powdered state:



- c) The size effect on the lattice parameter can be explained by two approaches (p. 47-49):

Thermodynamic approach

Laplace's law can be used to express the pressure P_{int} inside the grains to the pressure P_{ext} outside, the surface energy γ , and the grain diameter a :

$$P_{\text{int}} = P_{\text{ext}} + 4\gamma/a$$

The term $4\gamma/a$ is positive, since γ is an excess energy at the surface of the solid and hence necessarily positive. Hence, when the grain size a goes down, the term $4\gamma/a$ grows larger, leading to an increased pressure inside the grains. This would mean that the lattice parameter should decrease in every case. This is the result for the fcc metal nanoparticles.

For BaTiO_3 the opposite happens. A more careful analysis can explain this apparent paradox, showing that it is the surface stress that should appear in the last equation, rather than the surface energy. Thus, the pressure within the grain can be diminished if the stress is negative, resulting in an increase of the lattice parameter with decreasing nanoparticle size.

Microscopic approach

The atoms or ions are held together by attracting forces and repelled from each other by repulsive forces. The attracting forces can be long-range (Coulombic forces between oppositely charged ions, gravity) or short-range (covalent interaction, van der Waals forces).

In ionic crystals such as BaTiO_3 long-range forces will dominate. The lattice parameter will therefore expand because the effect of the long-range forces will be lower than it is in a bulk crystal.

In fcc metals, short-range forces will dominate. The effect of the short-range forces will be much the same as in a bulk crystal. The lattice parameter will decrease because of the pressure exerted on the nanoparticle by the surface atoms with lower coordination number.

PROBLEM 3

The atoms situated at corners and edges have lower coordination numbers (are bonded to fewer other atoms) than atoms situated on flat surfaces. The corner/edge atoms will thus bond more strongly to adsorbed species since they will have more electrons available for bonding to other atoms. The adsorption energy is therefore higher for species adsorbed on corners/edges.

The adsorbed species can be desorbed (removed) by heat-treatment. But as species adsorbed on corners/edges are bound more strongly to the particle atoms, it is necessary to heat-treat at a higher temperature to desorb the adsorbed species, compared to less strongly bound adsorbed species.