Introduction to nanotechnology:

Chapter 4 : Properties of Nanoparticles

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1. **Introduction:**
2. **Metal Nanoclusters**
3. **Metal Nanoclusters**
4. **Semiconducting Nanoclusters**
5. **Rare Gas and Molecular Clusters**
6. **Methods of Synthesis**

1 : Introduction

Scope 範疇

Macroscopic (巨觀) : Bulk
Mesoscopic (介觀) : cluster and nanoparticles
Microscopic (微觀) : atom and molecular

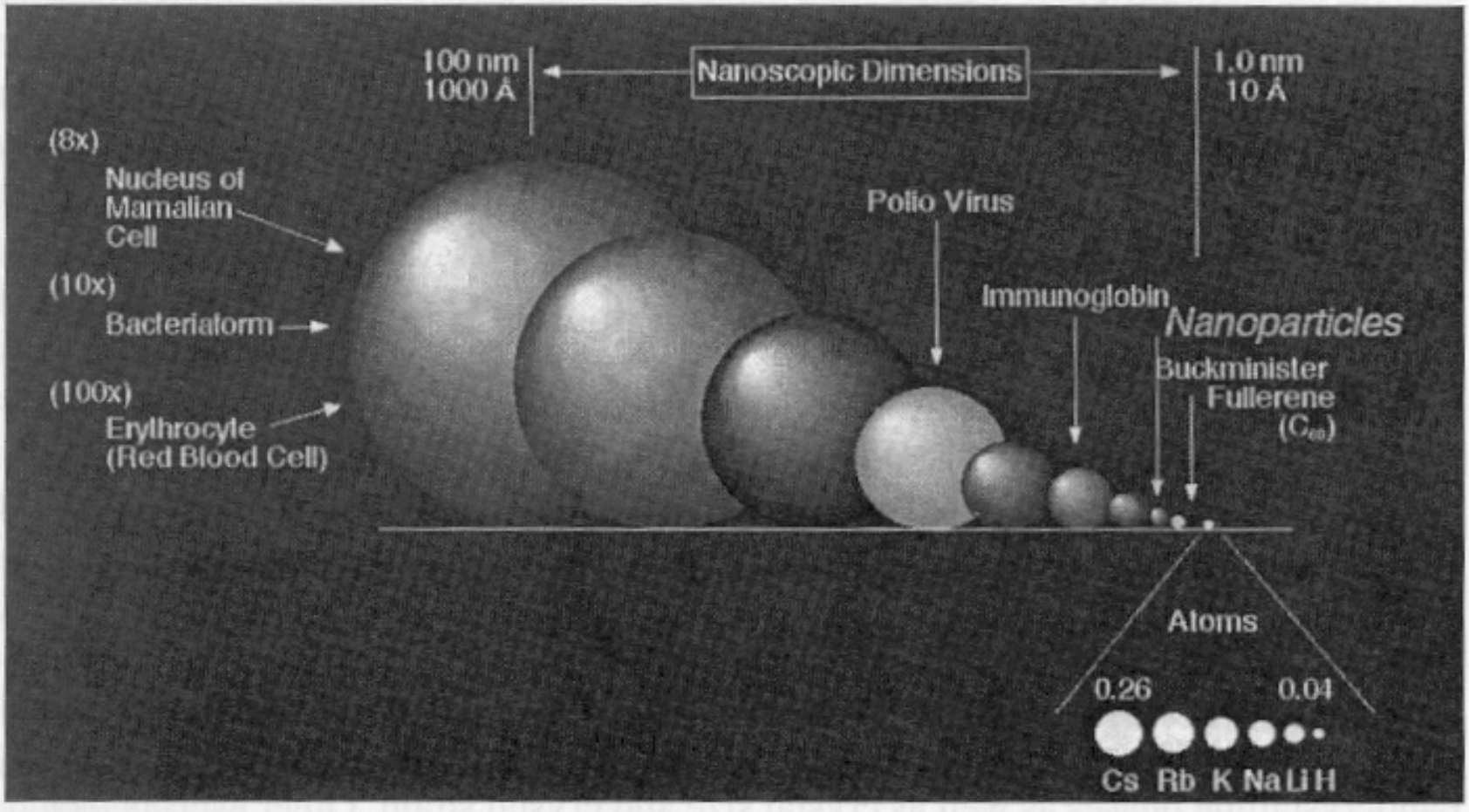


FIGURE 1.2 Size comparisons of nanocrystals with bacteria, viruses, and molecules.

II. Nanoparticle
奈米微粒1~100 nm~ 1000 nm

病毒 Virus　~10 nm~100 nm

紅血球 blood cell 200~300 nm

細菌 bacteria 200~600 nm

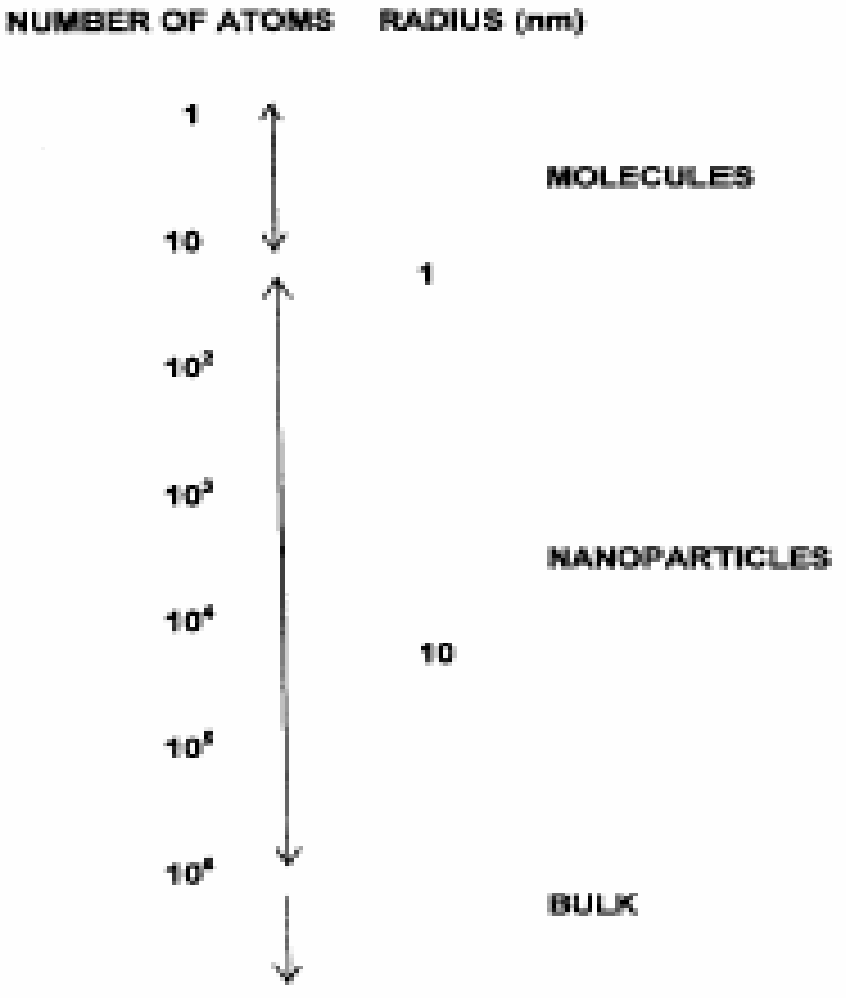


Figure 4.1. Distinction between molecules, nanoparticles, and bulk according to the number of atoms in the cluster.

