Outline

1. Properties of individual nanoparticles
2. Scanning tunneling microscopy
3. Atomic force microscopy and Scanning probe microscopy
4. Electron microscopy **(given by Prof. Hsu)**

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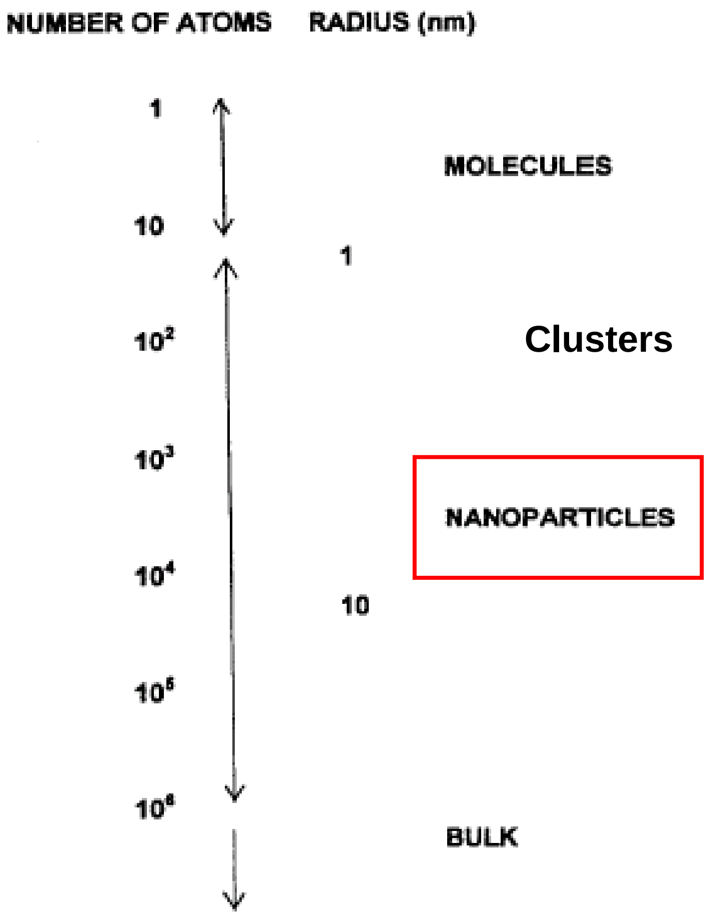
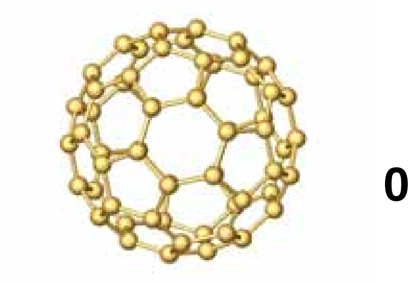
Properties of Individual Nanoparticles



1. **Very small (~1 nm to ~100 nm)-- difficult to image individual nanoparticles.**
2. **Unique physical and/or chemical properties (different from those of bulk material, electronic structure, conductivity, reactivity, melting temperature, mechanical properties, etc.) – size dependent.**
3. **Enhanced surface effects.**



C_{60}

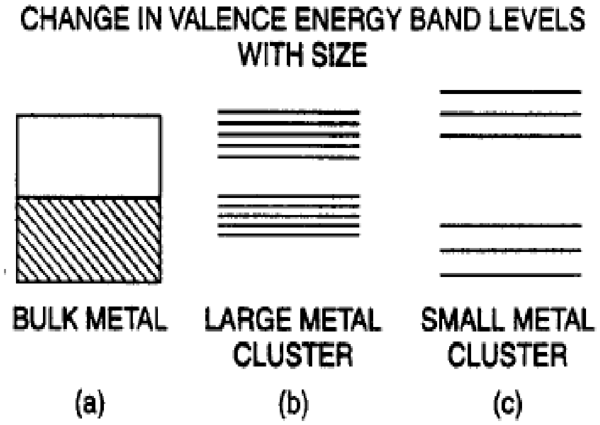
0.7 nm

Quantum Size Effects

Electronic structures of nanoparticles

1. **Discrete energy levels:** atom-like energy levels

2. **Separation of energy levels increases with decreasing particle size.**



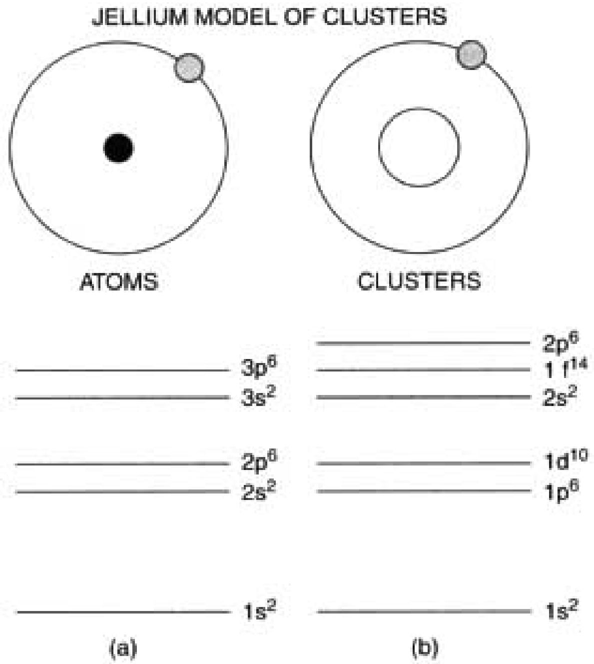
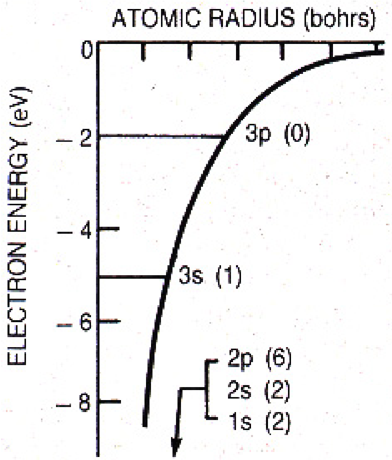
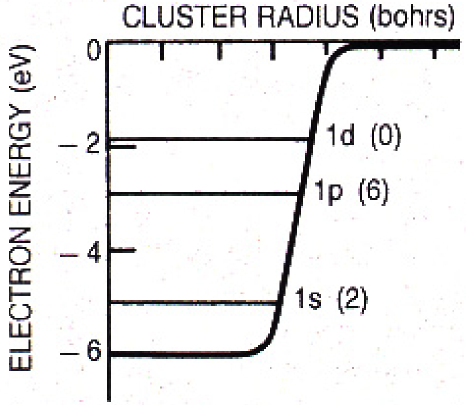


Figure 4.5. A comparison of the energy levels of the hydrogen atom and those of the jellium model of a cluster. The electronic magic numbers of the atoms are 2, 10, 18, and 36 for He, Ne, Ar, and Kr, respectively (the Kr energy levels are not shown on the figure) and 2, 18, and 40 for the clusters. [Adapted from B. K. Rao et al., *J. Cluster Sci.* **10**, 477 (1999).]





Jellium Model

The clusters are considered to be uniformly positively charged spheres filled with electrons.

Si Nanowires

Science **299**, 1874 (2003)

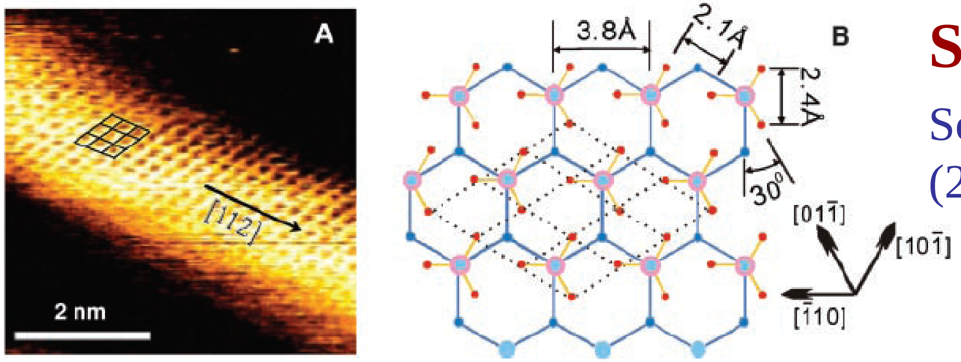
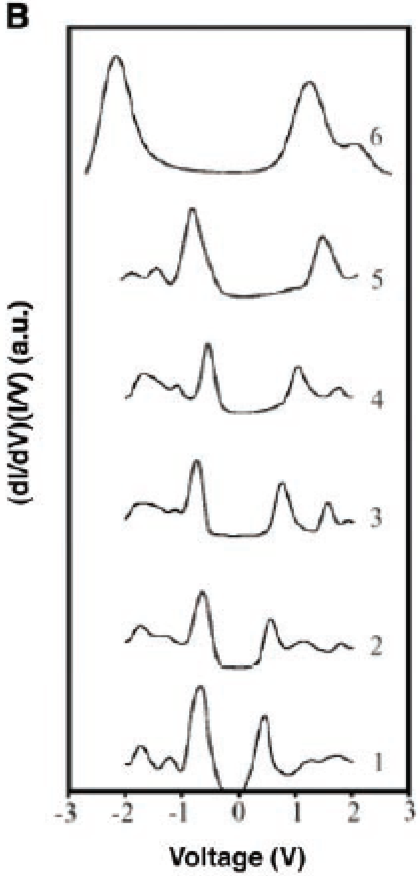
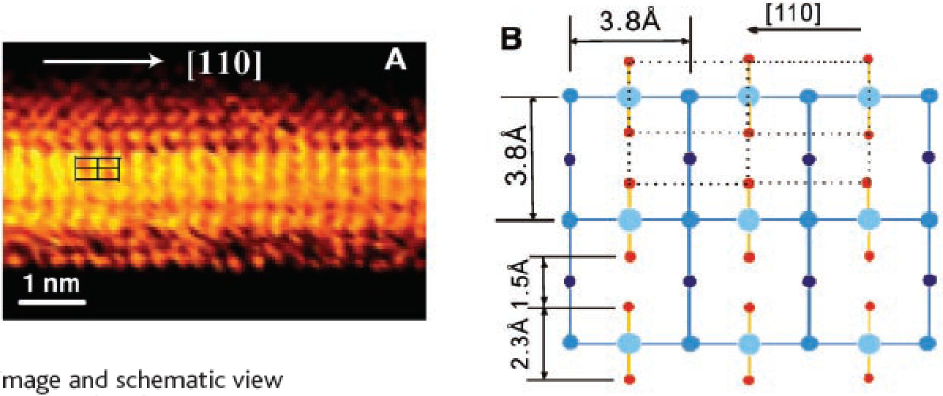


Fig. 1. STM image and schematic view of a SiNW with a Si (111) facet. Crystallographic directions are shown. (**A**) Constant-current STM image of a SiNW on a HOPG substrate. The wire's axis is along the [112] direction. (**B**) Schematic view of SiH_3 on Si (111) viewed along the [111] direction. Red and large blue circles represent the H atoms and Si atoms in the SiH_3 radical, respectively. Small blue circles represent Si (111) atoms in the layer below.





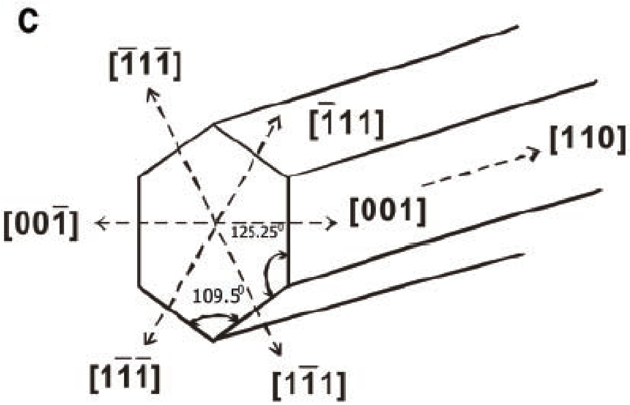
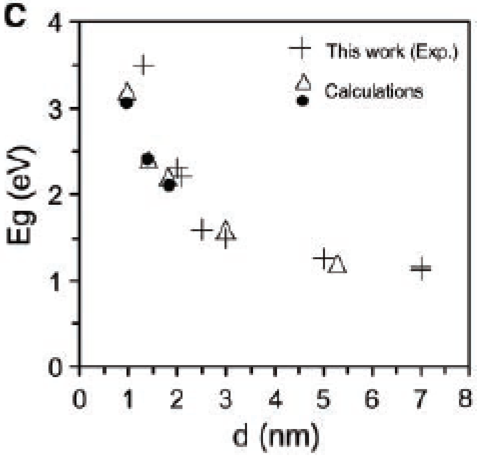


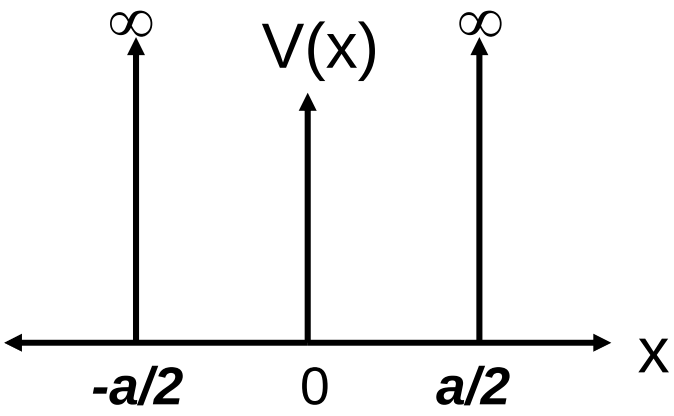
Fig. 2. STM image and schematic view of a SiNW with a Si (001) facet. Crystallographic directions are shown. (**A**) Constant-current STM image of a SiNW on a HOPG substrate. The wire's axis is along the [110] direction. (**B**) Schematic view of the dihydride phase on Si (001). Red and large blue circles represent H and Si atoms in the dihydride phase, respectively. Small blue circles correspond to Si atoms on the layers below. (**C**) Schematic view of a Si nanowire bounded by four ($\bar{1}$11)-type facets and two (001)-type facets. The wire's axis is along the [110] direction.

