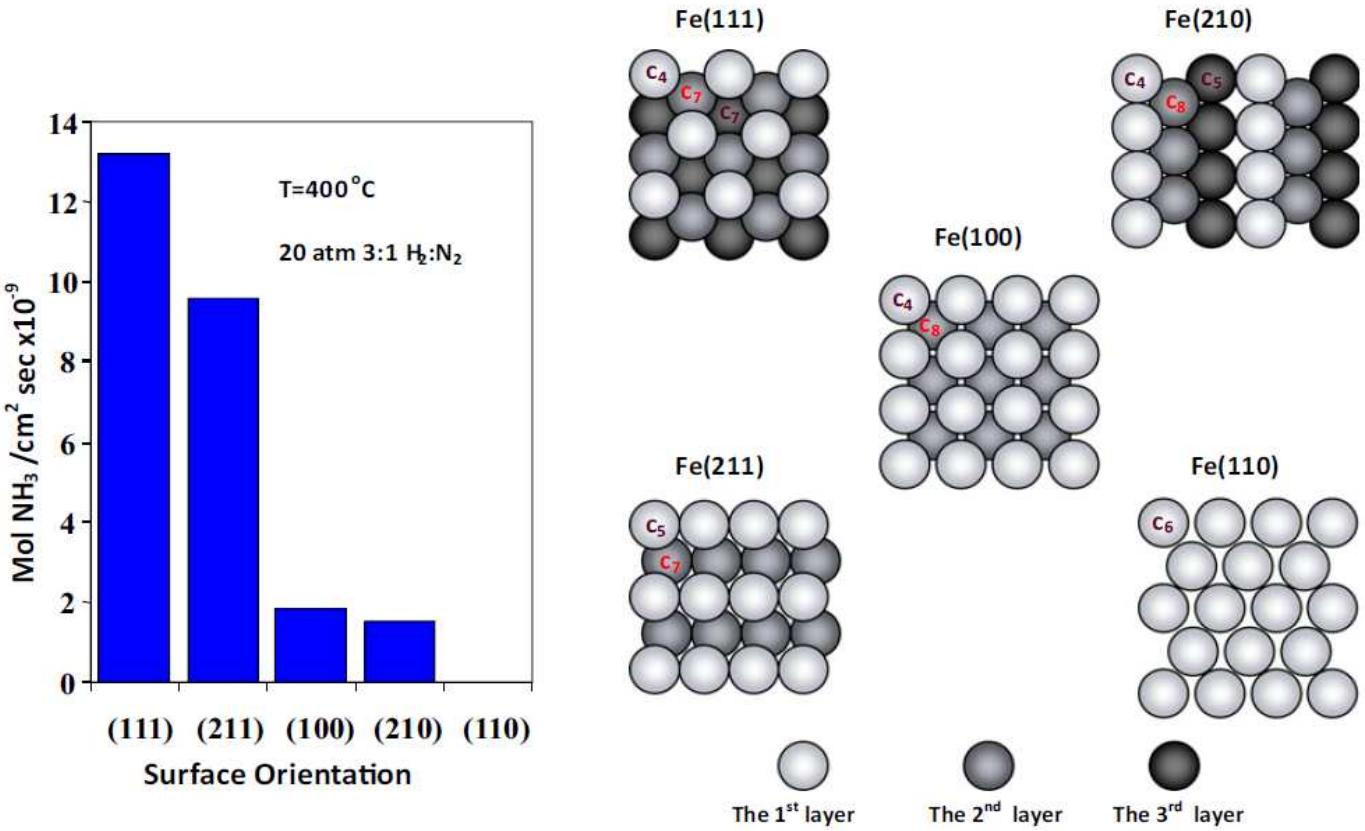
Surface Science and Catalysis

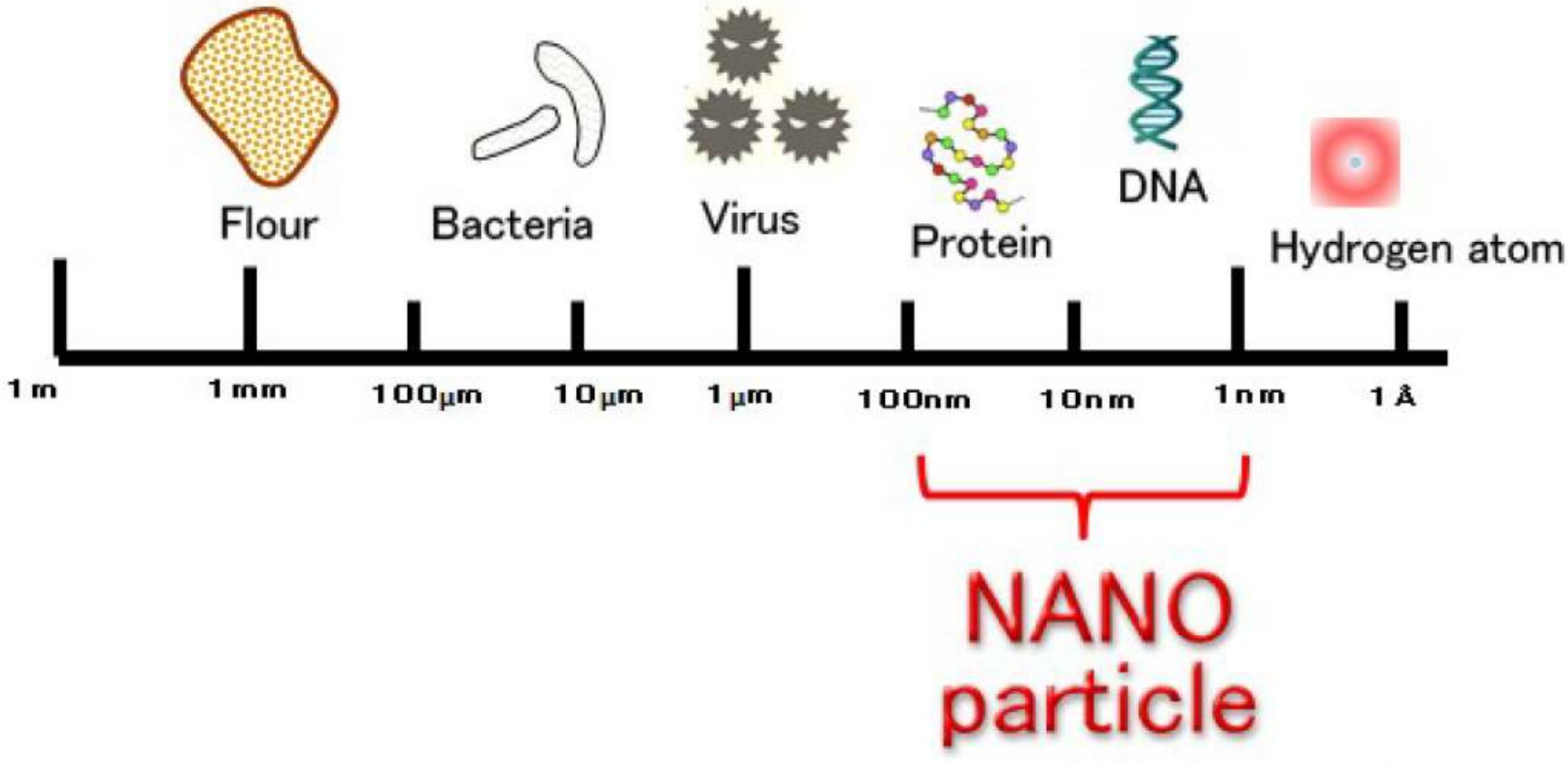
Theory and Applications

Surface structure vs. catalytic activity



The activities of ammonia synthesis over different Fe crystal faces and the structures of corresponding crystal faces, suggesting that the surface atoms with high coordination number (C7 and C8) are the active sites for ammonia synthesis.

Common in-situ-techniques to see the molecular-level surfaces



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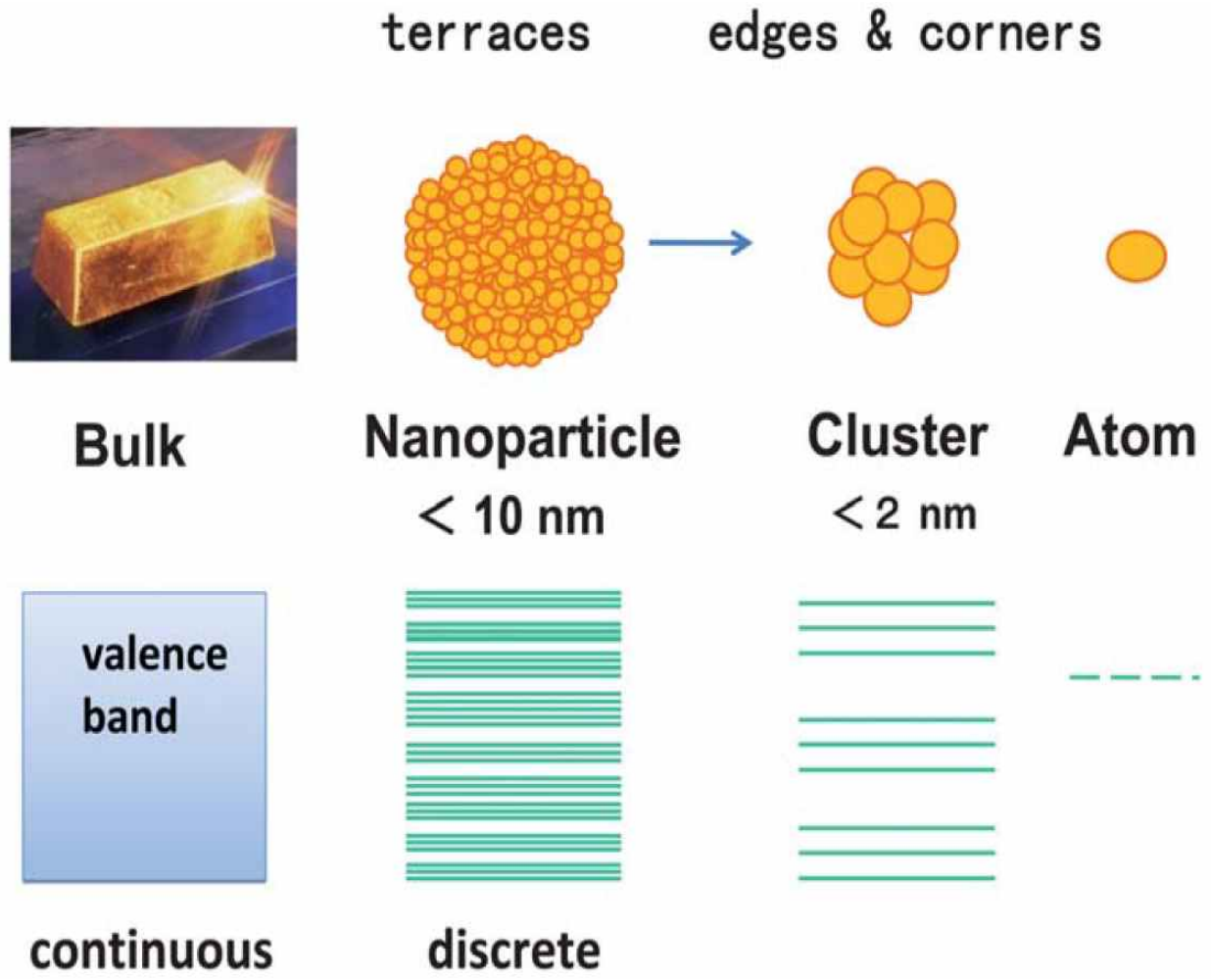
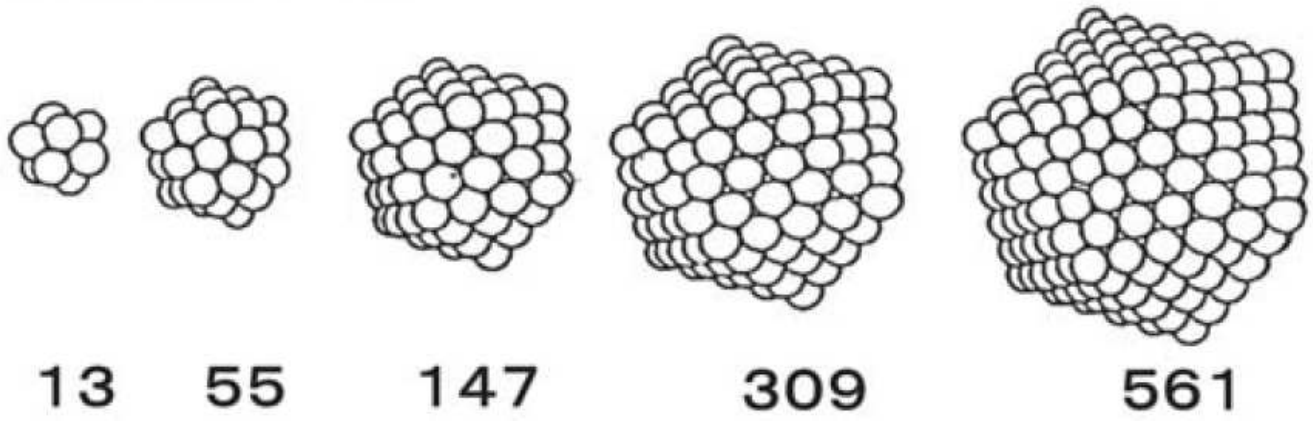
Techniques	Properties characterized
Transmission electron microscopy (TEM)	Surface/interface structure, the size, shape, and crystallinity of nanocrystals
X-ray diffraction (XRD)	Structure of micro- and mesoporous materials
Surface X-ray diffraction (SXRD)	Surface structure
Ambient pressure X-ray photoelectron spectroscopy (AP-XPS)	Surface chemical composition
Small Angle X-ray scattering (SAXS)	Characteristic distances of ordered nanomaterials
X-ray emission spectroscopy (XES)	Electronic structure of surfaces
Near-edge X-ray absorption fine structure (NEXAFS)	Surface chemical composition
Extended X-ray Absorption fine structure (EXAFS)	Chemical composition and bonding environment of nanoparticles
Polarization-modulated reflection–absorption infrared spectroscopy (PM–RAIRS)	Surface reaction intermediates
Surface enhanced Raman spectroscopy (SERS)	Surface reaction intermediates
Sum frequency generation spectroscopy (SFG)	Surface reaction intermediates
High pressure scanning tunneling microscopy (HP-STM)	Surface morphology and electronic structure
Atomic force microscopy (AFM)	Surface morphology, tribological properties, and work function