Size is smaller than critical length

- Mean free path or scattering length
- Coherence length
- Energy level spacing >> thermal energy KT

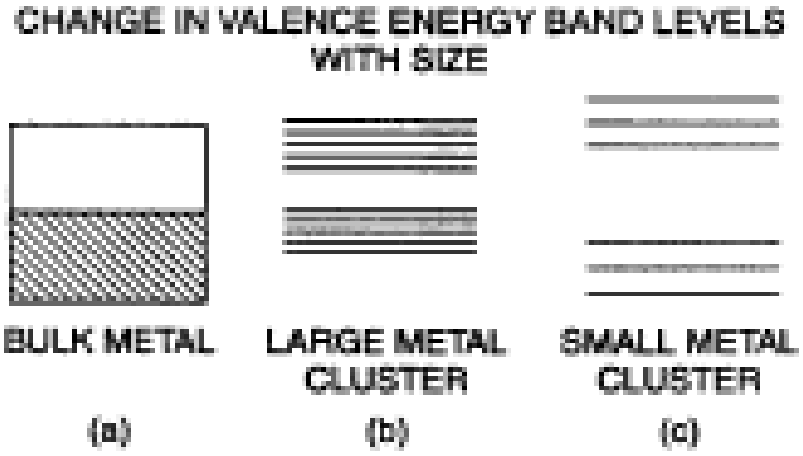


Figure 4.9. Illustration of how energy levels of a metal change when the number of atoms of the material is reduced: (a) valence band of *bulk metal*; (b) *large metal cluster* of 100 atoms showing opening of a band gap; (c) *small metal cluster* containing three atoms.

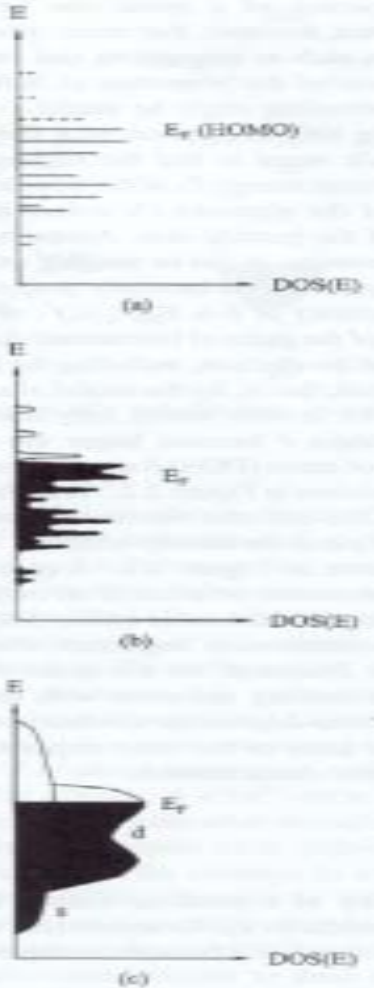


FIGURE 2.2 Formation of a band structure (a) from a molecular state, (b) from a nanosized particle with broadened energy states, and (c) the fully developed band structure consisting of *s* and *d* band. E_F = Fermi energy; DOS = density of states. In (a) E_F coresponds to the highest occupied molecular orbital (HOMO).

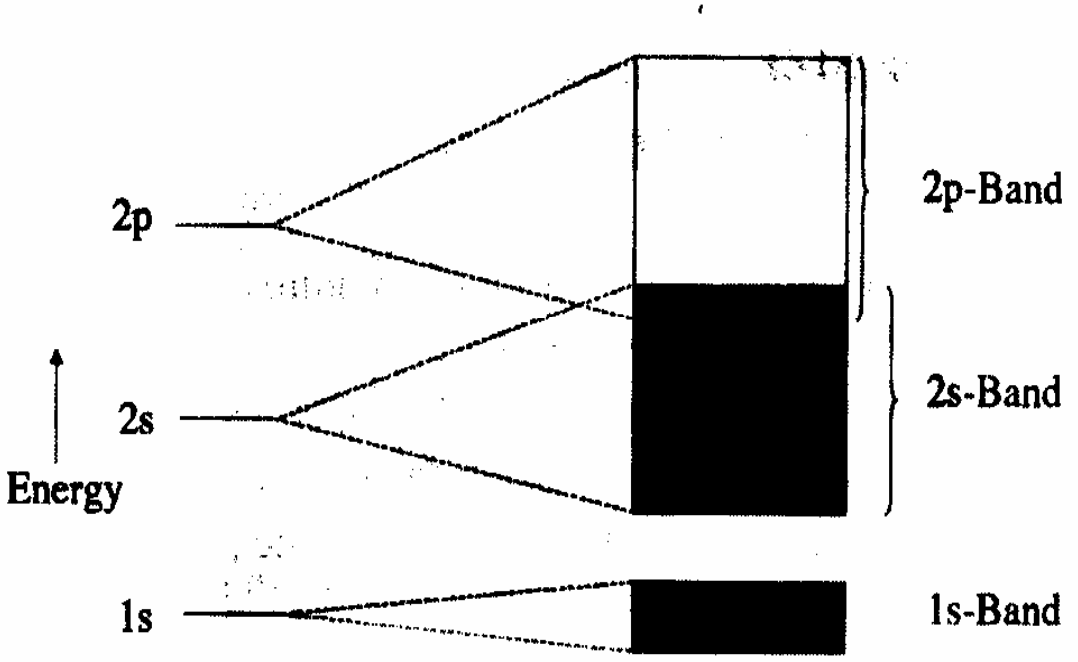


FIGURE 2.3 Overlap of the fully occupied 2*s* band with the empty 2*p* band in beryllium is responsible for the metallic behavior.

do 2D and 1D arrangements.