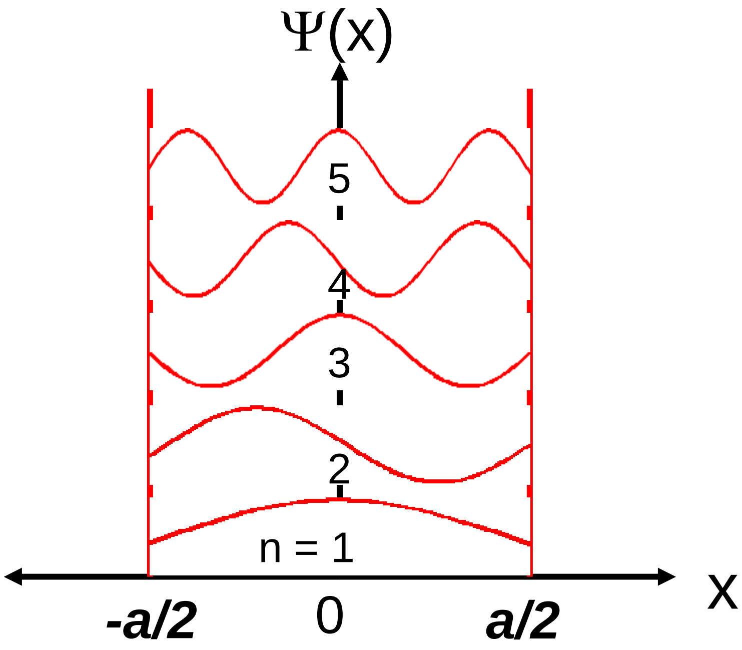


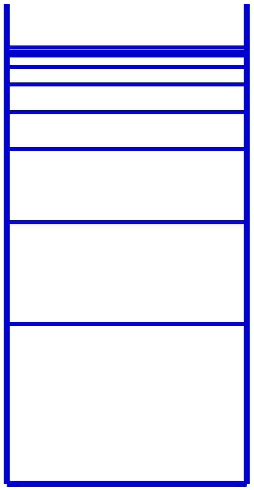
Quantum Confinement

One dimensional size effect

Particle in a box







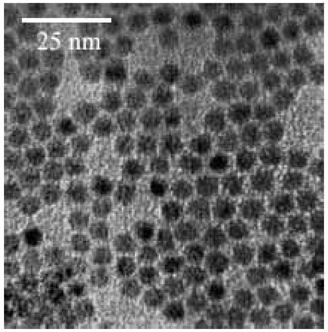
Atomic Levels

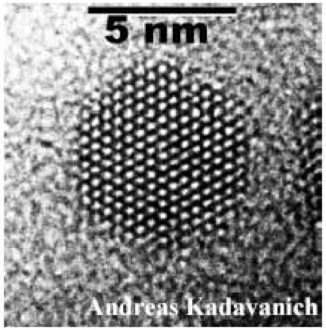
$$\Psi(x) = \begin{cases} \sin(n\pi x/a), \text{ n even} \\ \cos(n\pi x/a), \text{ n odd} \end{cases}$$

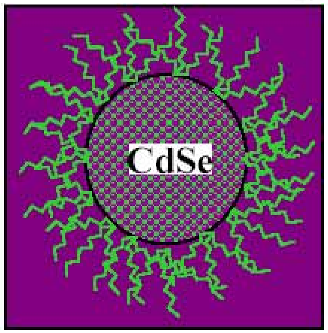
$$E = n^2\pi^2\hbar^2/2ma^2, \ n = 1,2,3\ldots$$

Optical Properties

1. The color of a material is determined by the wavelength of light that is absorbed by it.
2. The absorption occurs because electrons are induced by the photons of the incident light to make transitions between the lower-lying occupied levels and higher unoccupied energy levels of the materials.
3. Clusters of different sizes will have different electronic structures and different energy-level separations

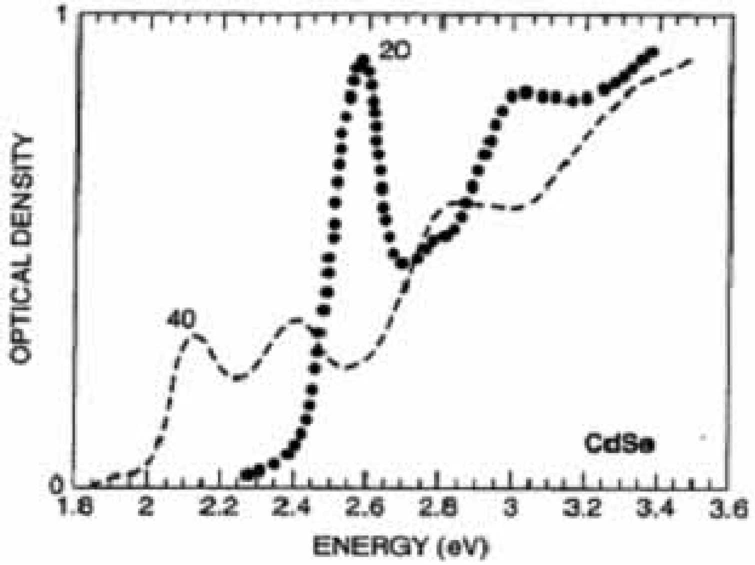




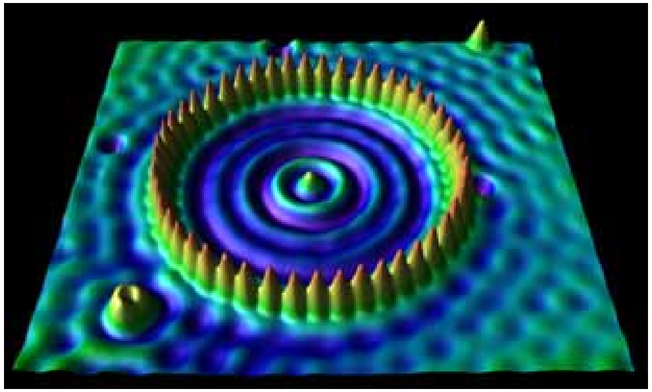


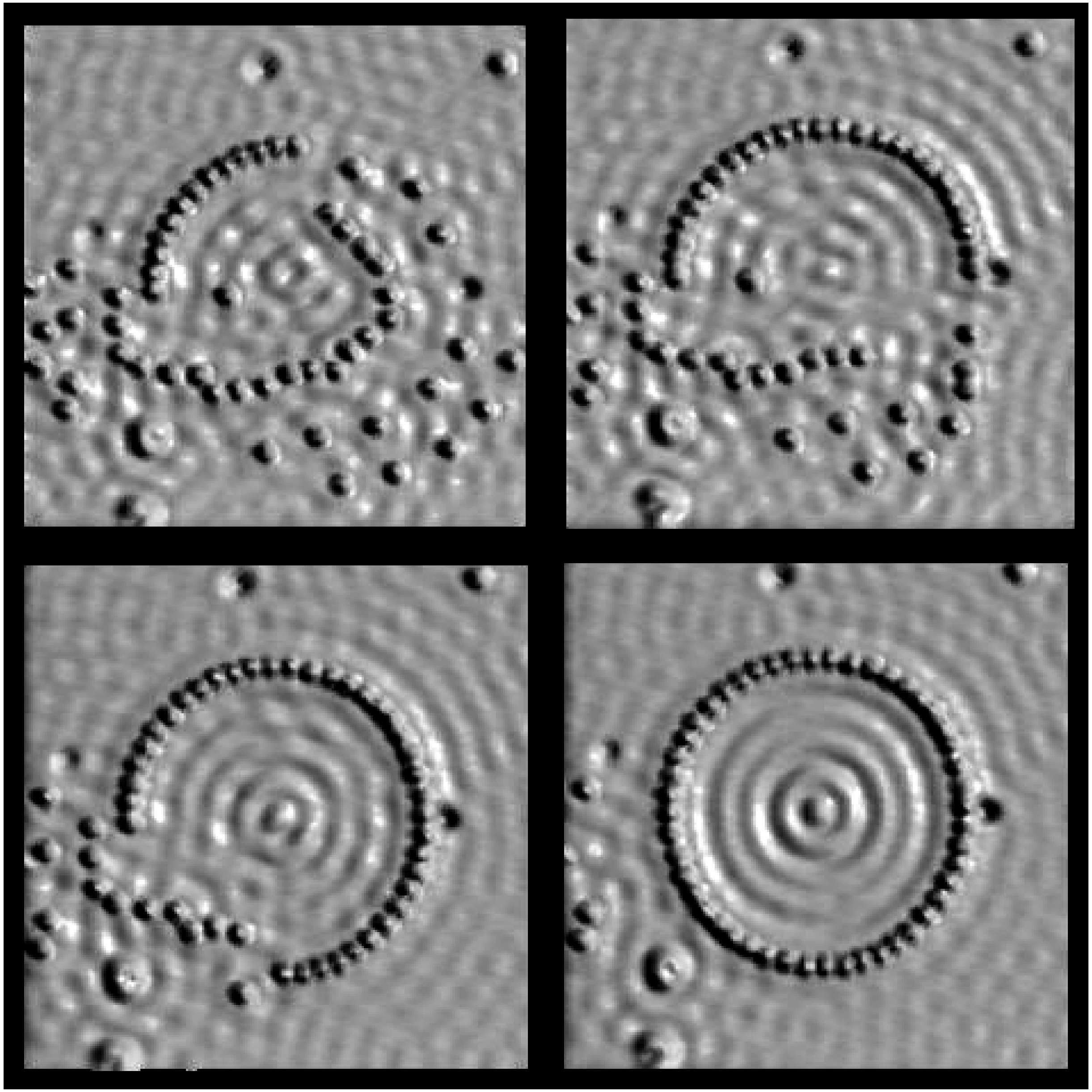
(Reproduced from Quantum Dot Co.)

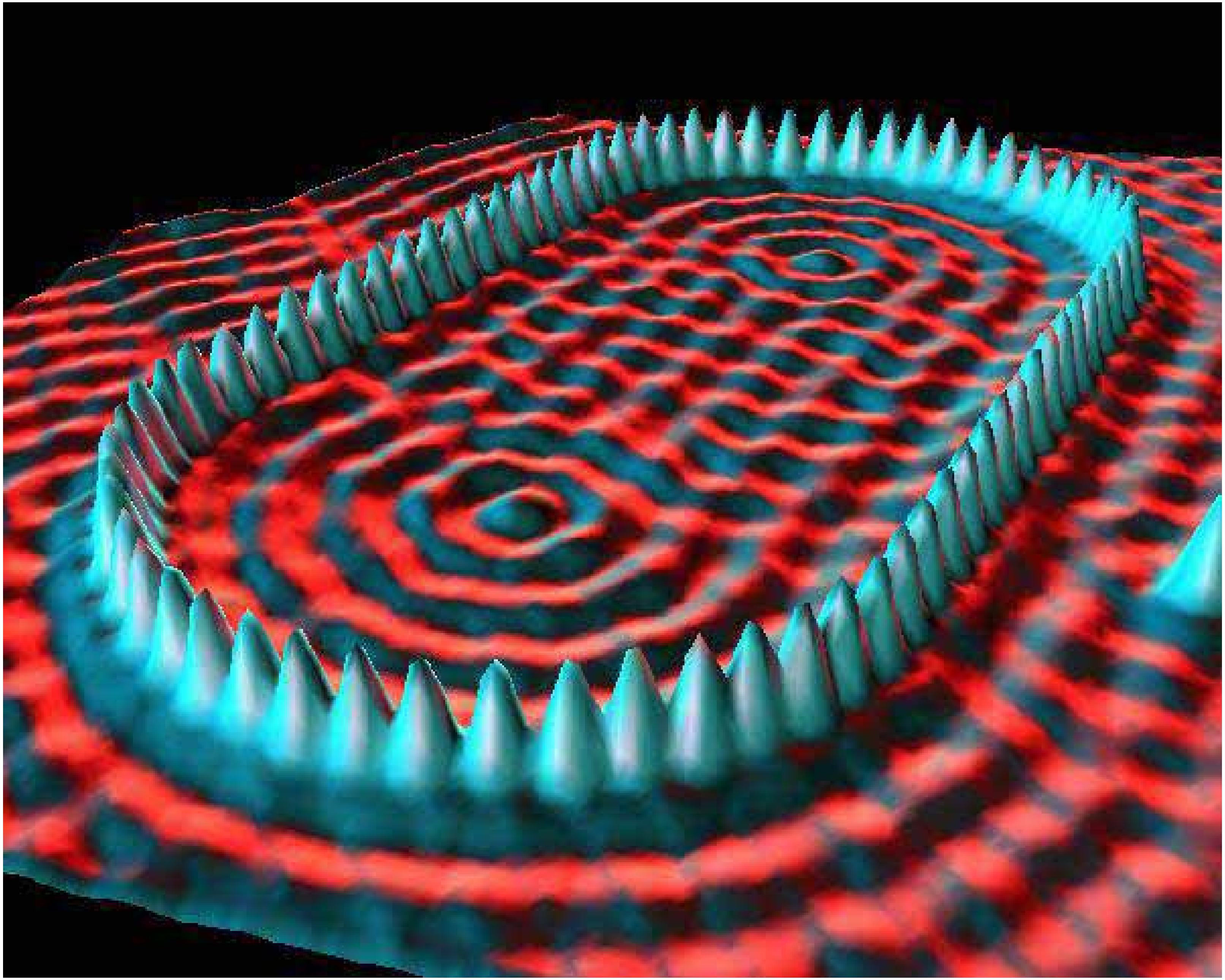
Optical absorption spectrum of CdSe for two nanoparticles having sizes 20 Å and 40 Å, respectively. [Adapted from D. M. Mittleman, *Phys. Rev.* **B49**, 14435 (1994).]

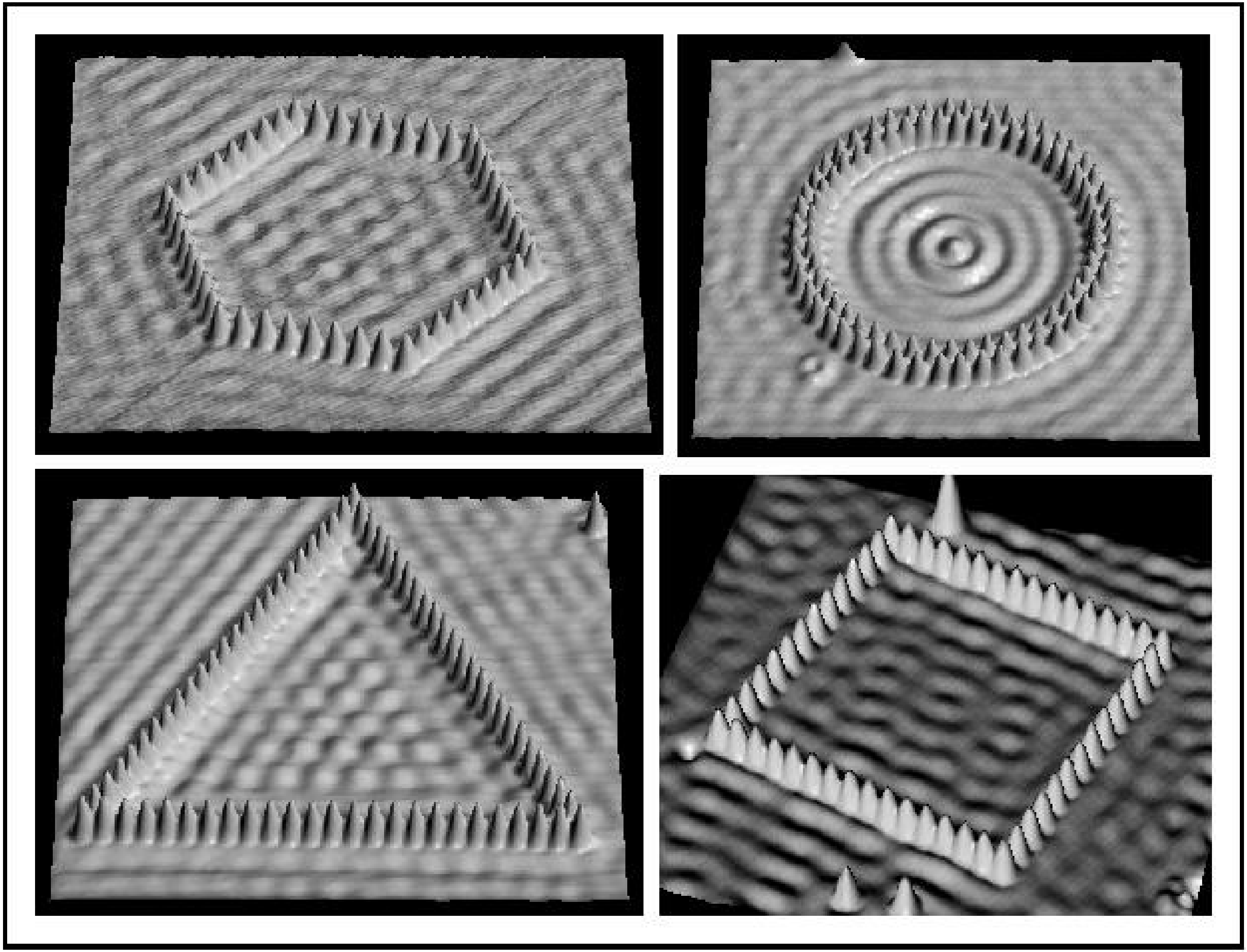


Quantum Corral 48 Fe adatoms on Cu(111) surface









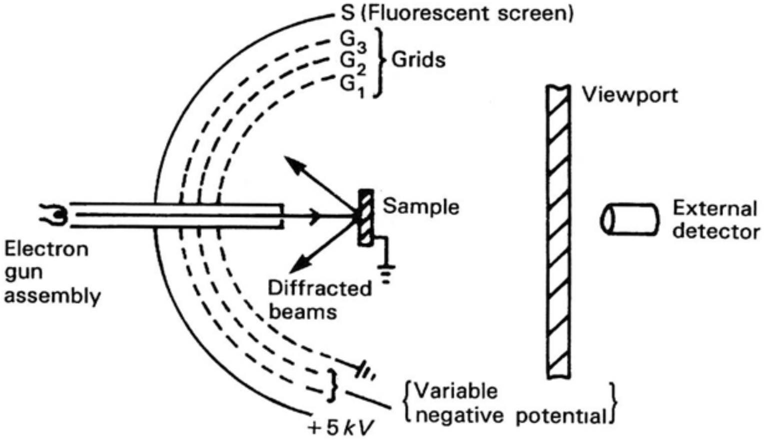
Wave Nature of Electrons

de Broglie's proposal:

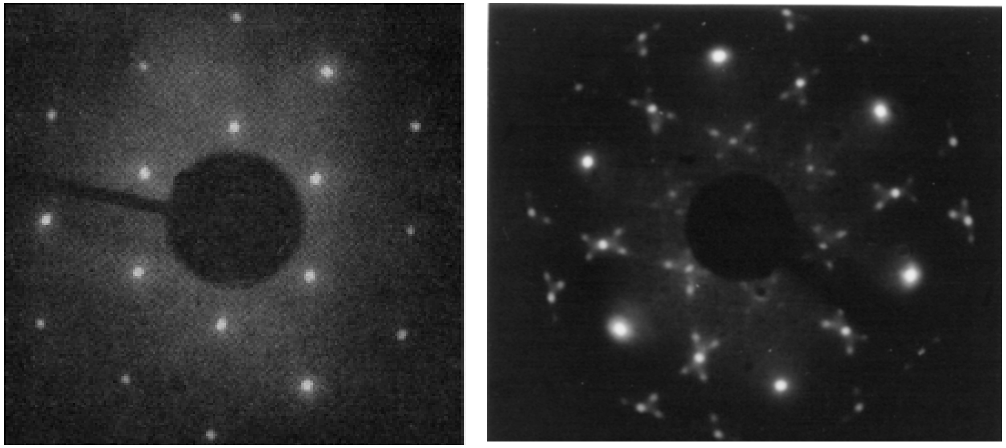
$\lambda = h/P$

For electrons:

$$\lambda\,(\text{Å}) = \sqrt{\frac{150}{E(eV)}}$$



Schematic diagram of conventional RFA-type LEED optics

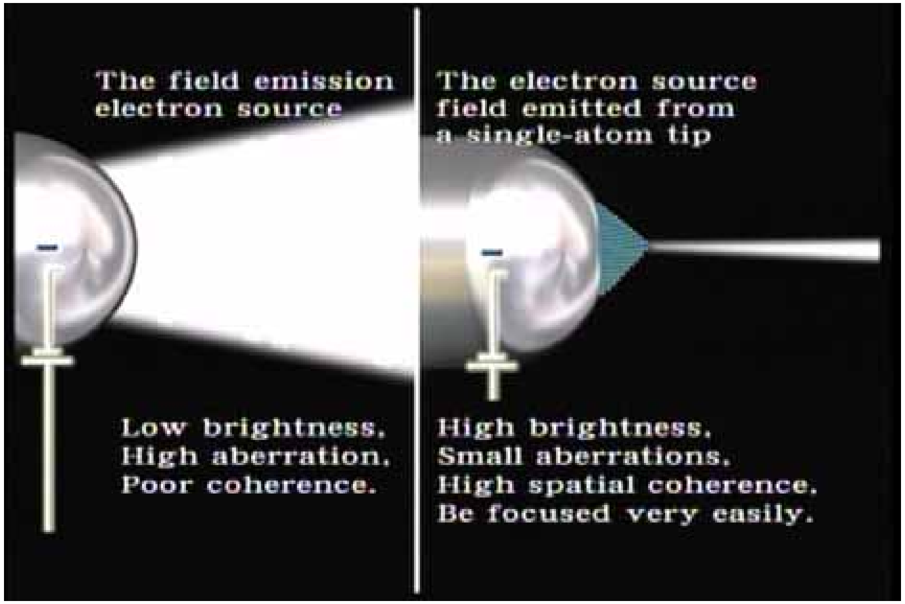


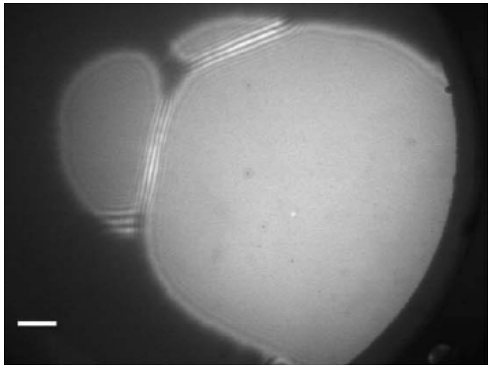
Electron diffraction patterns

Noble Metal/W(111) Pyramidal Single-Atom Tips

Traditional

Ideal electron point source

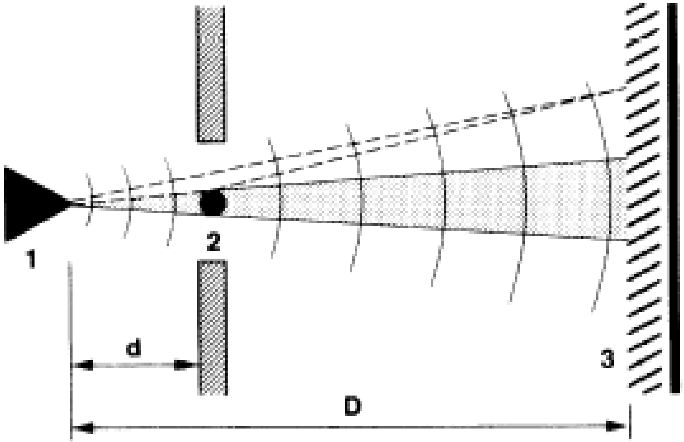


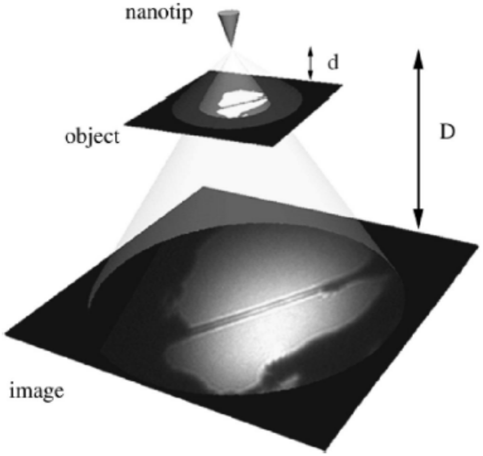


Rev. Sci. Instrum. 77, 043714 (2006)

Electron Projection Microscopes
(In-line holography)

$$M = D/d$$





Melting Temperature of Nanoparticles

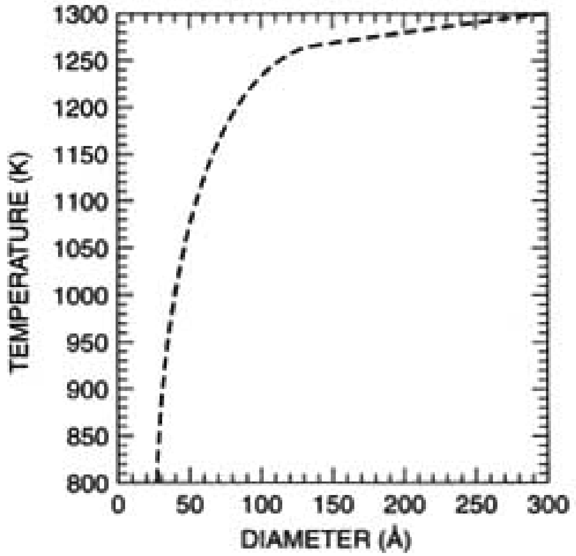
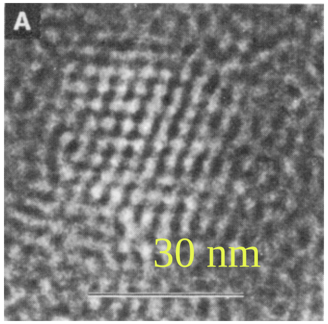
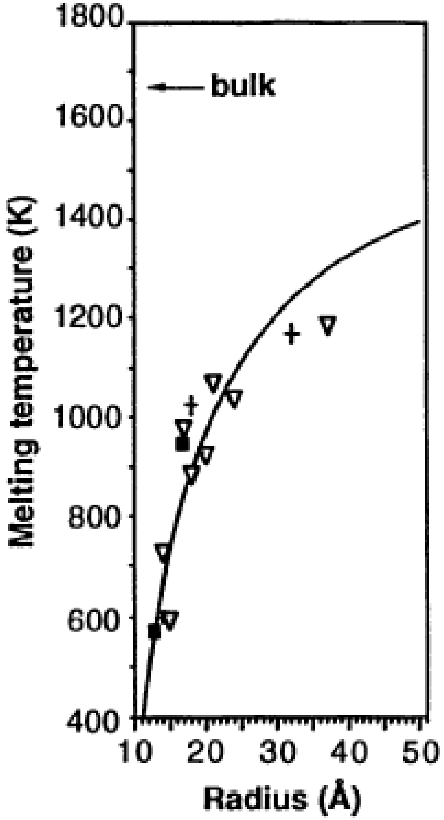


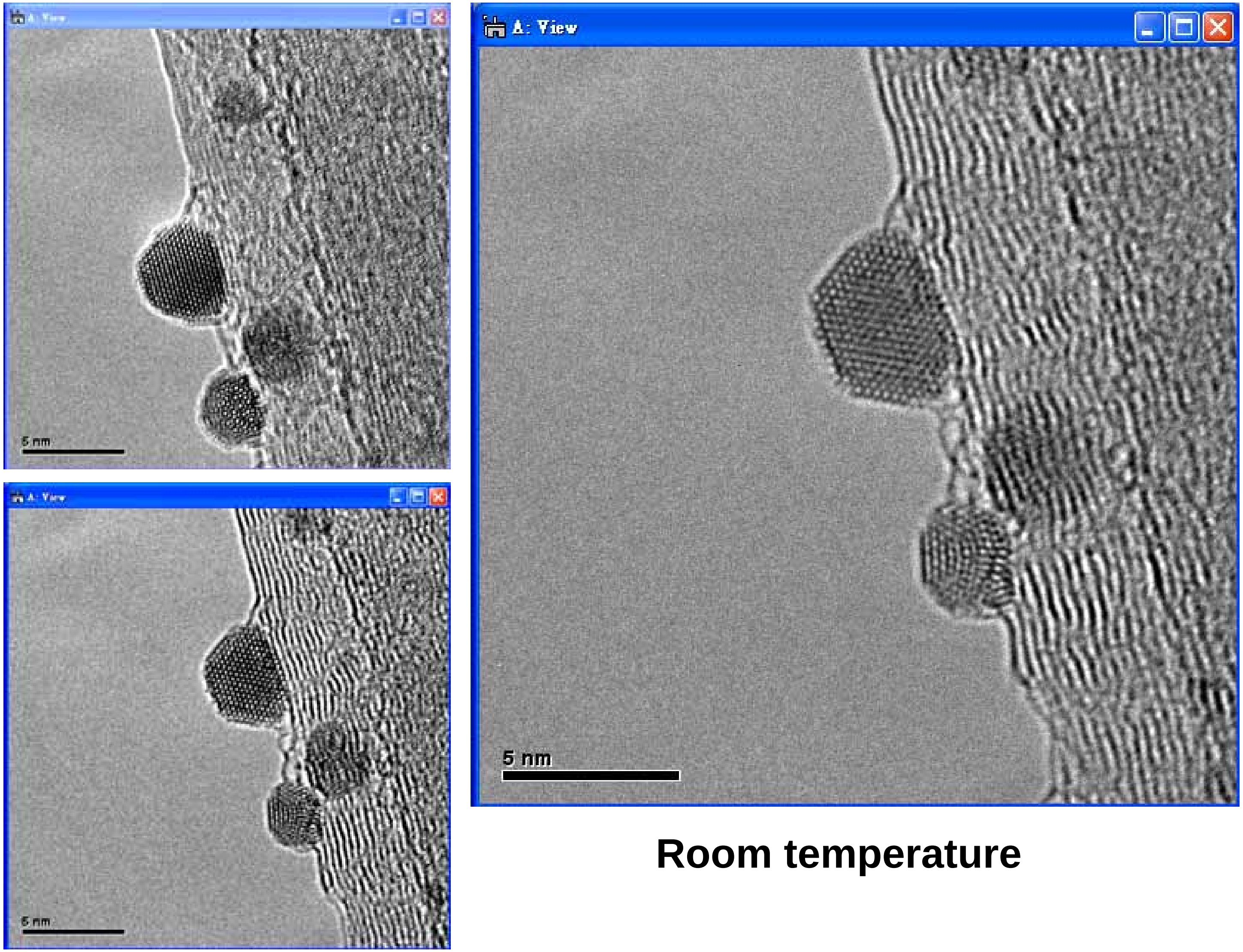
Figure 4.18. Melting temperature of gold nanoparticles versus particle diameter (10 Å = 1 nm). [Adapted from J. P. Borel et al., *Surface Sci.* **106**, I (1981).]