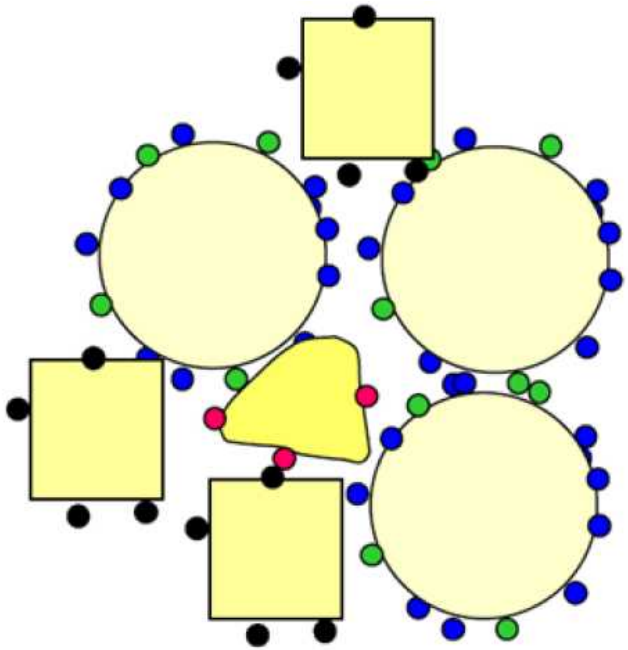
Geometric structures and valence bands



Particle size vs. edge and corner sites for icosahedrons



Particle size vs. edge and corner sites



Active site (for a particular reaction) one or more atoms in a particular configuration