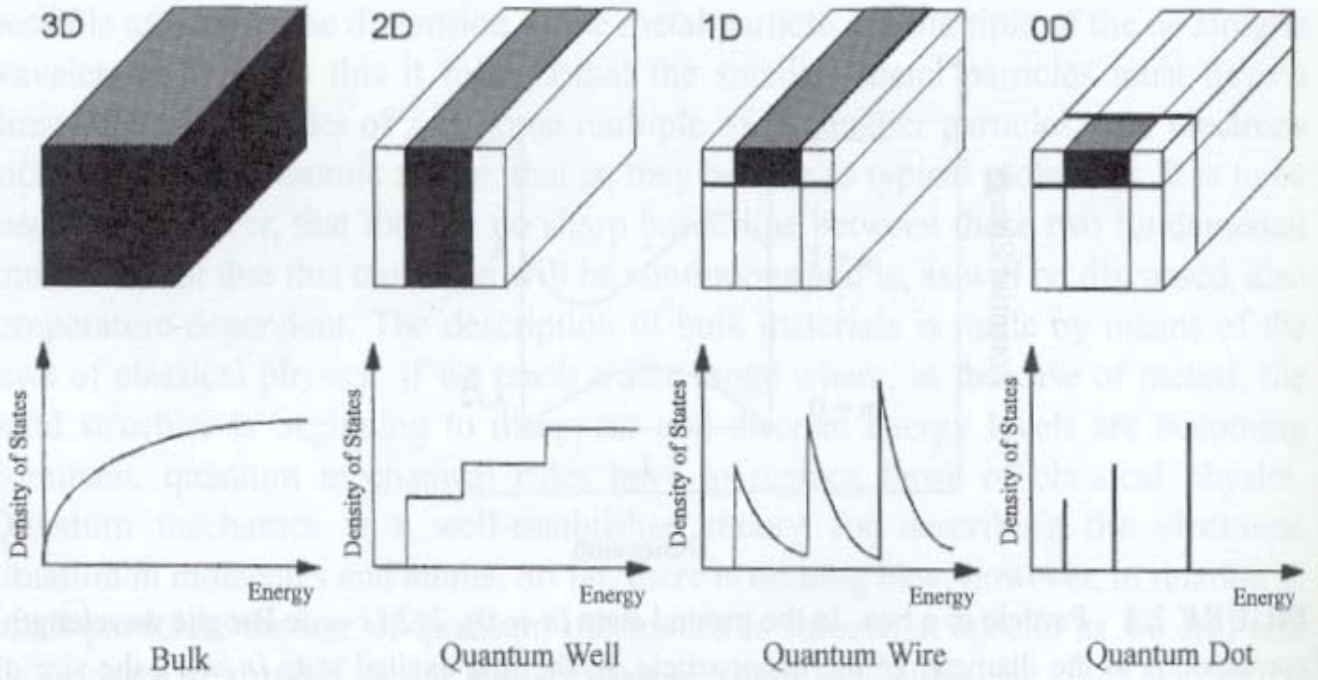


FIGURE 2.5 Formation of a zero-dimensional (0D) quantum dot by the formal reduction of dimensions, correlating with the continuing discretization of the energy states.

4.2.1 Magic numbers and structure

1. No. of electrons for an atom
2. No. of atoms for a nanoparticles

   The jellium model P75

   Density functional theory P78

   Molecular orbital theory P78

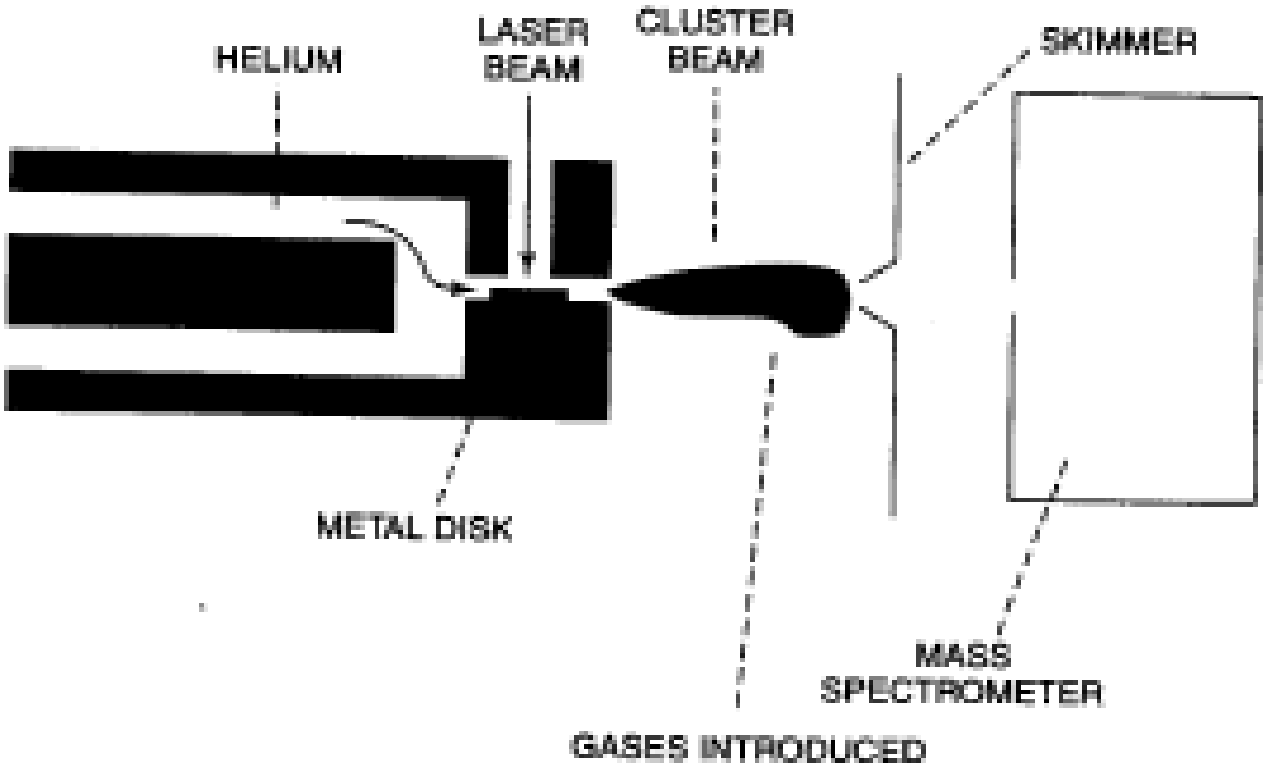


Figure 4.2. Apparatus to make metal nanoparticles by laser induced evaporation of atoms from the surface of a metal. Various gases such as oxygen can be introduced to study the chemical interaction of the nanoparticles and the gases. (With permission from F. J. Owens and C. P. Poole, Jr., *New Superconductors*, Plenum Press, 1999.)