3D CdS nanocrystal





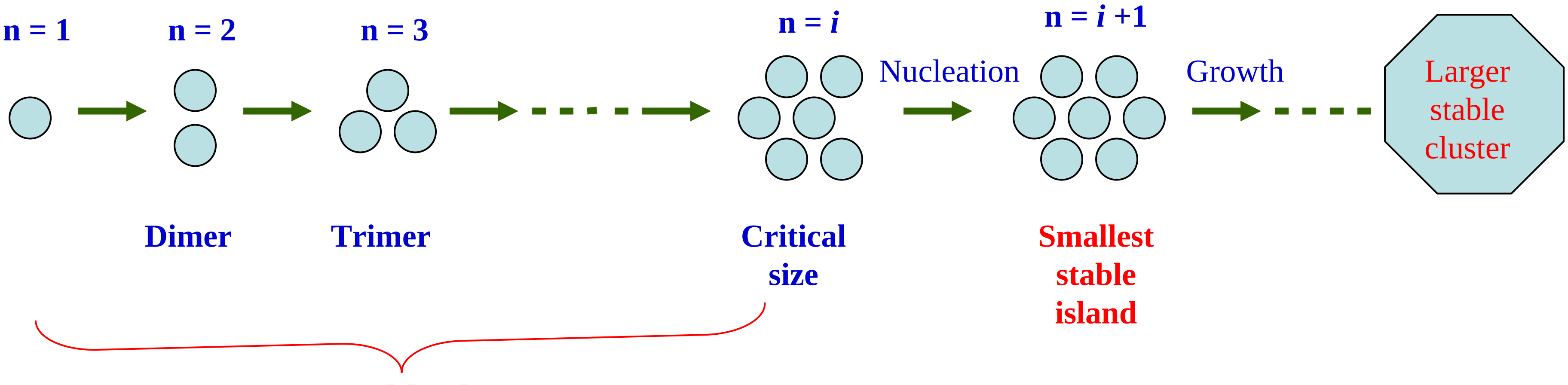
Goldstein, Echer, Alivisatos, Science **256**, 1425 (1992).



Room temperature

Stability of Nanoparticles

Traditional Picture of Nucleation and Growth



n = 1

n = 2

n = 3

n = *i*

Nucleation

n = *i* +1

Growth

Larger stable cluster

Dimer

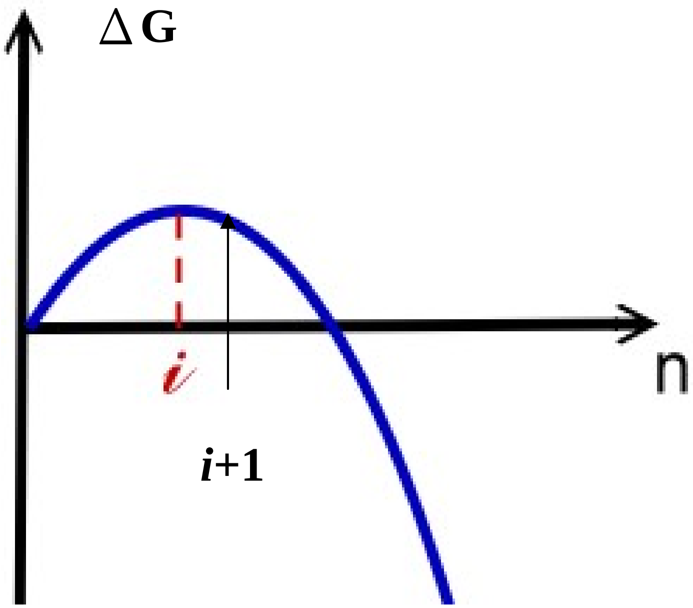
Trimer

Critical size

Smallest stable island

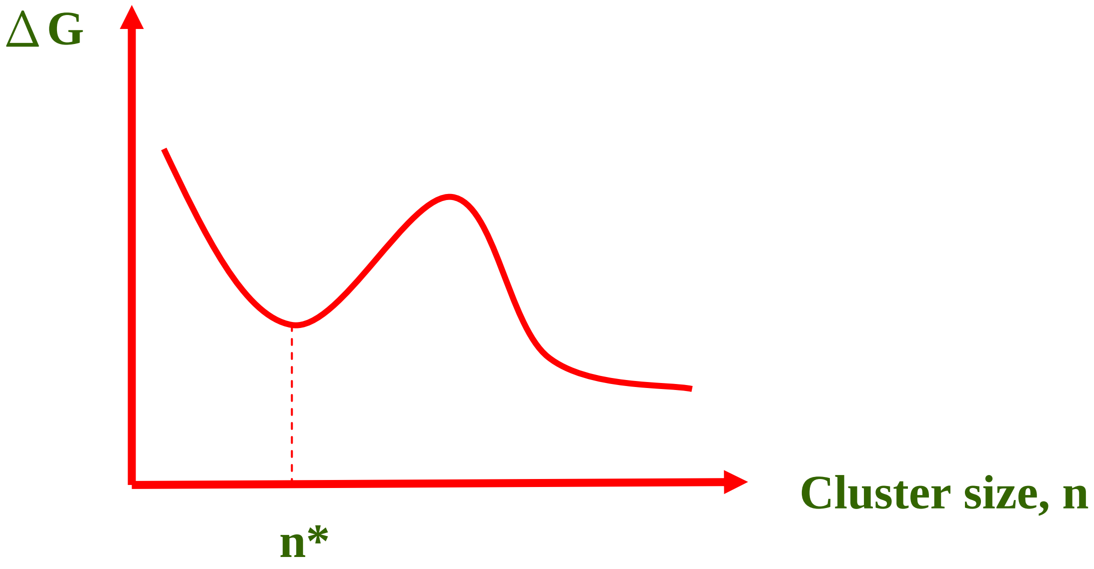
Unstable clusters

J. A. Venables et al., Rep. Prog. Phys. 47, 399 (1984).



Magic Clusters

1. Magic clusters exhibit enhanced stability relative to clusters either slightly larger or smaller than the magic size. Thus, it is energetically unfavorable for magic clusters to grow in size by adding one or a few atoms.
2. Traditional nucleation theories: The cluster with a size of *i**+1 is "stable" in a sense that they tend to grow larger by incorporating more atoms. That also means they have a higher free energy than that of clusters of larger sizes. They are not really stable!



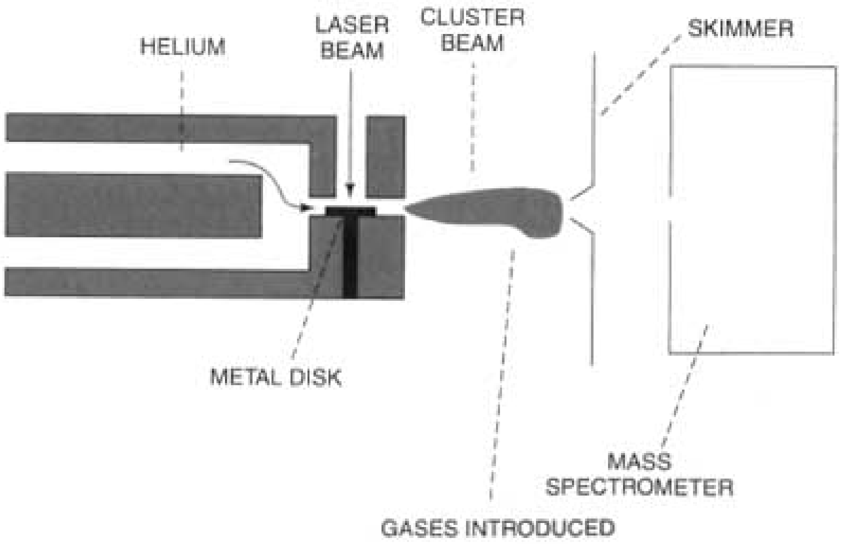


Figure 4.2. Apparatus to make metal nanoparticles by laser induced evaporation of atoms from the surface of a metal. Various gases such as oxygen can be introduced to study the chemical interaction of the nanoparticles and the gases. (With permission from F. J. Owens

1. **Laser evaporation**
2. **Metal atoms are swept away by a burst of He and passed through an orifice into a vacuum where the expansion of the gas causes cooling and formation of clusters of the metal atoms.**
3. **These clusters are ionized and passed into a mass spectrometer.**

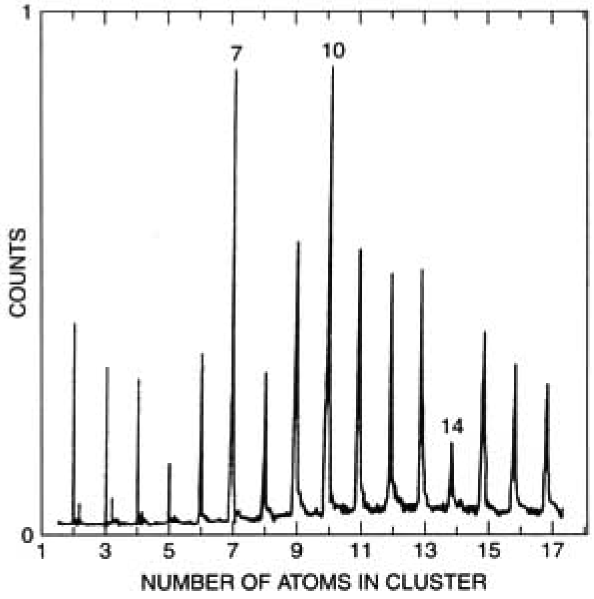


Figure 4.3. Mass spectrum of Pb clusters. [Adapted from M. A. Duncan and D. H. Rouvray, *Sci. Am.* 110 (Dec. 1989).]

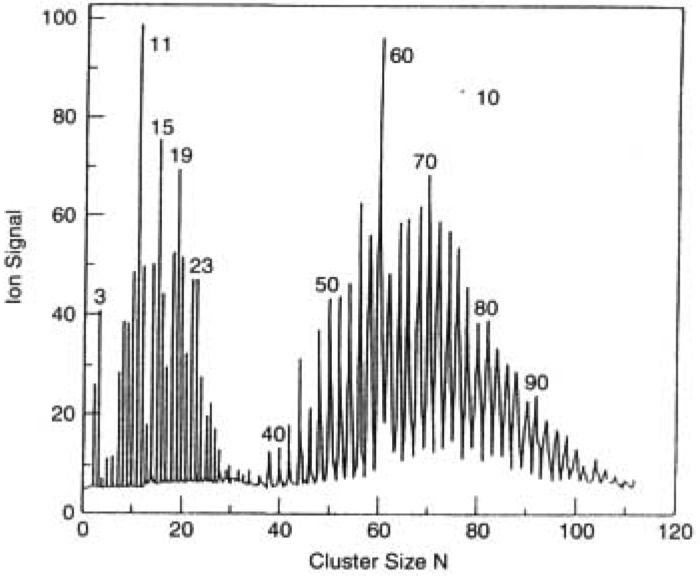


Figure 5.3. Mass spectrum of carbon clusters. The C_{60} and C_{70} fullerene peaks are evident. (With permission from S. Sugano and H. Koizuni, in *Microcluster Physics*, Springer-Verlag, Heidelberg, 1998.)

Mass Analyzer

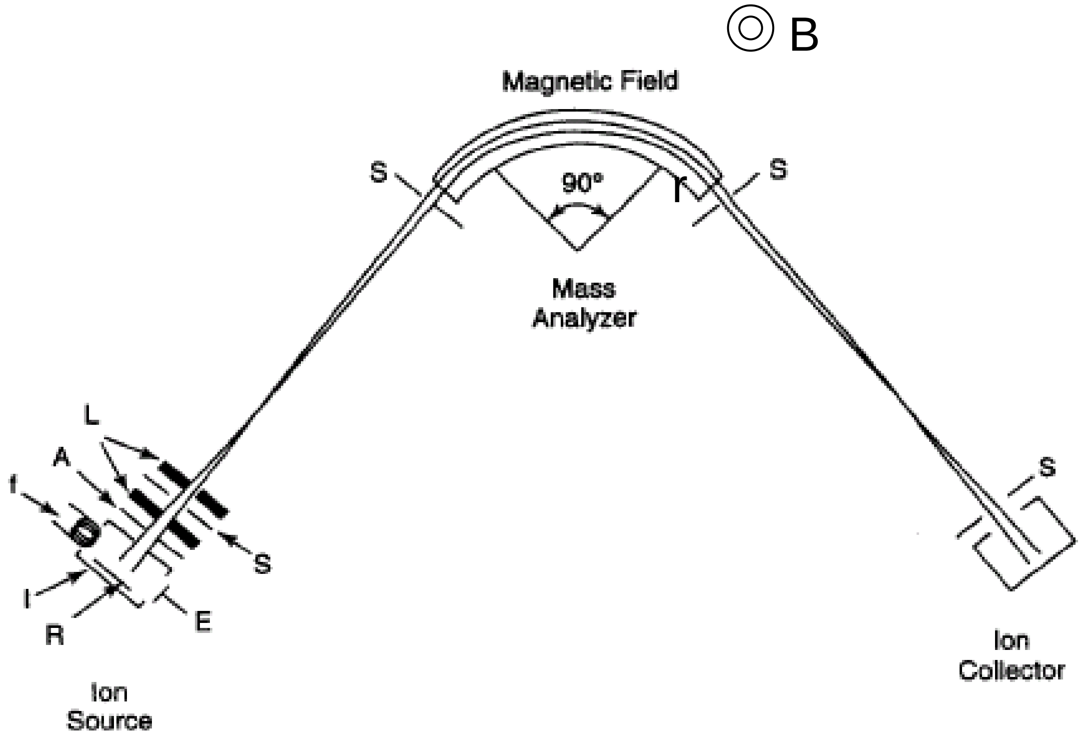


Figure 3.8. Sketch of a mass spectrometer utilizing a 90° magnetic field mass analyzer, showing details of the ion source: A—accelerator or extractor plate, E—electron trap, f—filament, I—ionization chamber, L—focusing lenses, R—repeller, S—slits. The magnetic field of the mass analyzer is perpendicular to the plane of the page.

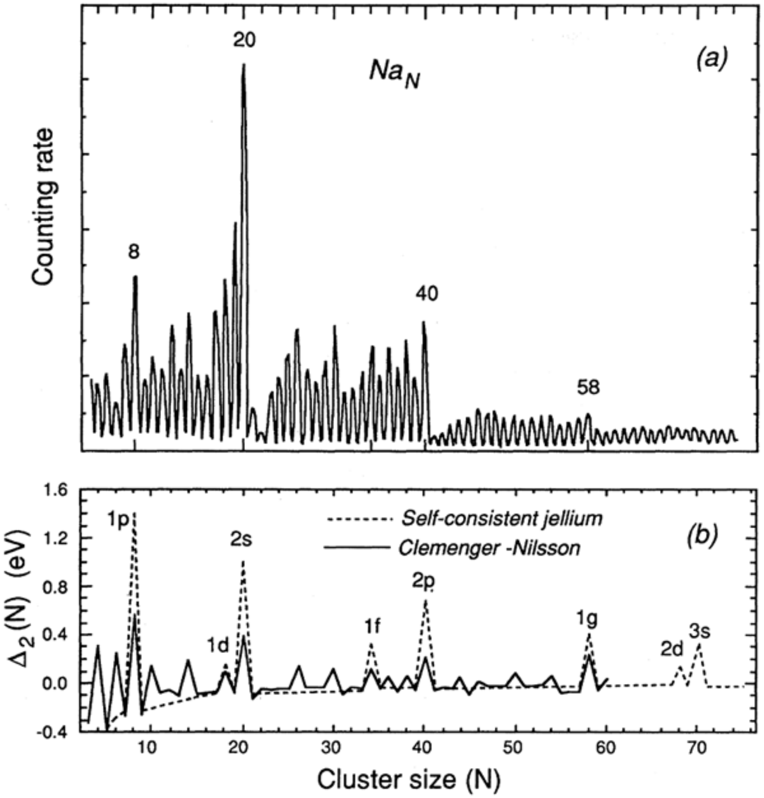
$$qV = \frac{1}{2} mv^2$$

$$F = qvB = mv^2/r$$

$$m/q = \frac{1}{2} B^2r^2/V$$

Electronic Magic Numbers

Clusters in which the number of valence electrons matches the spherical shell closing numbers are produced more abundantly.