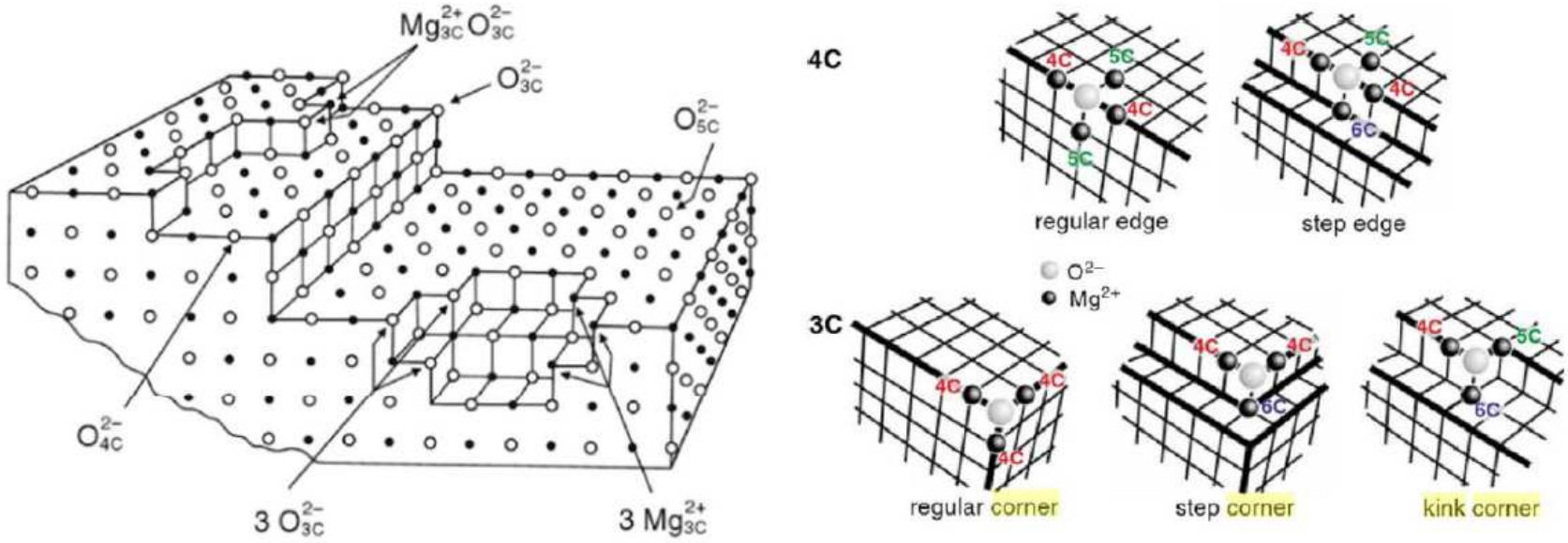
Hugh Scott Taylor

Proc. Roy. Soc. A108, 105 (1925)

Particle size vs. edge and corner sites for icosahedrons

Even a single crystal surface has some defects!
Sites/atoms: terraces, edges, step edges, kinks, adatoms, vacancies, corners….

Scheme of MgO surface: defects



Surface Science

☐ **Surface**

- the boundary layer between a solid and a vacuum, gas, or liquid
- Occasionally surface also refers to the boundary between liquid and gas phase.

☐ **Surface differs from the interior of the solid both in chemical composition and physical properties**

- Unsaturated atoms exist for binding or adsorption.
- As the dimension of a solid becomes smaller in nanometer range, the ratio of surface atoms increases dramatically.

- For a large bulk material, the surface layer is generally only a tiny fraction of the total solid.

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☐ **Surface science**

- the study of physical and chemical phenomena that occur at the surfaces

☐ **Surface science includes:**

- surface chemistry
- surface physics
- some related practical applications
- surface engineering.

  - o heterogeneous catalysis
  - o semiconductor devices
  - o corrosion and adhesion
  - o metal/alloy surface
  - o behavior and function of biological membranes

(Continued)

☐ **Surface chemistry**

- the study of chemical reactions at interfaces, aiming at modifying the chemical composition of a surface by incorporation of selected elements or functional groups that produce various desired effects or improvements in the properties of the surface or interface

- particular importance to the field of heterogeneous catalysis

☐ **Surface physics**

- the study of physical changes that occur at interfaces

- surface states, surface diffusion, surface reconstruction, surface phonons and plasmons, epitaxy and surface enhanced Raman scattering, the emission and tunneling of electrons, spintronics, and the self-assembly of nanostructures on surface

(Continued)

☐ **At atomic process,**

No distinction between surface chemistry and physics!

☐ **Traditionally, a physical change in a substance doesn't change what the substance is. In a chemical change where there is a chemical reaction, a new substance is formed and energy is either given off or absorbed.**

- cutting up a piece of paper into small pieces -> still paper
- if burned, different substances (not paper)

- at atomic scale, these two cases different?

☐ **Traditionally defined, physical changes can be reversed, chemical changes cannot be reversed with the substance changed back without extraordinary means, if at all.**

- a cup of water -> frozen -> heated -> a liquid

- at atomic scale, these two cases different?

Clean surface

☐ **A concentration of atoms on the surface of a solid:**

~ 10^{15} molecules/cm^2

☐ **From the kinetic theory of gases, the flux of molecules that strike the surface of unit area at a given ambient pressure is expressed by:**

$$F = \frac{N_A P}{\sqrt{2\pi M\, RT}}$$

N_a: Avogadro's number
P: pressure
M: average molecular weight of the gaseous species
R: gas constant
T: temperature

$$F\left(\frac{atom\ s}{cm^2 \cdot sec}\right) = 3.51 \times 1022\ \frac{P\ (Torr)}{\sqrt{M\left(\frac{g}{mole}\right)T}}$$

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☐ **Assuming P = 3 x 10^{-6} Torr, M = 28 g/mole (N_2), T = 300 K, and a sticking coefficient of unity**

$$F = \sim 10^{15} \text{ molecules/cm}^2 \cdot \text{sec}$$

- gas exposure unit: Langmuir (L)