準分子雷射濺鍍 (Excimer Laser Ablation簡稱 ELA)(建於 2003/3) 及奈米成長真空系統(建於1993/1)。

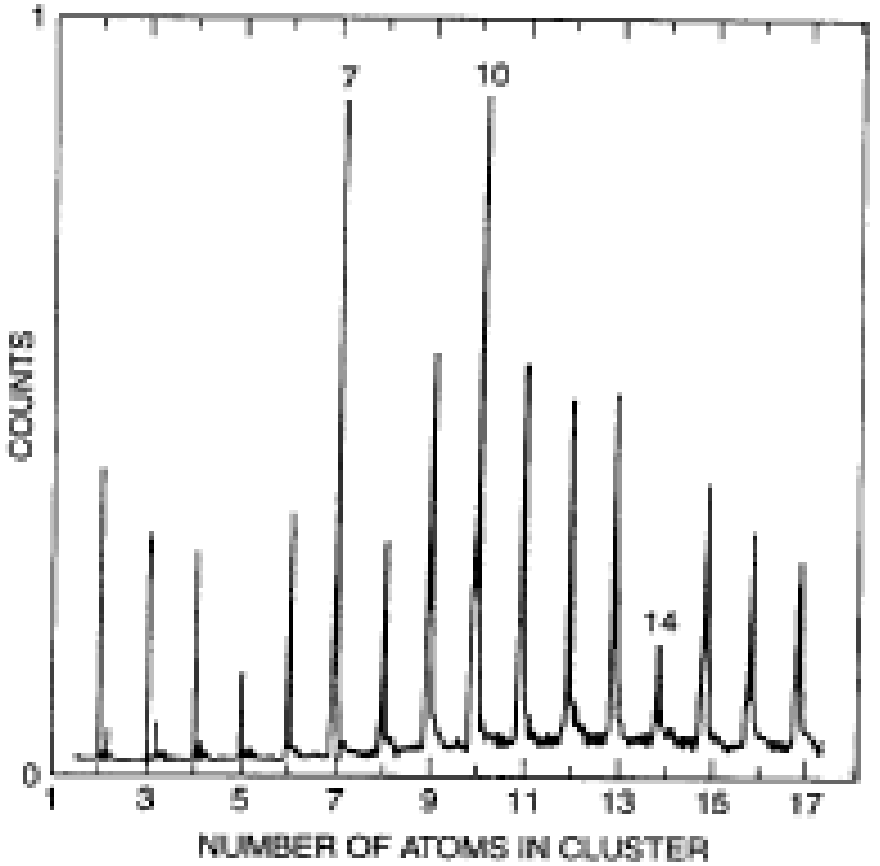
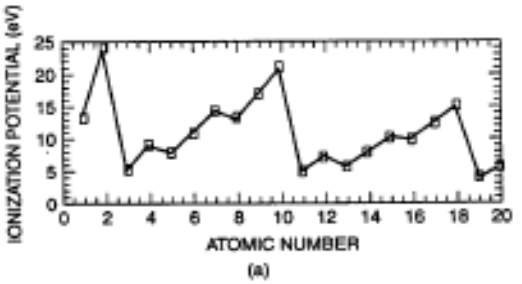
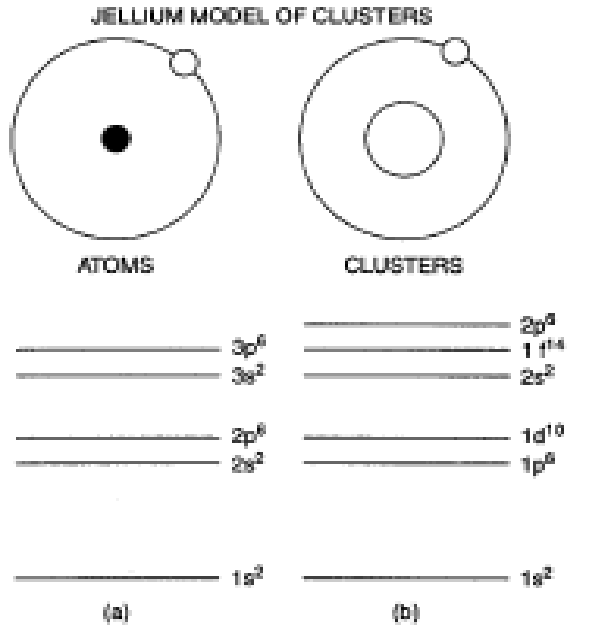


Figure 4.3. *Mass spectrum of Pb clusters.* [Adapted from M. A. Duncan and D. H. Rouvray, *Sci. Am.* 110 (Dec. 1989).]

4.2.2 Theoretical Modeling of Nanoparticles



ıre 4.4. (a) A plot of the ionization energy of single atoms versus the atomic number. The ıation energy of the sodium atom at atomic number 11 is 5.14 eV (b) plot of the ionization rgy of sodium nanoparticles versus the number of atoms in the cluster. [Adapted from ierman et al., *J. Chem. Phys.* **80**, 1780 (1984).]



Electronic magic numbers

Structural magic number

TABLE 2.1 The relation between the total number of atoms in full shell clusters and the percentage of surface atoms

Full-shell Clusters		Total Number of Atoms	Surface Atoms (%)
1 Shell		13	92
2 Shells		55	76
3 Shells		147	63
4 Shells		309	52
5 Shells		561	45
7 Shells		1415	35