Reviews of Modern Physics, Vol. 65, No. 3, July 1993

closed electronic shell

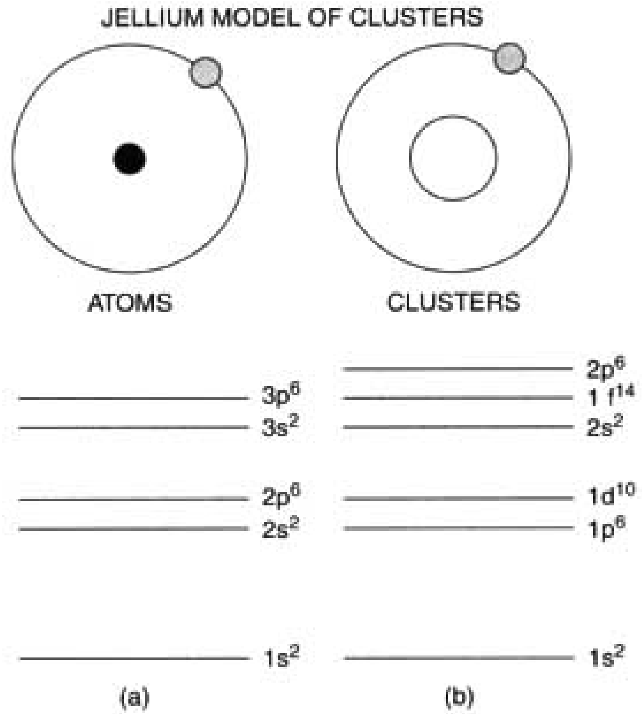
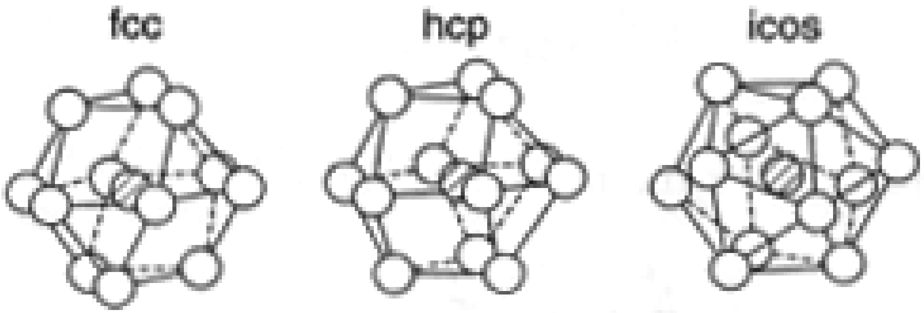


Figure 4.5. A comparison of the energy levels of the hydrogen atom and those of the jellium model of a cluster. The electronic magic numbers of the atoms are 2, 10, 18, and 36 for He, Ne, Ar, and Kr, respectively (the Kr energy levels are not shown on the figure) and 2, 18, and 40 for the clusters. [Adapted from B. K. Rao et al., *J. Cluster Sci.* **10**, 477 (1999).]

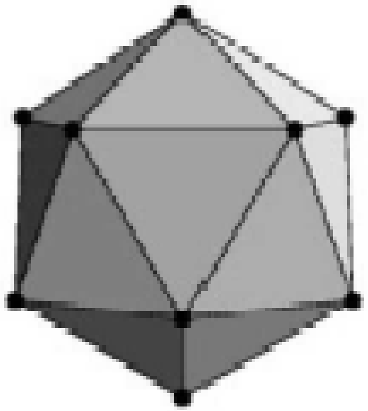
The clusters are considered to be uniformly positively charged spheres filled with electrons.

Structural Magic Numbers

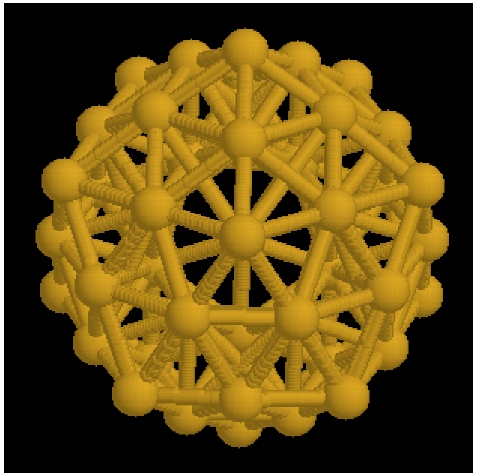
Al_{13}



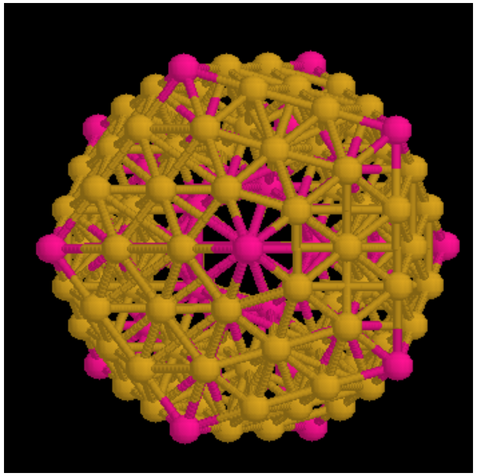
Mackay Icosahedra



P = 1



P = 2



P = 3

20 fcc(111) faces

$$N = 1 + \Sigma\ (10p^2 + 2)$$

Xe Magic Clusters

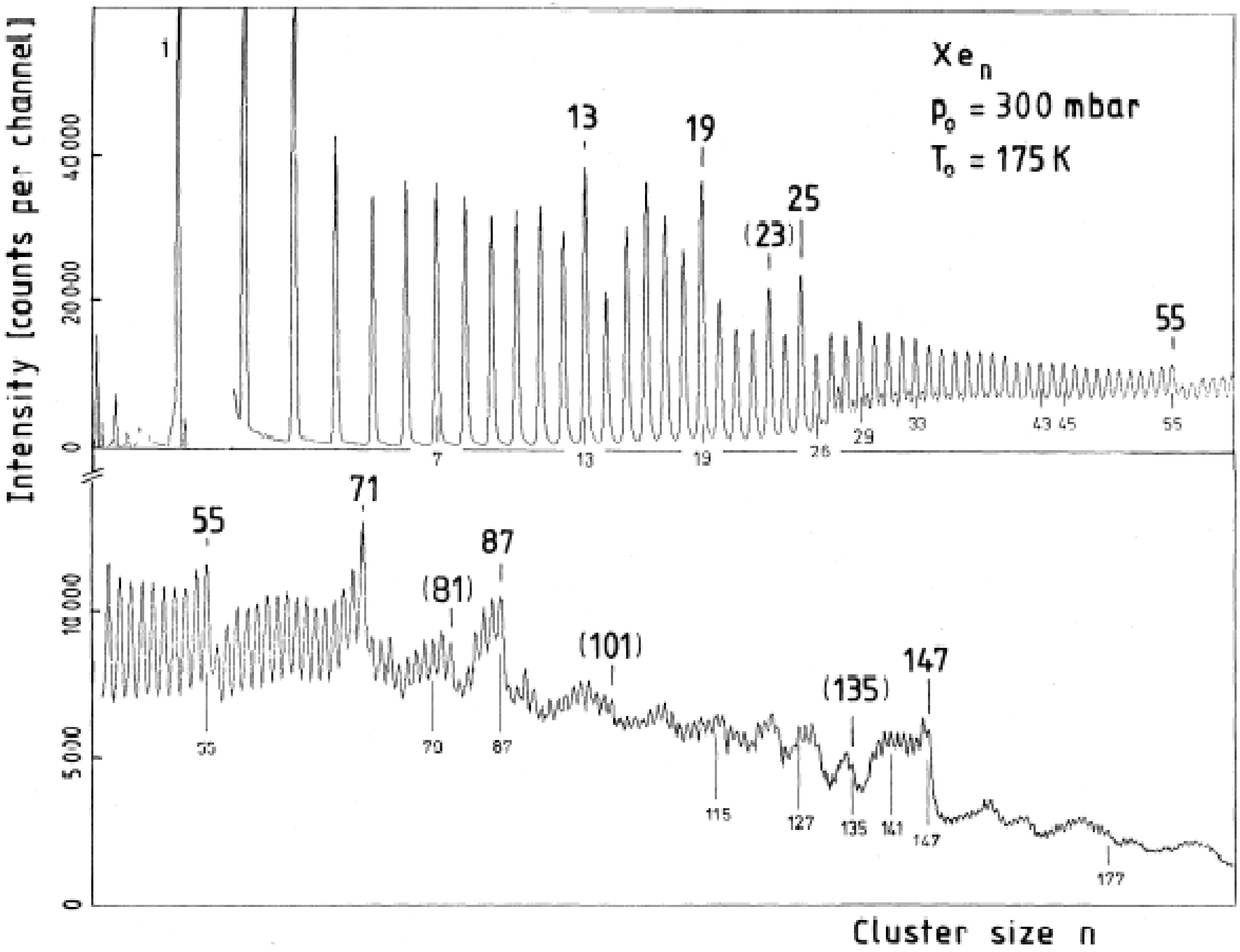


FIG. 1. Mass spectrum of xenon clusters. Observed magic numbers are marked in boldface; brackets are used for numbers with less pronounced effects. Numbers below the curve indicate predictions or distinguished sphere packings.

Fullerene

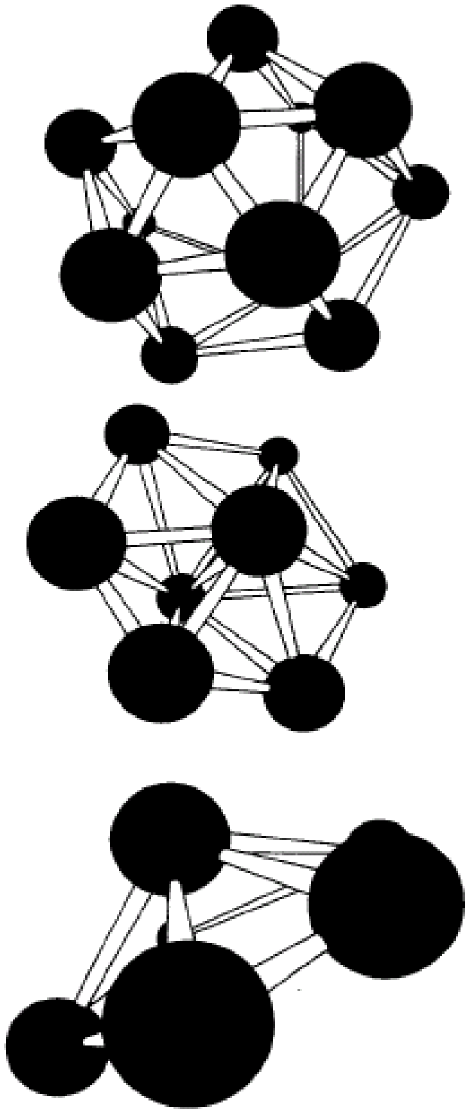
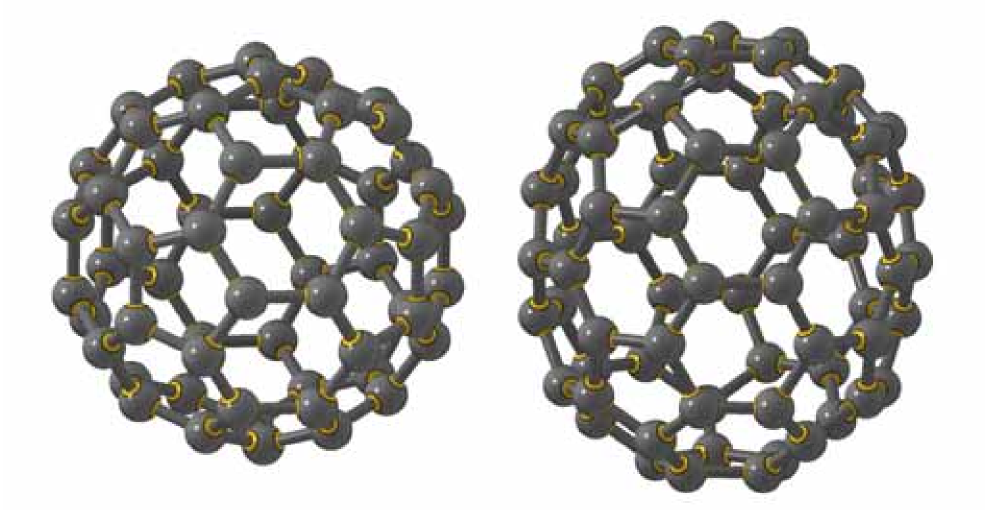


Figure 4.8. Illustration of some calculated structures of small boron nanoparticles. (F. J. Owens, unpublished.)