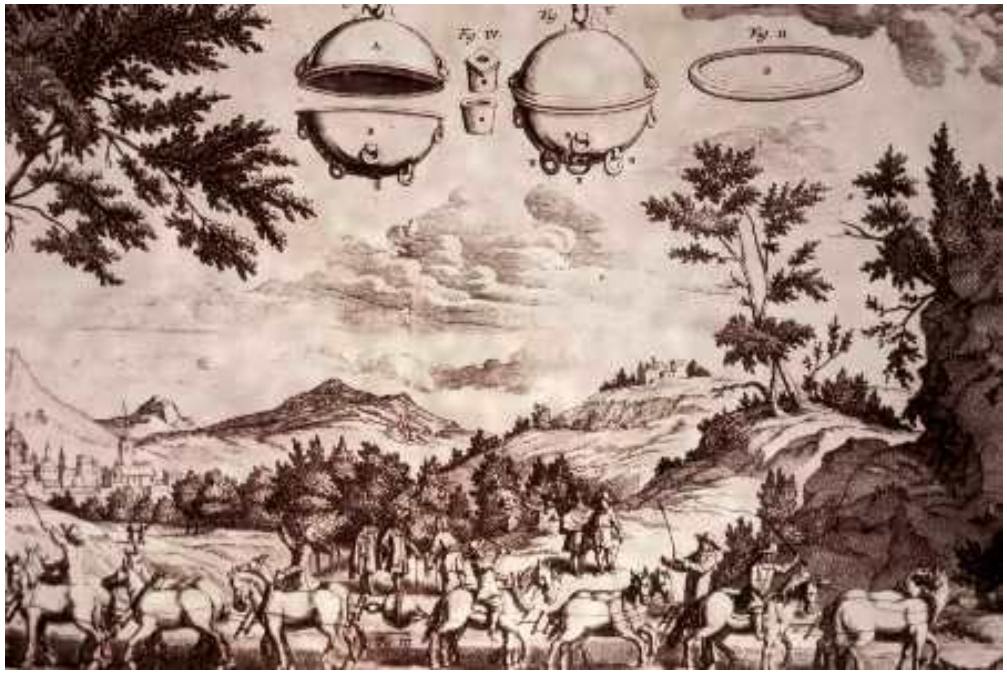
- 1 L = 10^{-6} Torr·sec

☐ **At pressures on the order of 10^{-9} Torr, it takes 1,000 sec.**

- *Ultrahigh dynamic vacuum* < 10^{-9} Torr *for maintaining a clean surface for about 1 h*

Magdeburg hemispheres experiments

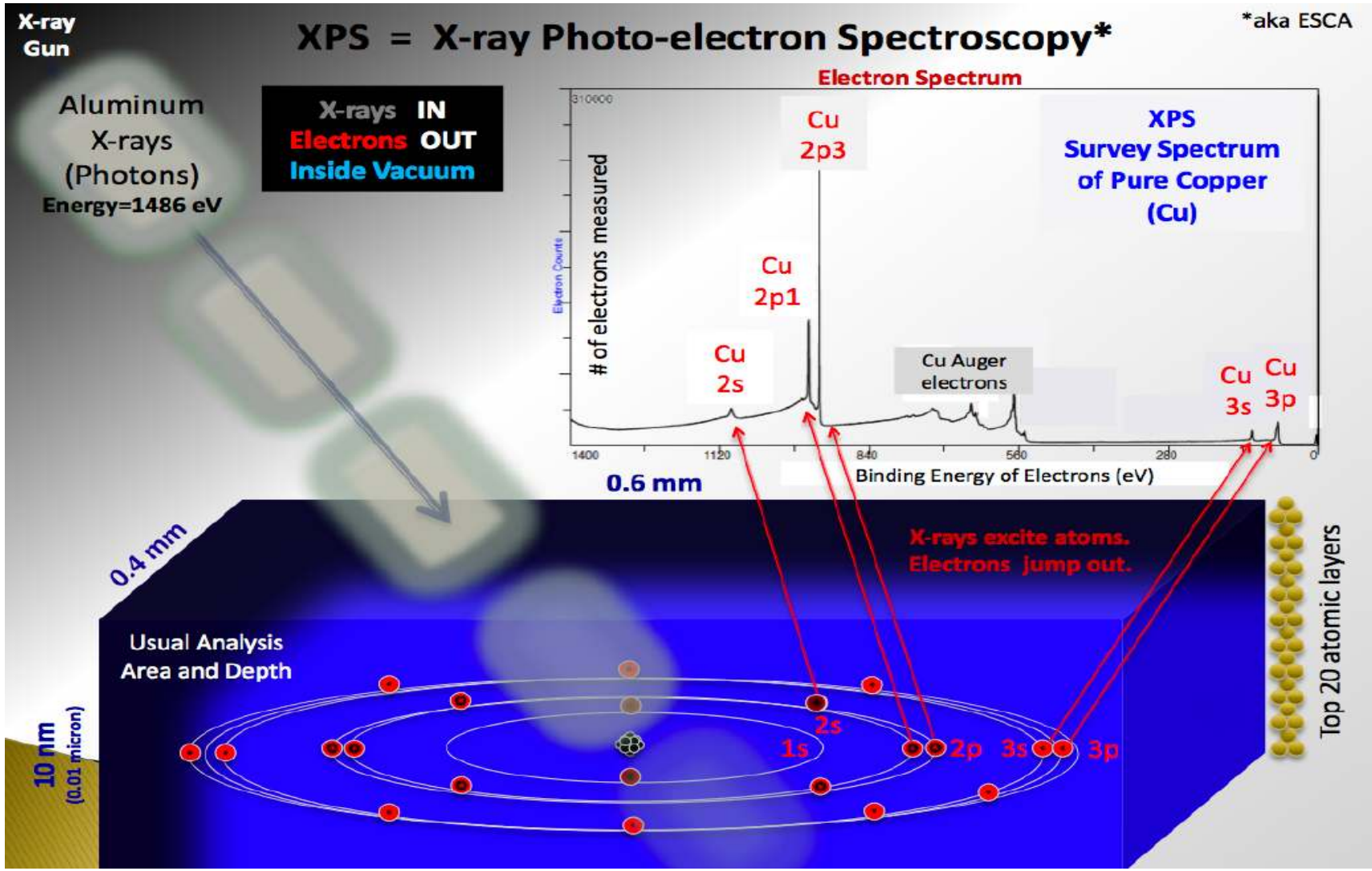
- invention of an air pump
- performed in 1657 at Magdeburg by Otto von Guericke (1602-1686), the mayor of this city
- to pull apart the two evacuated hemispheres with a diameter of ca. 50 cm, eight horses on the right and eight horses on the left, ~2.2 ton-force