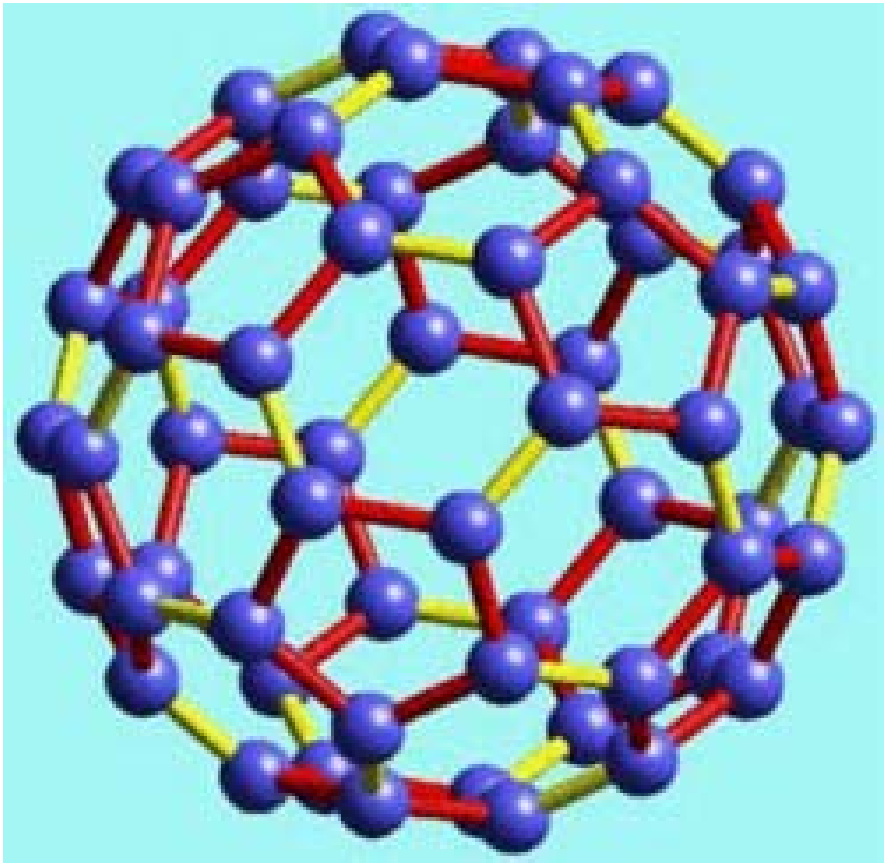
With FCC structure

Chapter 2 ：Nanostructure

奈米結構

I. Cluster ：Fe_n, Cu_n S_m, C_nH_m, C_{60}, C_{70}

Magic number：C_{20}, C_{24}, C_{28}, C_{32}, C_{36}, C_{50}, C_{60}, C_{70}



4.2.3 Geometric Structure

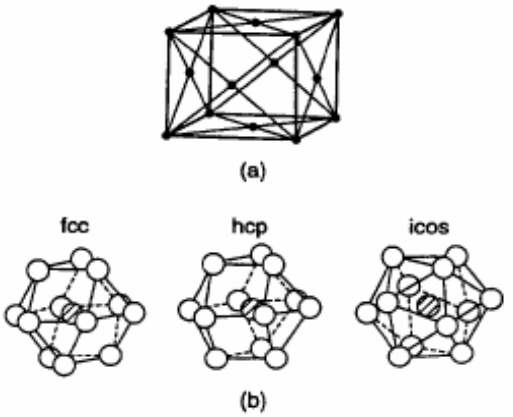


Figure 4.6. (a) The unit cell of bulk aluminum; (b) three possible structures of Al_{13}: a face-centered cubic structure (FCC), an hexagonal close-packed structure (HCP), and an icosahedral (ICOS) structure.

Table 4.1. Calculated binding energy per atom and atomic separation in some aluminum nanoparticles compared with bulk aluminum

Cluster	Binding Energy (eV)	Al Separation (Å)
Al_{13}	2.77	2.814
Al_{13}^-	3.10	2.75
Bulk Al	3.39	2.86

Structure of Indium nanoparticles

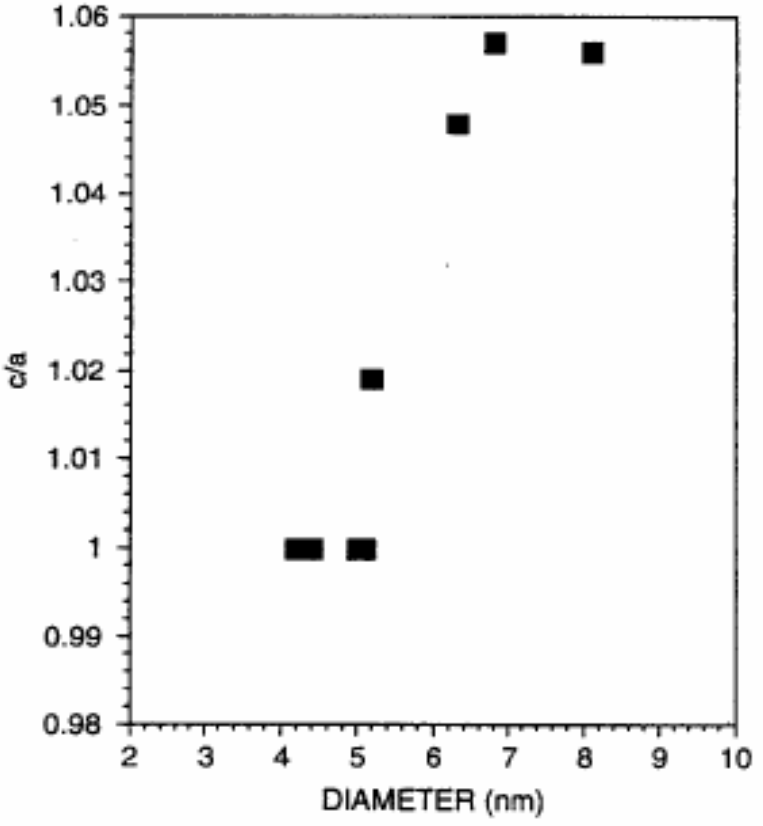
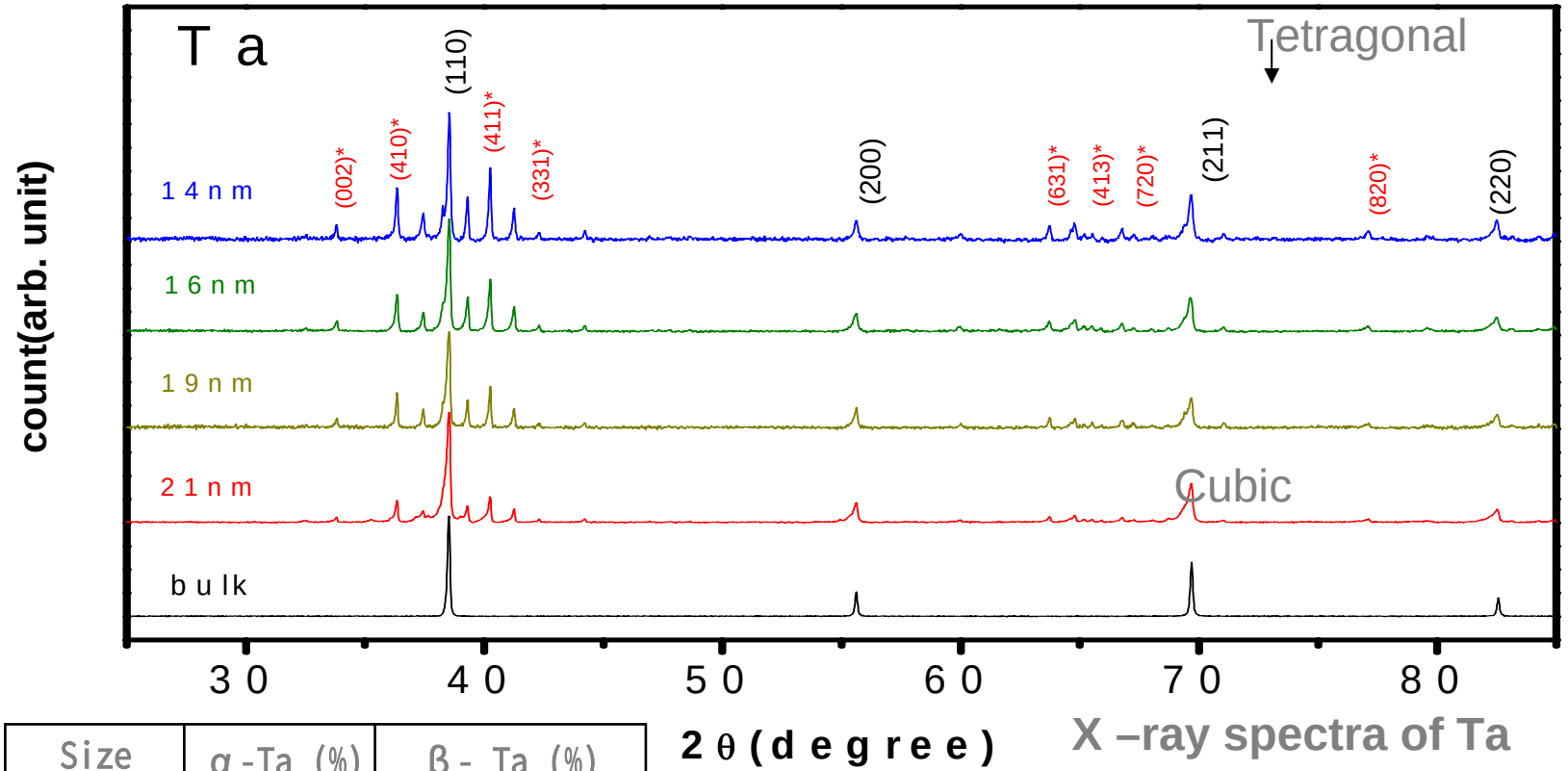