C_{60} C_{70}

Reactivity of Nanoclusters

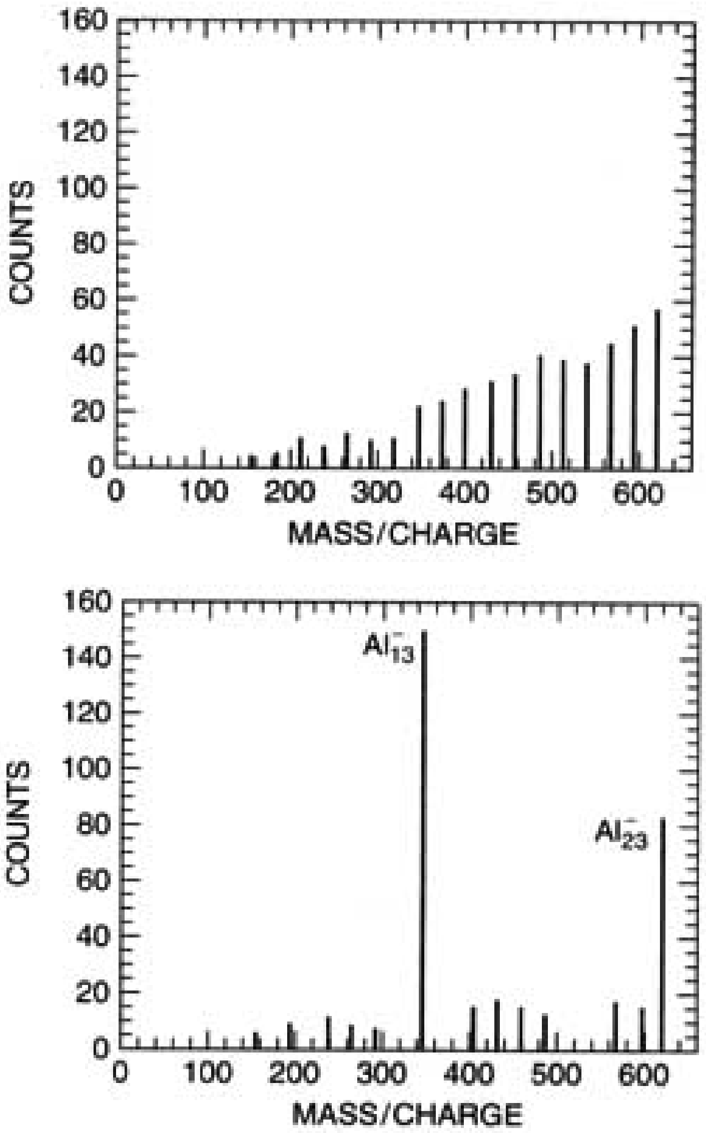
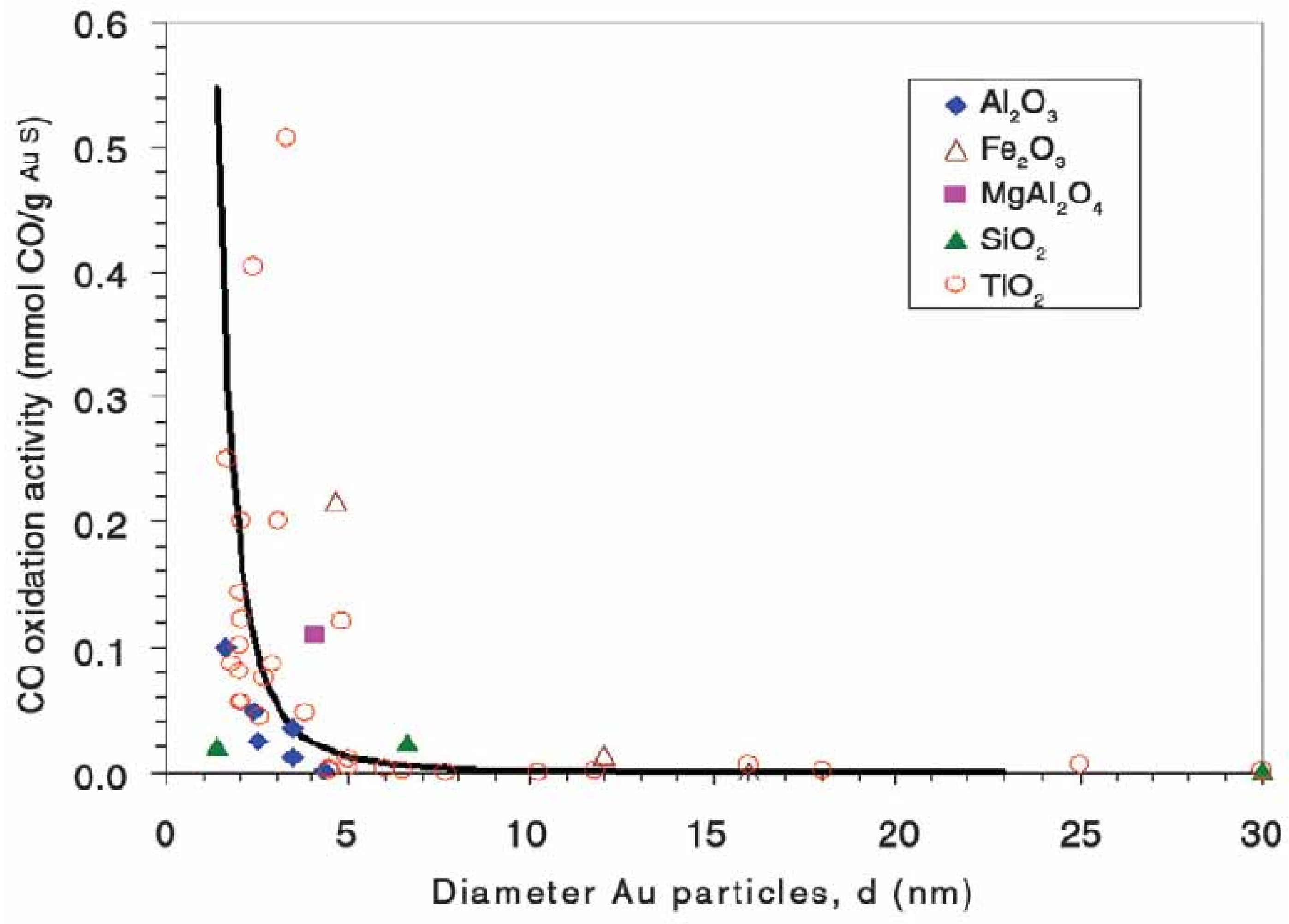


Figure 4.13. Mass spectrum of Al nanoparticles before (top) and after (bottom) exposure to oxygen gas. [Adapted from R. E. Leuchtner et al., *J. Chem. Phys.*, **91**, 2753 (1989).]

Catalytic Activities of Au Nanoparticles

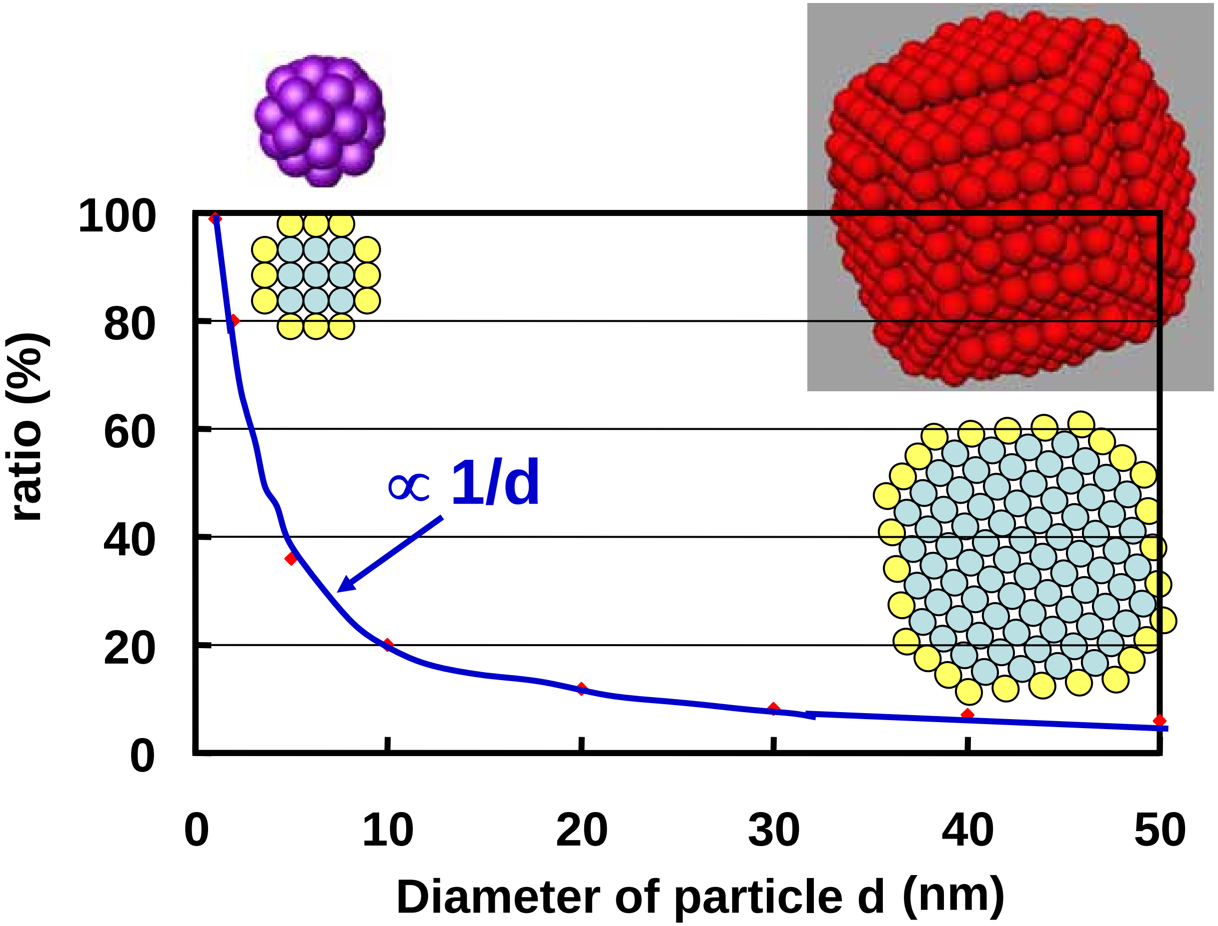


Au is usually viewed as an inert metal, but surprisingly it has been found that Au nanoparticles less than 3–5 nm in diameter are catalytically active for several chemical reactions.

Nano Today
AUGUST 2007

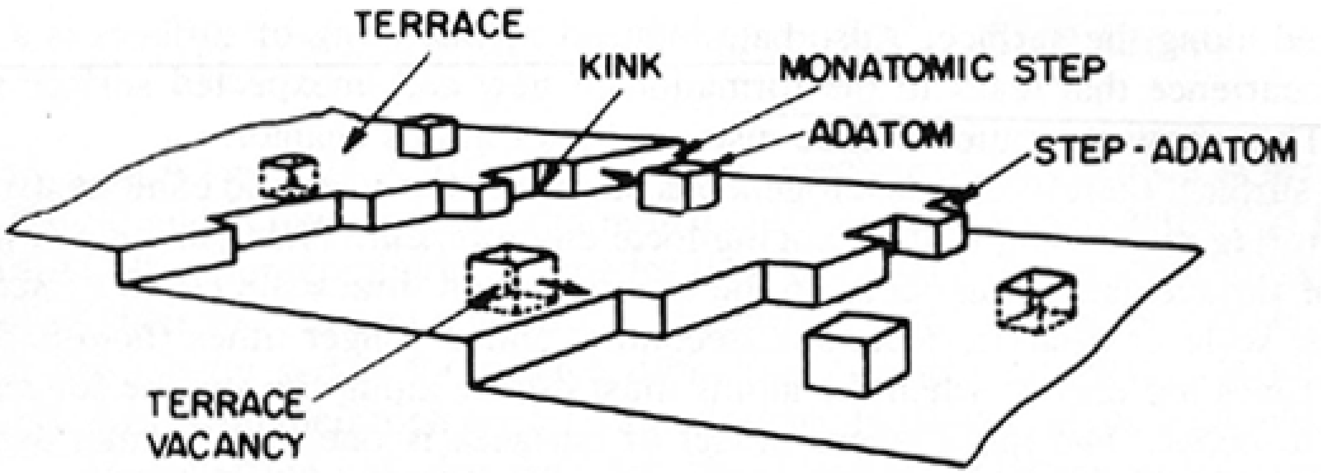
Catalytic activities for CO oxidation at 273 K as a function of Au particle size

Ratio of surface atoms



The Structure of Surface

Atoms on a surface of a solid have an environment that differs markedly from that of atoms in the bulk of the solid. They have fewer neighbors than do bulk atoms.



Model of a heterogeneous solid surface depicting different surface sites. These sites are distinguishable by their number of nearest neighbors.

On clean surface, two important structure changes can occur.

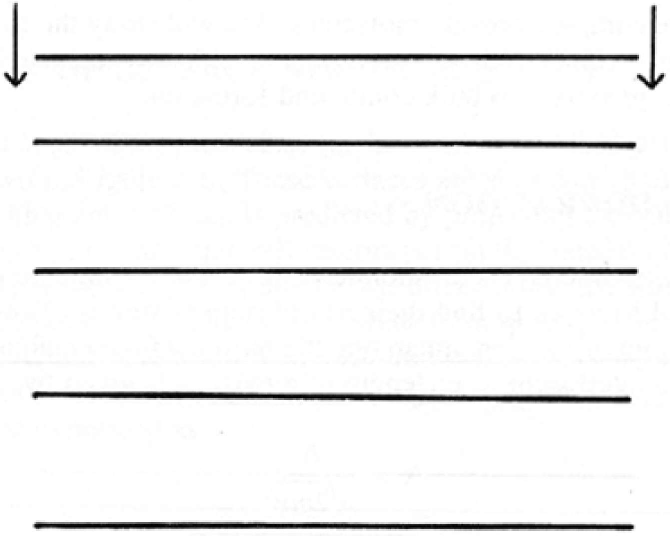
1.Bond-length contraction or relaxation

2.Reconstruction

Bond-length Contraction or Relaxation

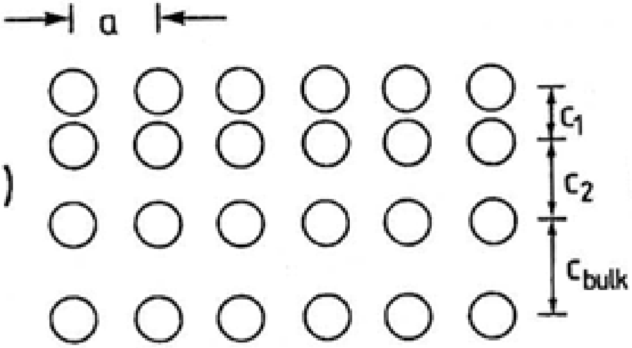
1. In vacuum, virtually all surfaces relax. The spacing between the first and second atomic layers is significantly reduced from the spacing characterizing the bulk.

2. For a close-packed metal with a less close-packed surface, the interlayer spacing between the topmost and the second atomic layer is smaller than the bulk spacing. The perturbation caused by this surface relaxation propagates a few layers into the bulk. In fact, there is often a compensating expansion between the second and the third metal layer (on the order of 1%), accompanied by a small but detectable change in the next layer.



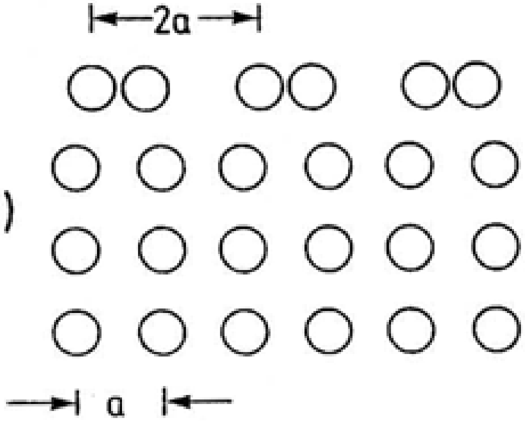
Schematic representation of the contraction in interlayer spacing usually observed at clean solid surfaces.

a)



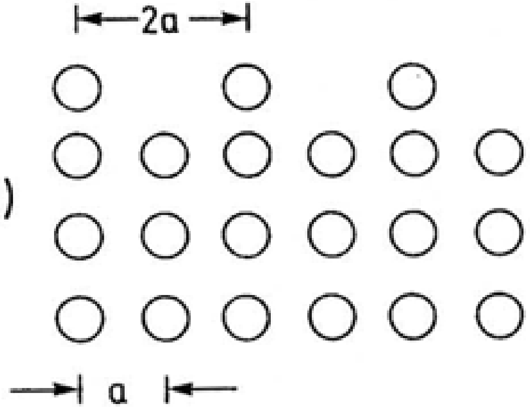
Relaxation

b)



Reconstruction

c)



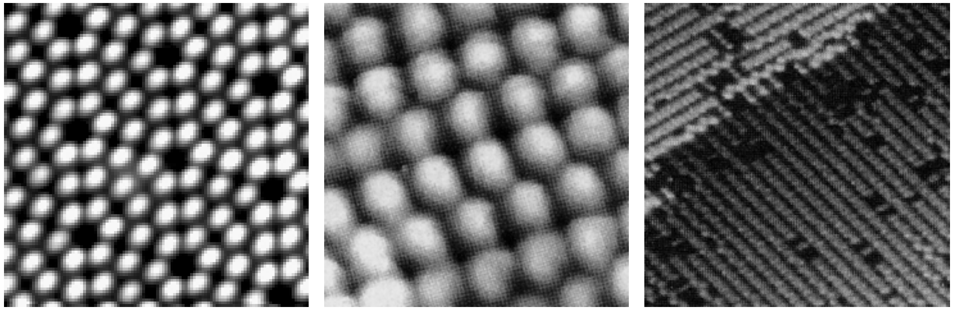
Missing row

reconstruction

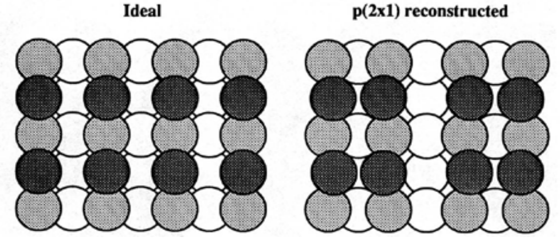
Reconstruction

The surface can assume an atomic structure that differs fundamentally from the structure one would expect if the bulk structure terminated abruptly at the surface.