A sketch by Gaspar Schott

Deutsches Museum in Munich

Examples


X-ray Gun
XPS = X-ray Photo-electron Spectroscopy*
*aka ESCA
Aluminum X-rays (Photons)
Energy=1486 eV
X-rays IN
Electrons OUT
Inside Vacuum
Electron Spectrum
# of electrons measured
Cu 2p3
Cu 2p1
Cu 2s
Cu Auger electrons
Cu 3s
Cu 3p
XPS Survey Spectrum of Pure Copper (Cu)
1400
1120
840
560
280
0
Binding Energy of Electrons (eV)
0.6 mm
0.4 mm
X-rays excite atoms.
Electrons jump out.
Usual Analysis Area and Depth
10 mm
(0.01 micron)
1s
2s
2p
3s
3p
Top 20 atomic layers

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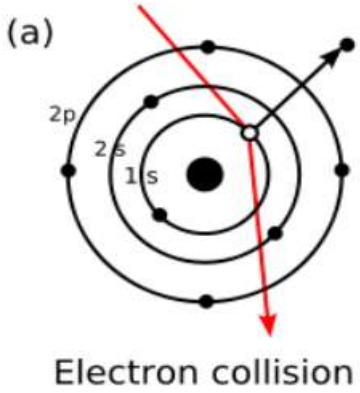
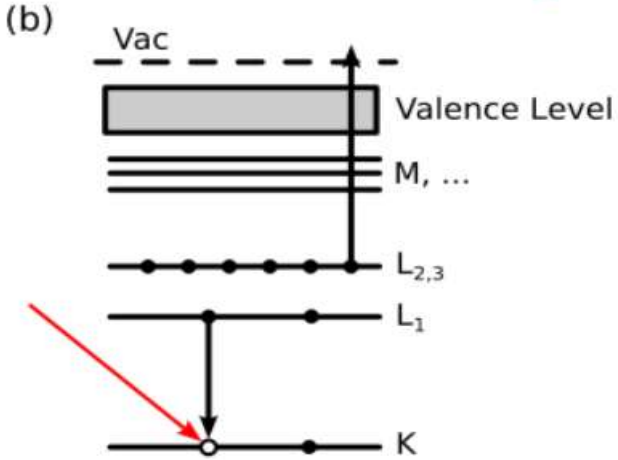
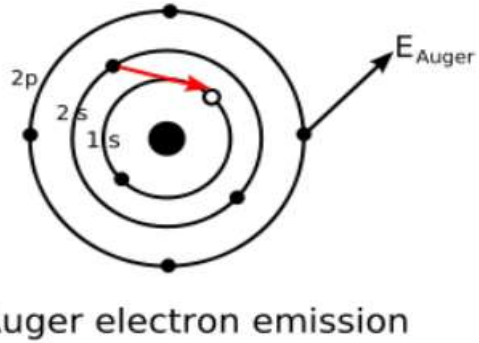
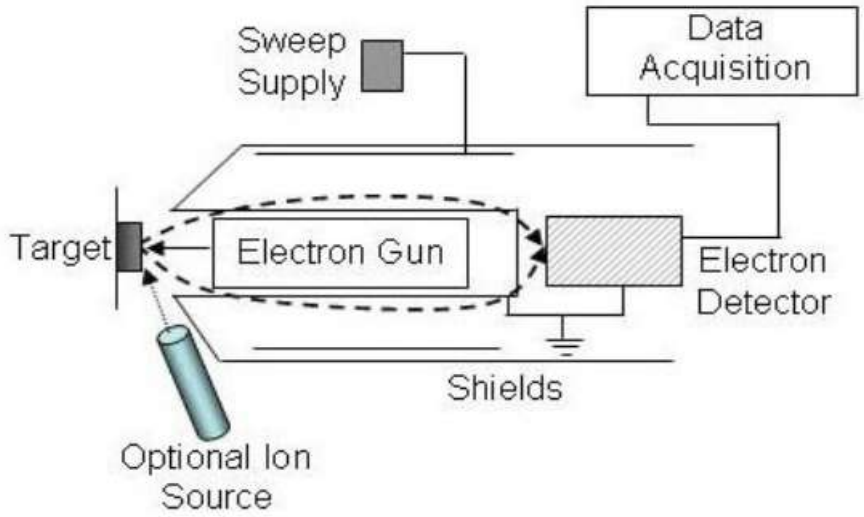
Auger electron spectroscopy