Figure 4.7. Plot of the ratio of the length of the *c* axis to the *a* axis of the tetragonal unit cell of indium nanoparticles versus the diameter of nanoparticles. [Plotted from data in A. Yokozeki and G. D. Stein, *J. Appl. Phys.* **49**, 224 (1978).]



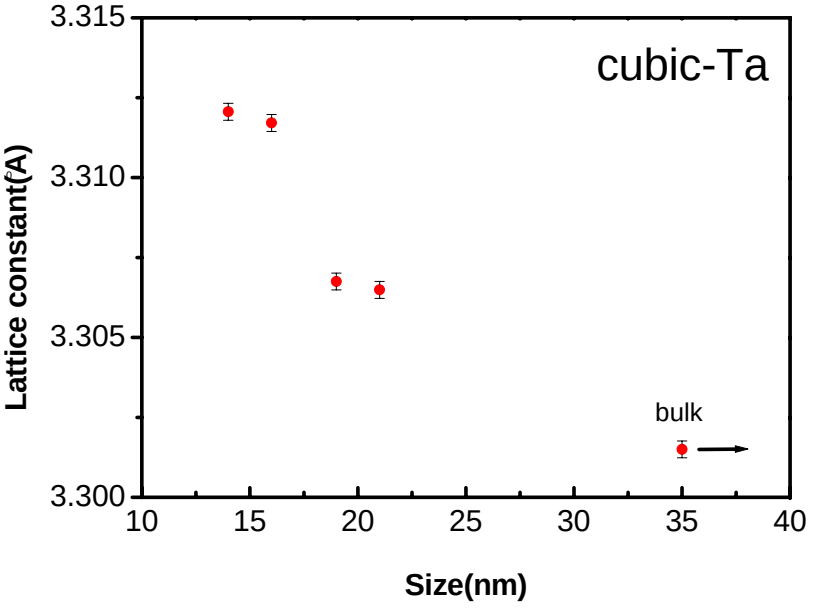
X –ray spectra of Ta

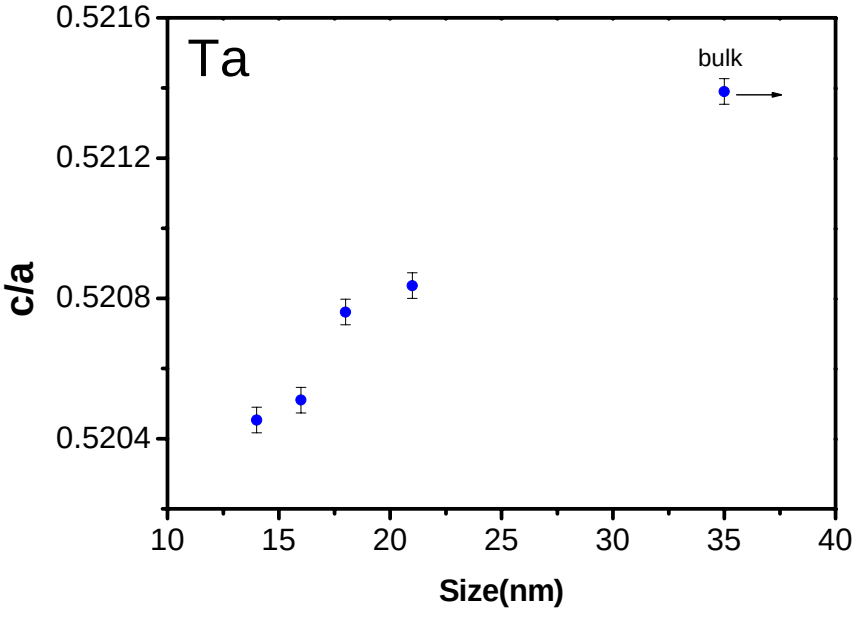
Size (nm)	α-Ta (%) Cubic	β- Ta (%) Tetragonal
14	42.4	57.6
16	44.7	55.3
19	47.8	52.2
21	66.7	33.3
bulk	100	0