For semiconductor surfaces, which are covalently bonded, the dangling bonds created at the surface cannot easily be satisfied except through more drastic rearrangements of these atoms. Example: Si(111)-7×7, Ge(111)-c(2×8), Si(001)-(2×1).

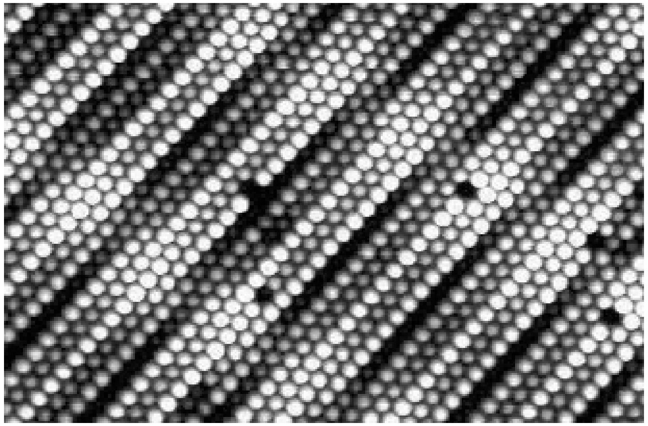


Si(001)

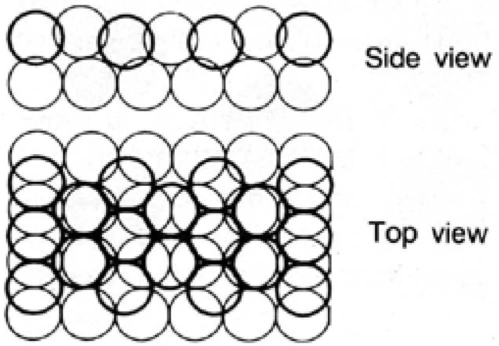


Many metal surfaces also reconstruct. Examples: Ir(100), Pt(100), Au(100)
Hexagonally close-packed surface layer on square lattice.

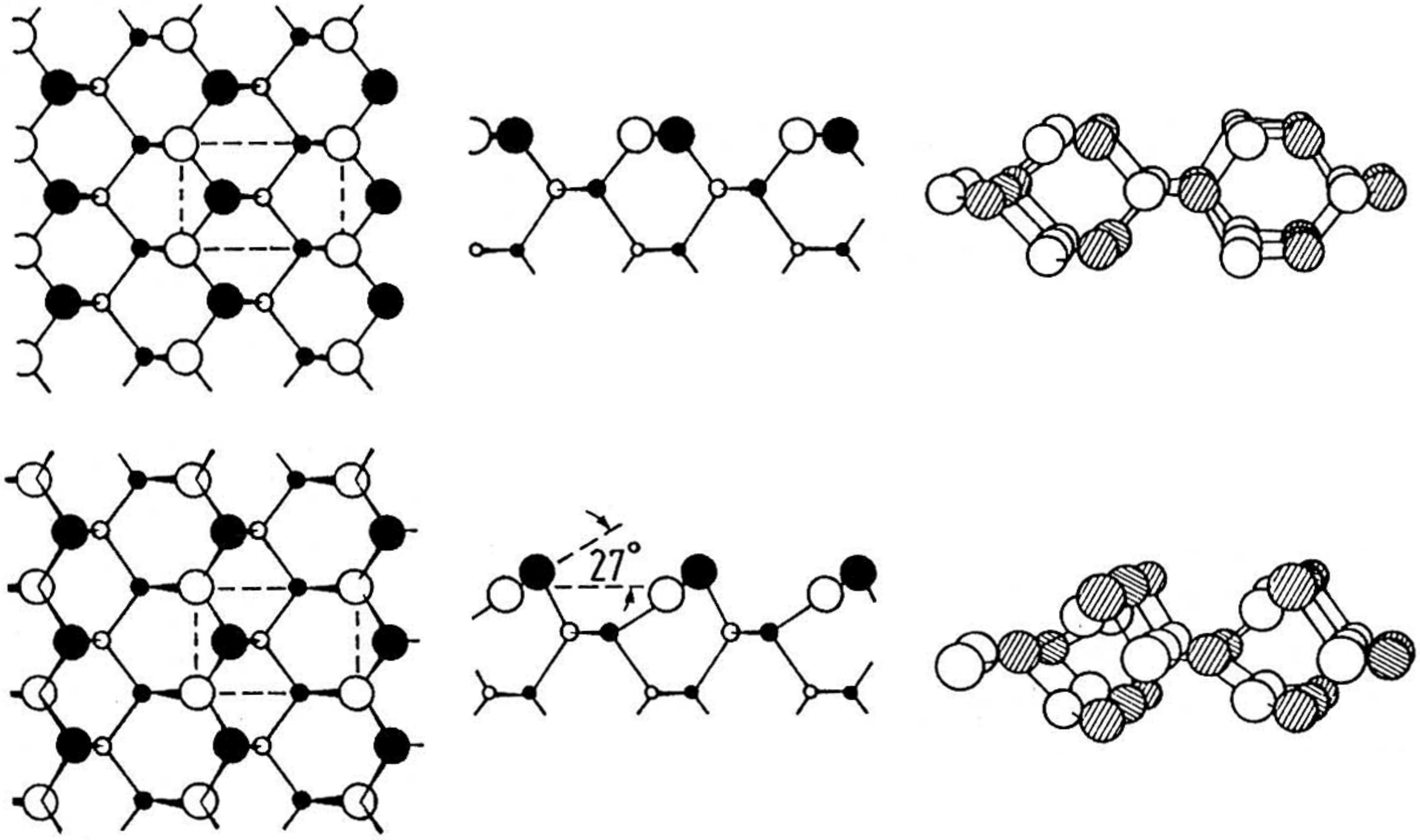
Pt(100)



Ir(100)-(1x5)



GaAs(110)-(1x1)



Top view

Side view

Sphere model (side view)

Non-reconstructed

Relaxed

Open circles designate Ga atoms and *shaded circles* As.

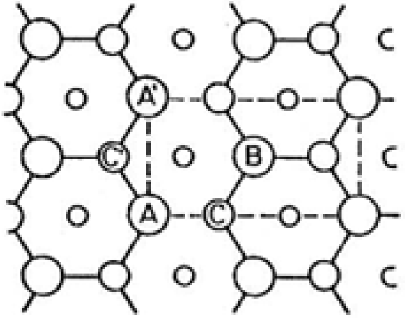
Si(111)-(2x1)

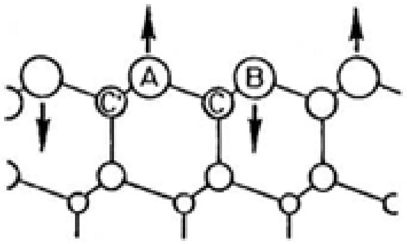
Top view

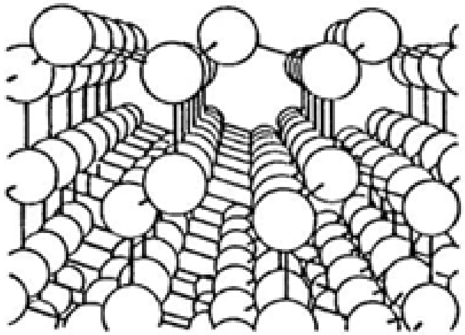
Side view

Sphere model (side view)

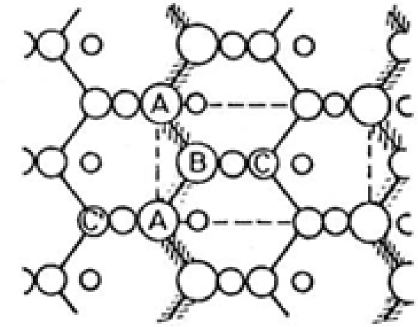
Non-reconstructed

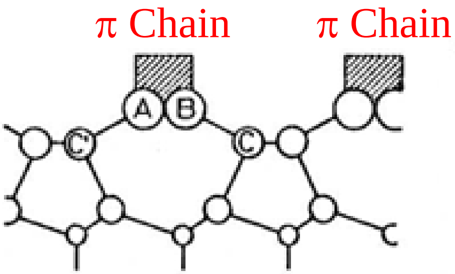


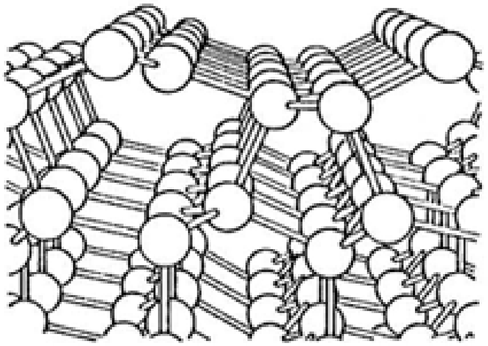




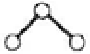
π Chain model

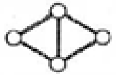


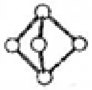


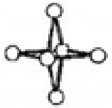


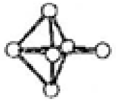
Lowest Energy Geometries proposed for the Si_n ($n \leq 11$) neutrals in the literature


n=3, C_{2v}

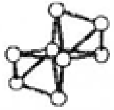

n=4, D_{2h}

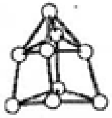

n=5, D_{3h}

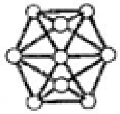

n=6, D_{4h}

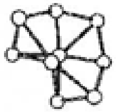

n=6, C_{2v}

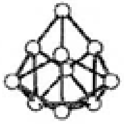

n=7, D_{5h}

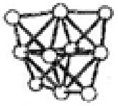

n=8, C_{2h}

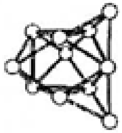

n=9, C_{2v}(I)

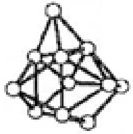

n=9, C_{2v}(II)

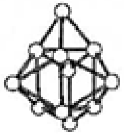

n=9, C_s

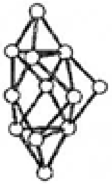

n=10, C_{3v}

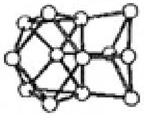

n=10, T_d

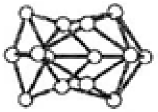

n=11, C_{2v}

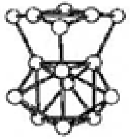

n=11, C_s (II)

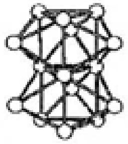

n=11, C_s (I)

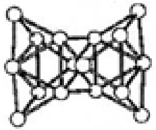

n=12, C_{2v}

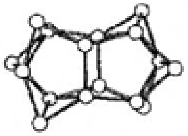

n=13, C_s

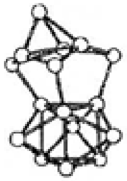

n=14, C_s

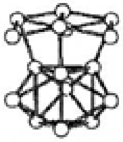

n=15, C_{3v}

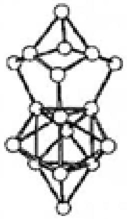

n=15, D_{3h}

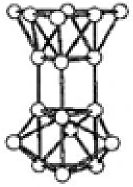

n=16, C_{2h} (I)

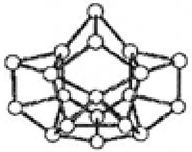

n=16, C_{2h} (II)