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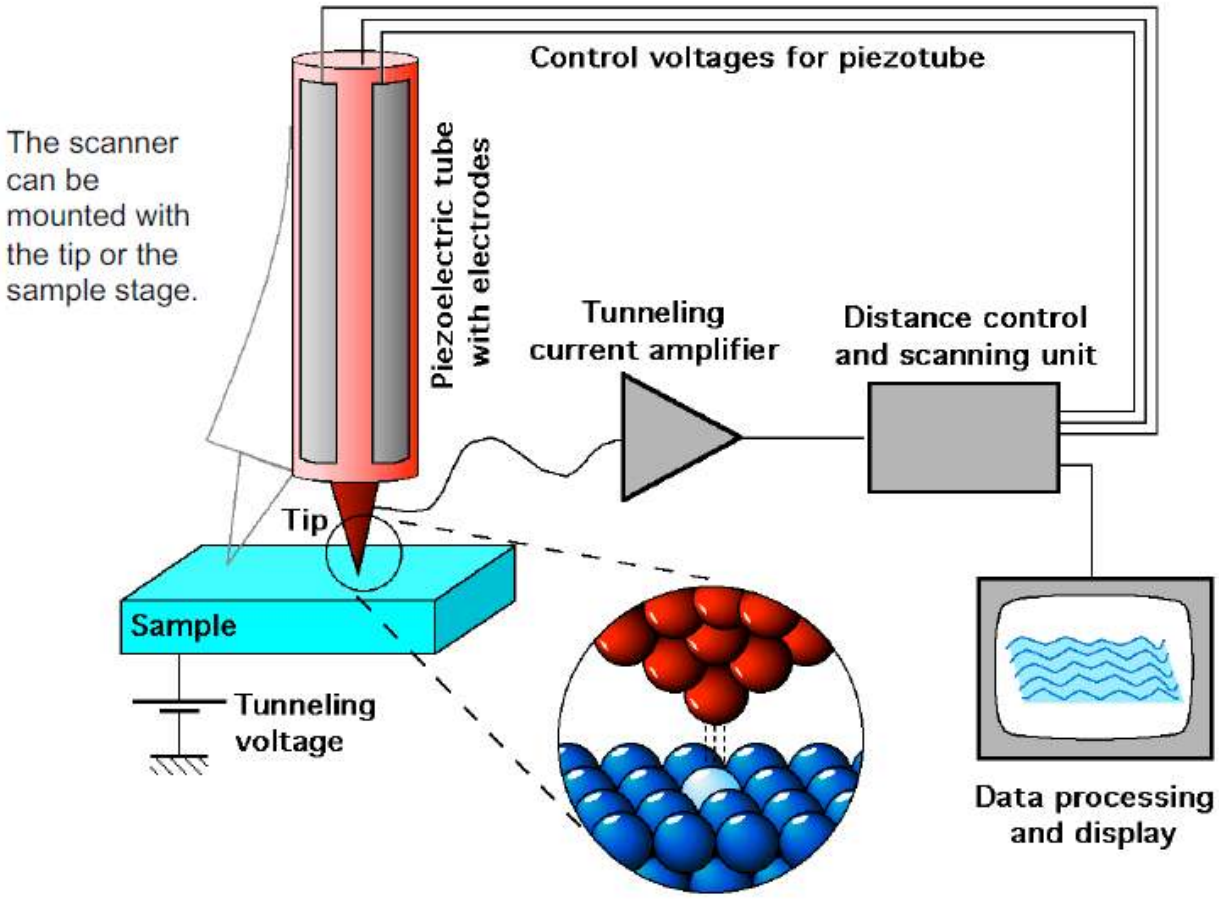

Five basic components:

1. Metal tip,
2. Piezoelectric scanner,
3. Current amplifier (nA),
4. Bipotentiostat (bias),
5. Feedback loop (current).

- Tunneling current from tip to sample or vice-versa depending on bias;
- Current is exponentially dependent on distance;
- Raster scanning gives 2D image;
- Feedback is normally based on constant current, thus measuring the height on surface.

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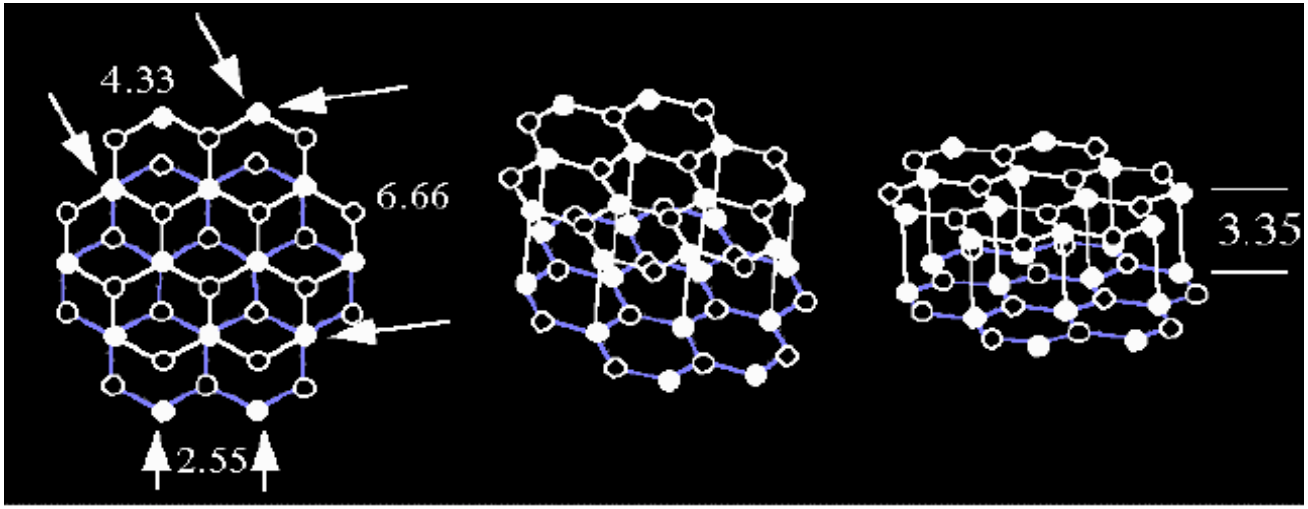