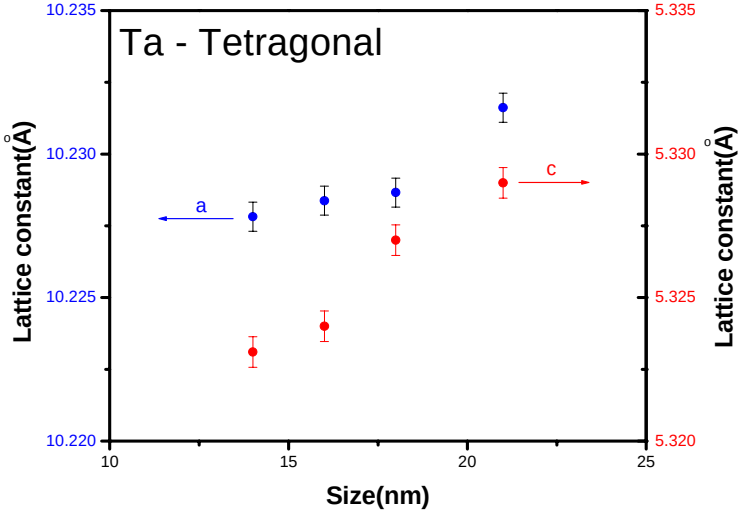
Size dependence of phase compositions

彭翊凱 陳致文

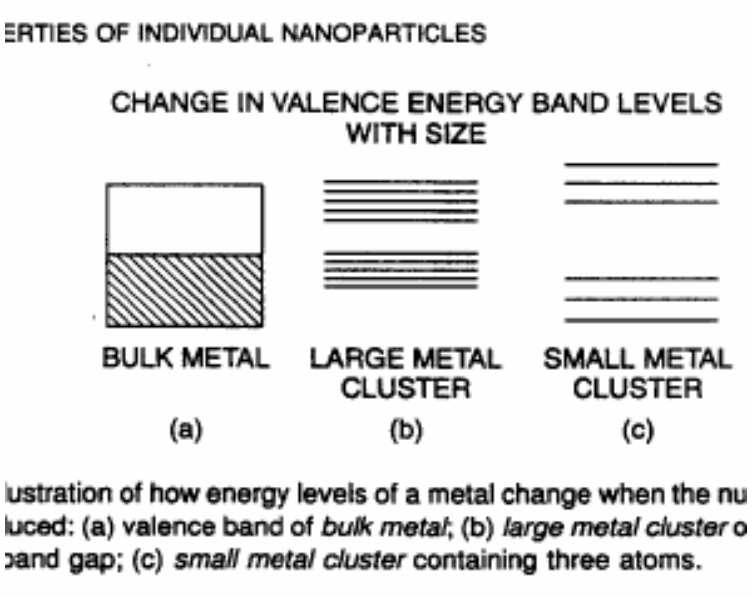
lattice constant of Ta







Electronic Structure



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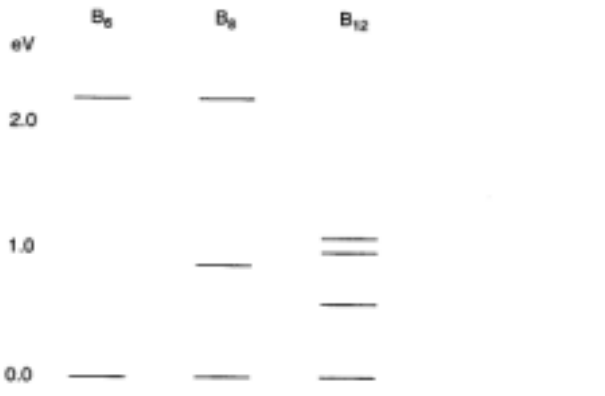
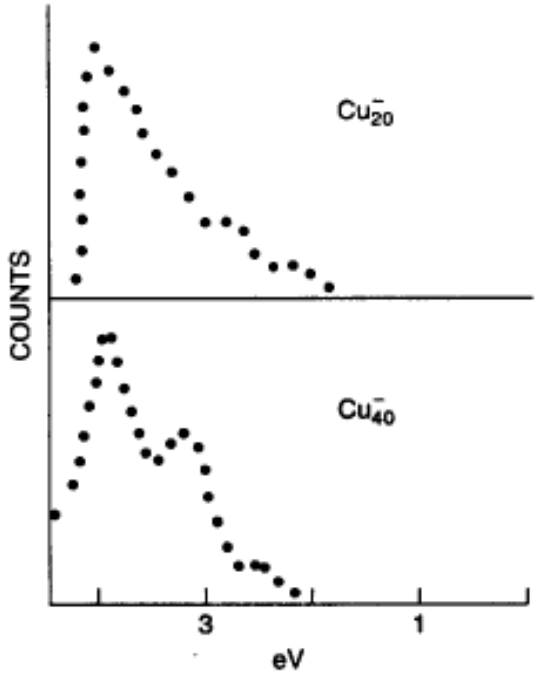


nsity functional calculation of excited state energy levels of B_6, B_9, and B_{12} hoton-induced transitions between the lowest level and the upper levels lor of the particles. (F. J. Owens, unpublished.)

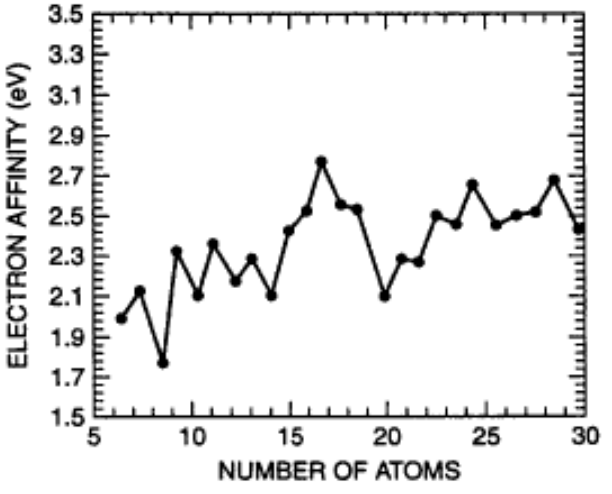
Quantum Size Effect :
Energy level spacing >> K_BT

Light-induced transitions between these levels determines the color

Electron affinity



1. UV photoelectron spectrum in the valence band region of copper



4.12. Plot of measured electron affinity of copper versus size of nanoparticle.

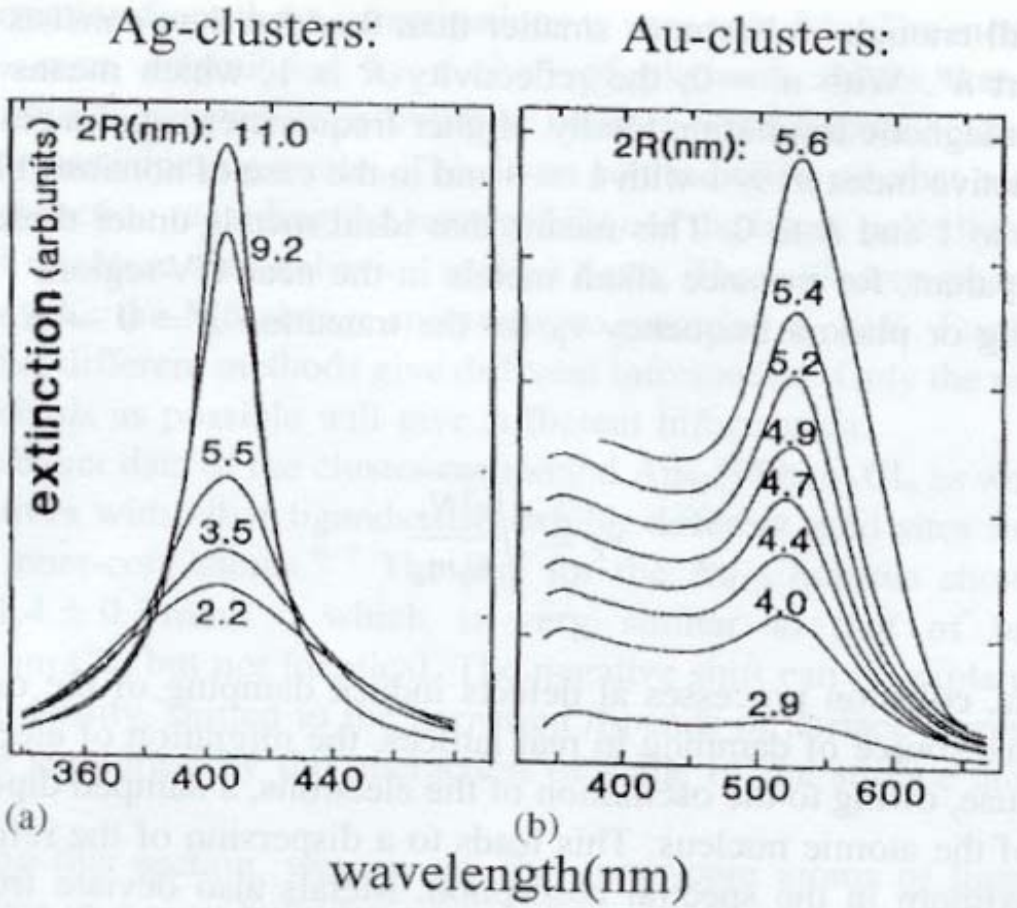


FIGURE 2.10 Absorbance spectra of (a) silver and (b) gold clusters of different sizes. Reprinted with permission from *Handbook of Optical Properties*, Vol. II (ed Hummel and Wissmann) **1997**. Copyright CRC Press, Boca Rata, Florida.[12]