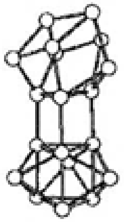

n=16, C_s

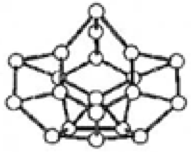

n=16, C_{3v}

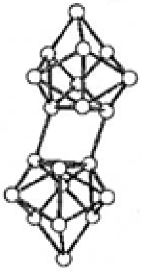

n=17, C_{3v}


n=18, C_{3v}


n=19, C_{2v}

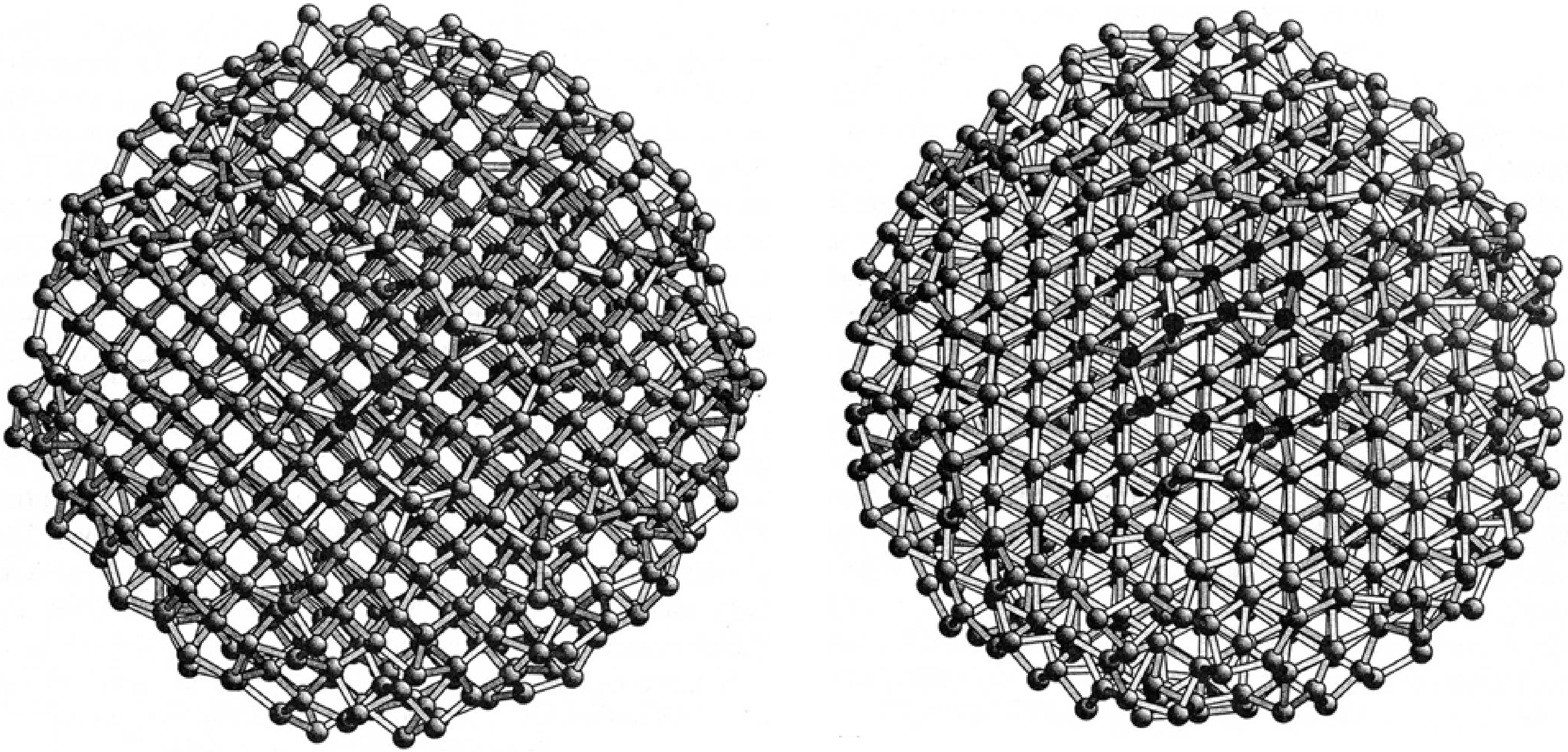

n=19, C_s


n=20, C_s


n=20, C_2

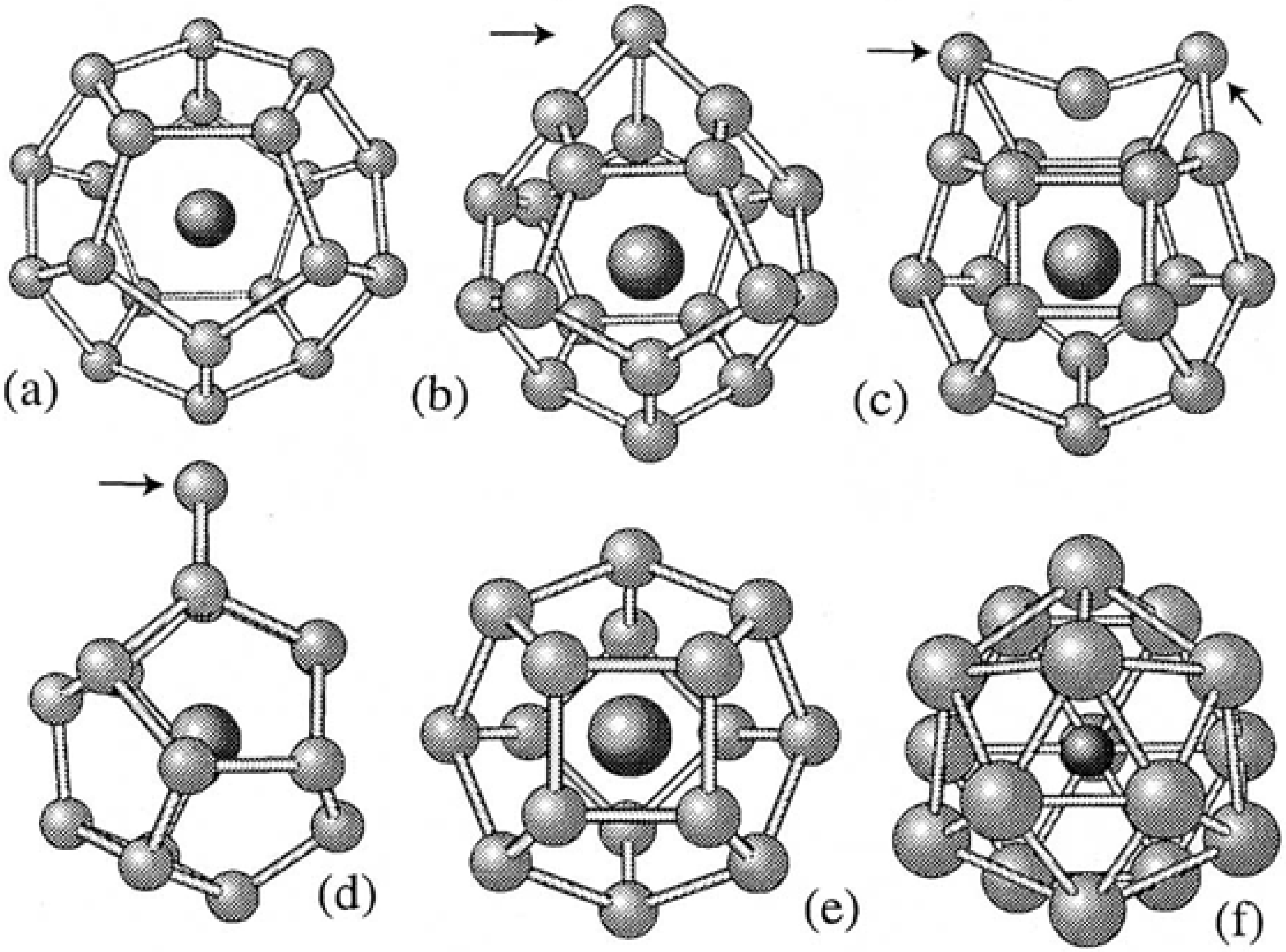
J. Chem. Phys., Vol. 109, No. 21, 1 December 1998

Theoretical Model of Si_{1000} Clusters



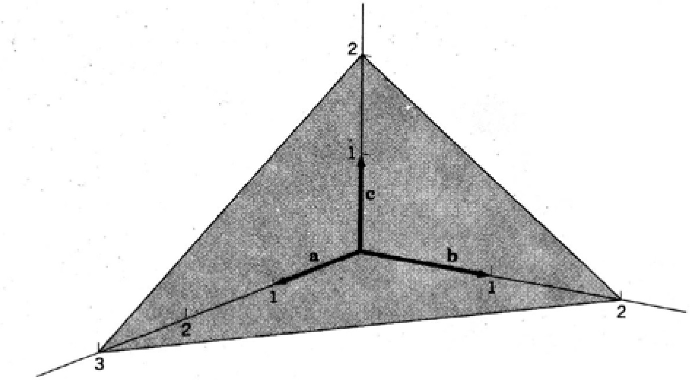
Phys. Rev. B 57, 3799 (1998)

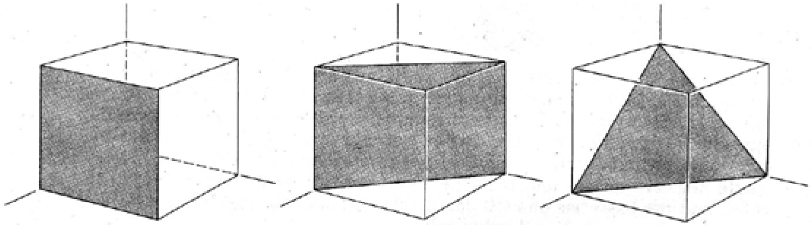
Theoretical Model for Metal-encapsulated Si$_n$ Clusters

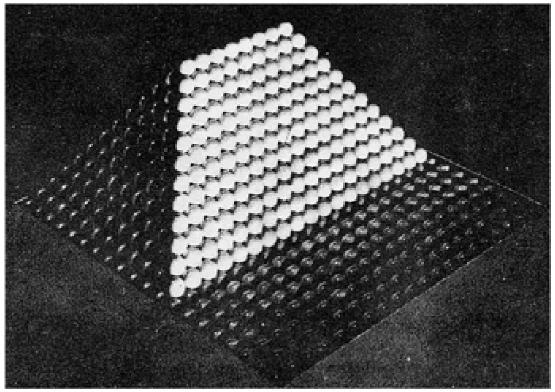


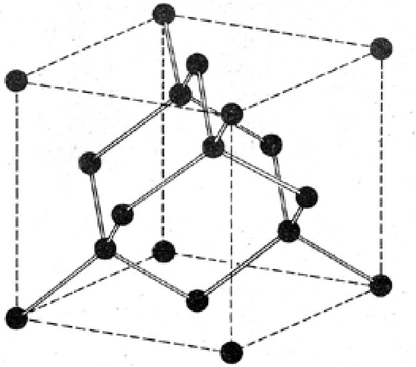
Phys. Rev. Lett. 87, 045503 (2001)

Miller Indices of a Plane

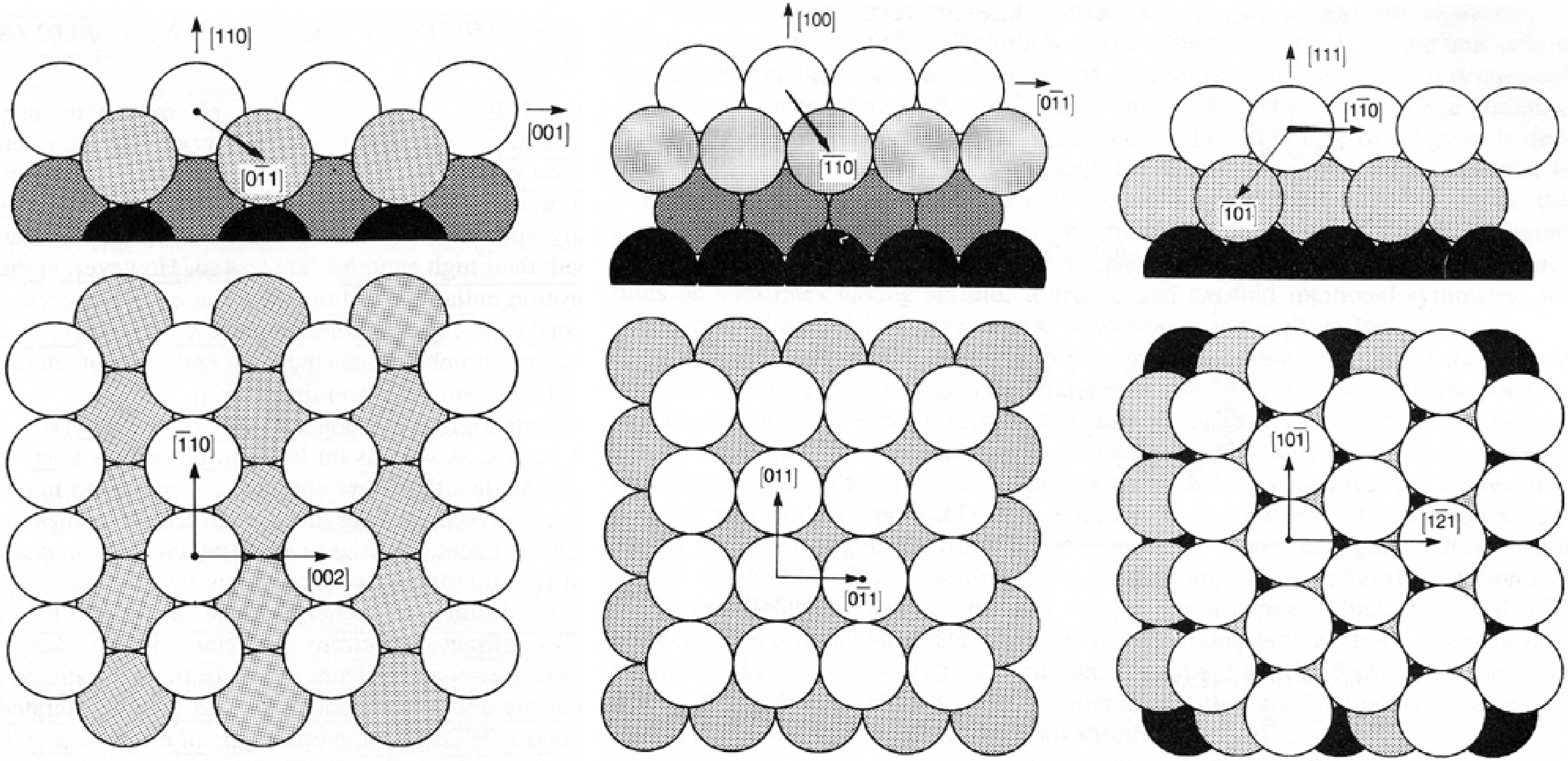



(100)
(110)
(111)




Crystal structure of diamond, showing the tetrahedral bond arrangement.

Face-Centered Cubic (fcc) Crystal Surfaces

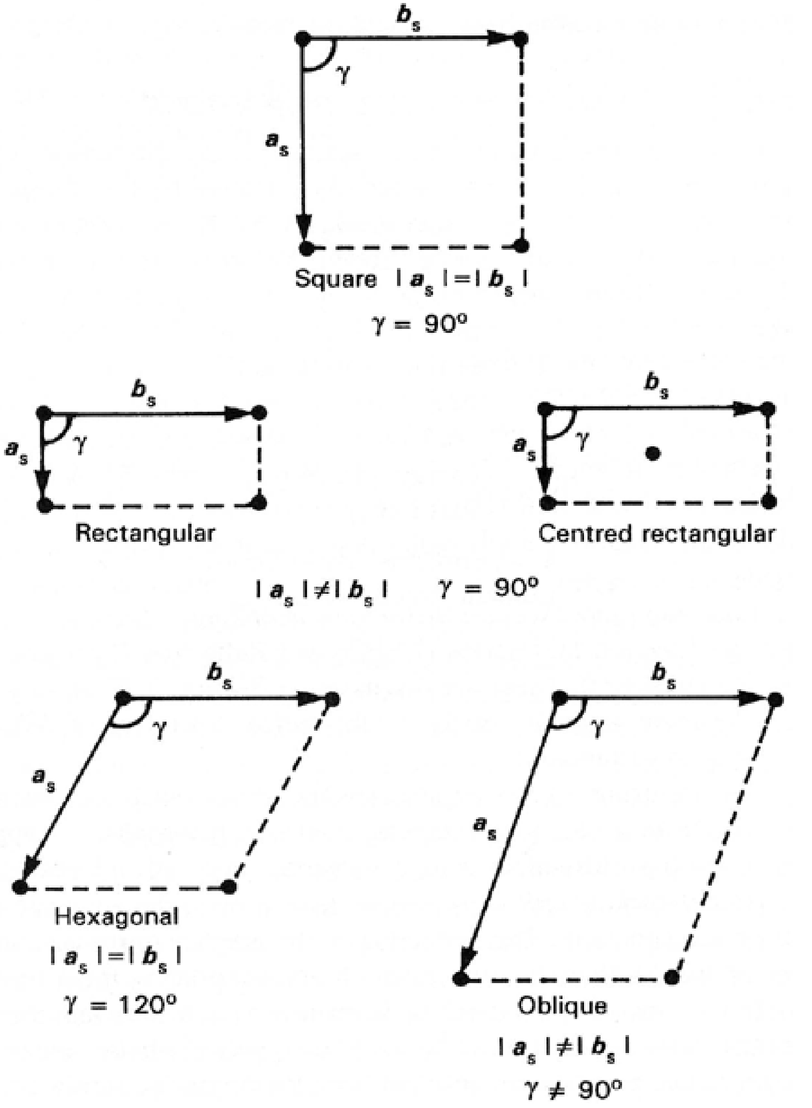


fcc (110)

fcc (100)

fcc (111)

The Five Surface Net



Notation of Surface Structures

1. If the translation vectors of the surface, *a'* and *b'*, *a'* = M*a*, *b'* = N*b*, where *a* and *b* are the translation vectors of the ideal, unreconstructed surface. The nomenclature for this structure is (M×N). If, in addition, the surface net is rotated with respect to the underlying substrate lattice by an angle ϕ degrees, the notation becomes (M×N)Rϕ. If the surface net is best described using a centered, rather than a primitive net, this is indicated as c(M×N). If the overlayer consists of an adsorbate, rather than simple reconstructed substrate atoms, this is also usually indicated. An arrangement of surface atoms identical to that in the bulk unit cell is called the substrate structure and is designated (1×1) (i.e. unreconstructed).

2. The surface unit-cell vectors *a'* and *b'* can be expressed in terms of the unit-cell vectors, *a* and *b*, obtained from the bulk projection.

$$a' = m_{11}a + m_{12}b,$$

$$b' = m_{21}a + m_{22}b,$$

$$M = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix}$$

A surface structure that has a unit cell different from the bulk-projected substrate unit cell is often called a "superlattice".

(2×2) correspond to the $\begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$ matrix notation.