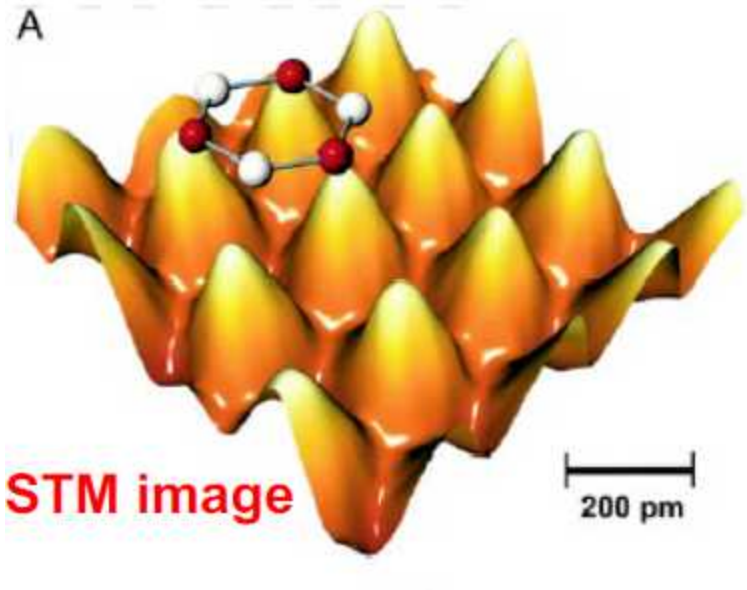

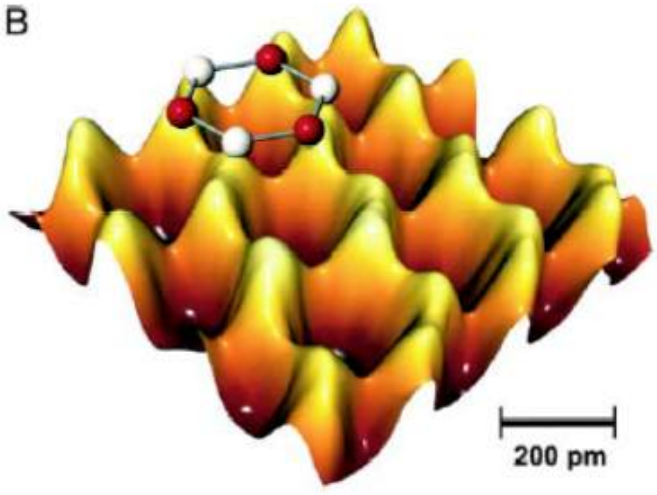

AFM image

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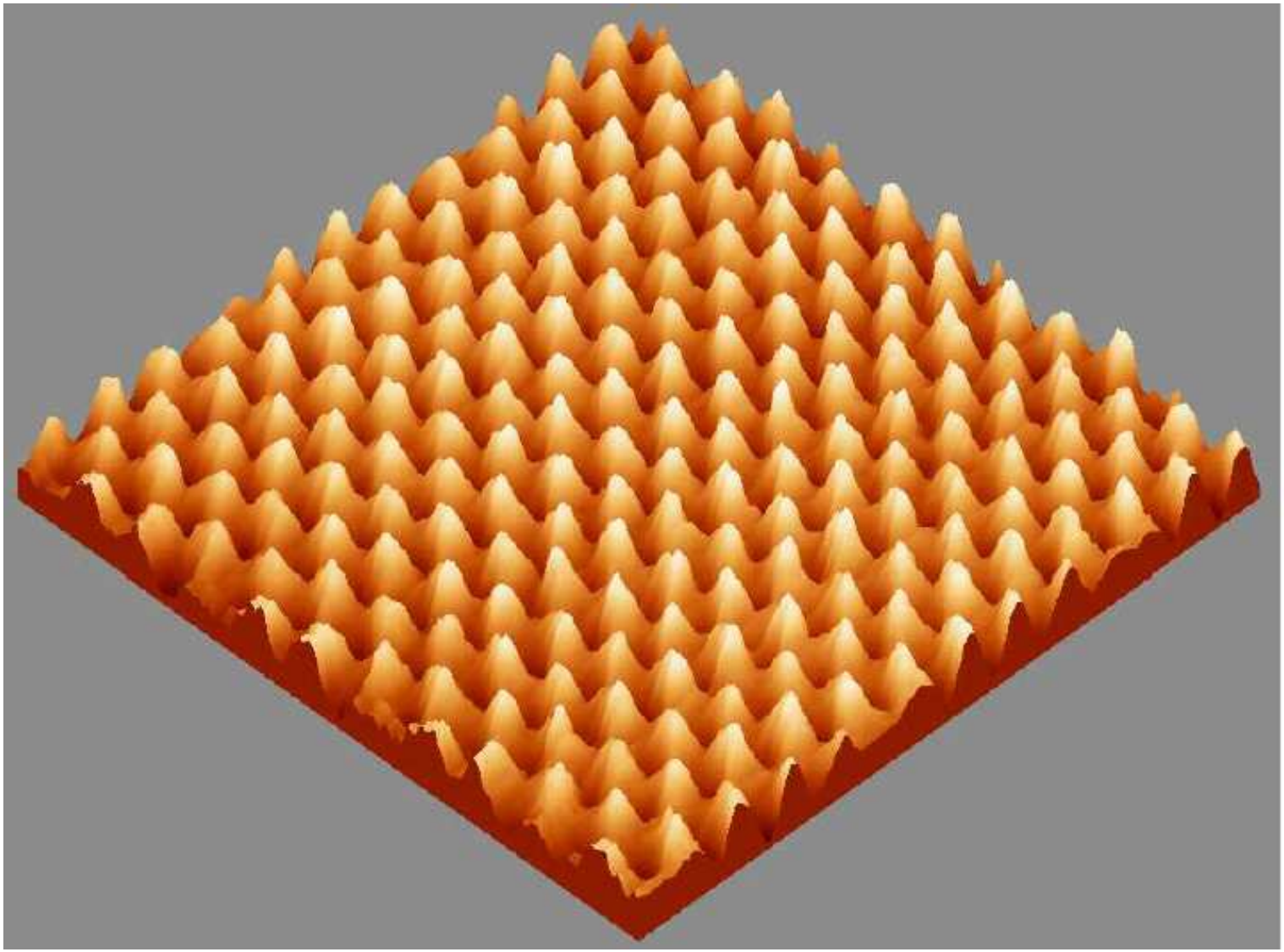

STM for a single crystal NaCl