4.2.5 Reactivity

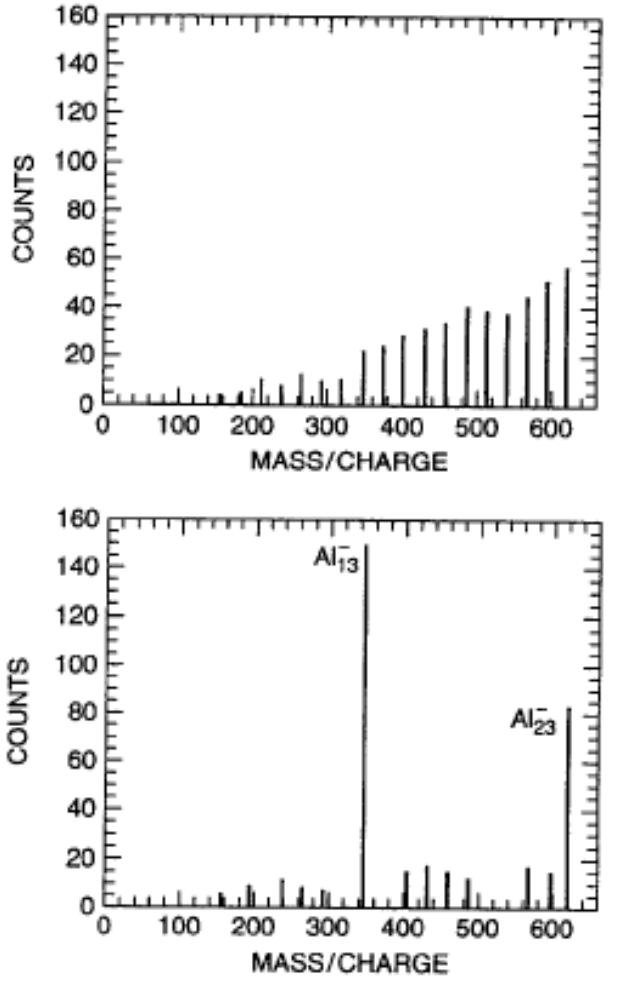


Figure 4.13. Mass spectrum of Al nanoparticles before (top) and after (bottom) exposure oxygen gas. [Adapted from R. E. Leuchtner et al., *J. Chem. Phys.*, **91**, 2753 (1989).]

4.2.6 Fluctuations

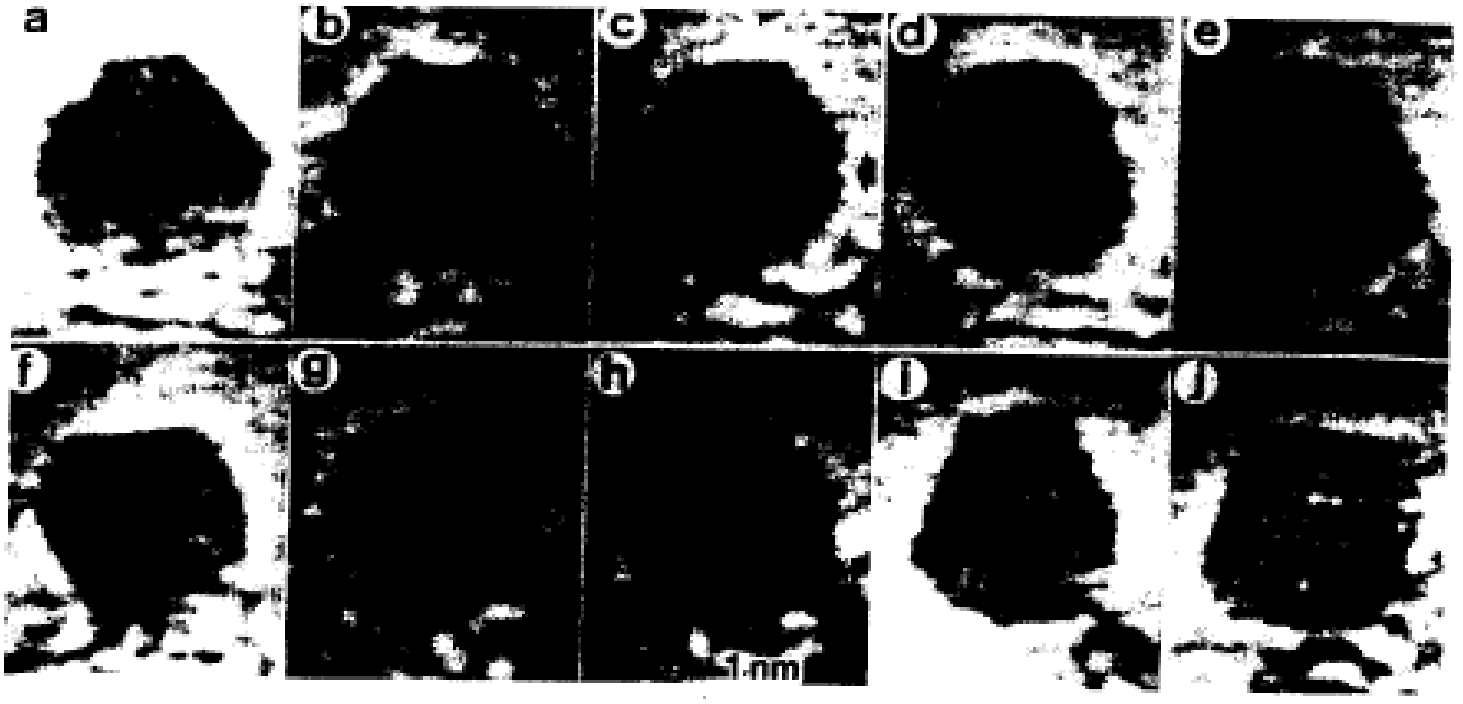


Figure 4.15. A series of electron microscope pictures of gold nanoparticles containing approximately 460 atoms taken at various times showing fluctuation-induced changes in the structure. (With permission from S. Sugano and H. Koizumi, in *Microcluster Physics*, Springer, Berlin,