4.2.7 Magnetic cluster

- Magnetized cluster
- Nonmagnetic- magnetic transition

Superparamagnetism

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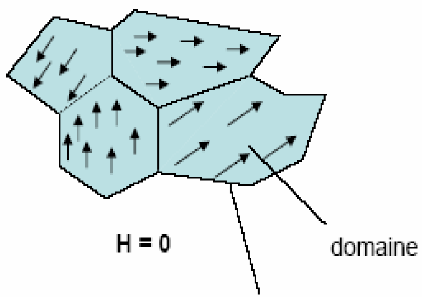
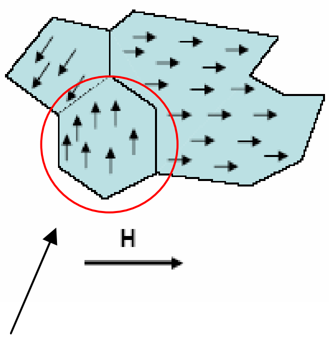
Ferro-magnetisme:





Single domain

Materials: Fe, Co, Ni, Gd

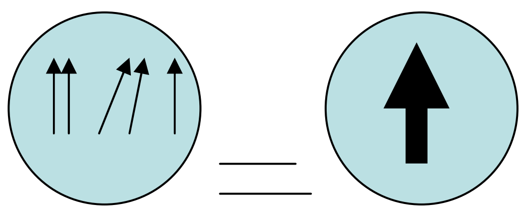
Spins of unfilled d-bands spontaneously align parallel inside a *domain* below a critical temperature T_C (Curie)

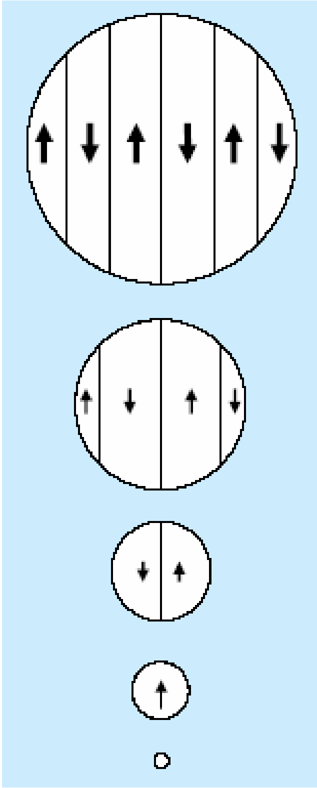
Laws:

$$B = H + 4\pi \cdot \chi \cdot H$$

$$M = \chi \cdot H$$

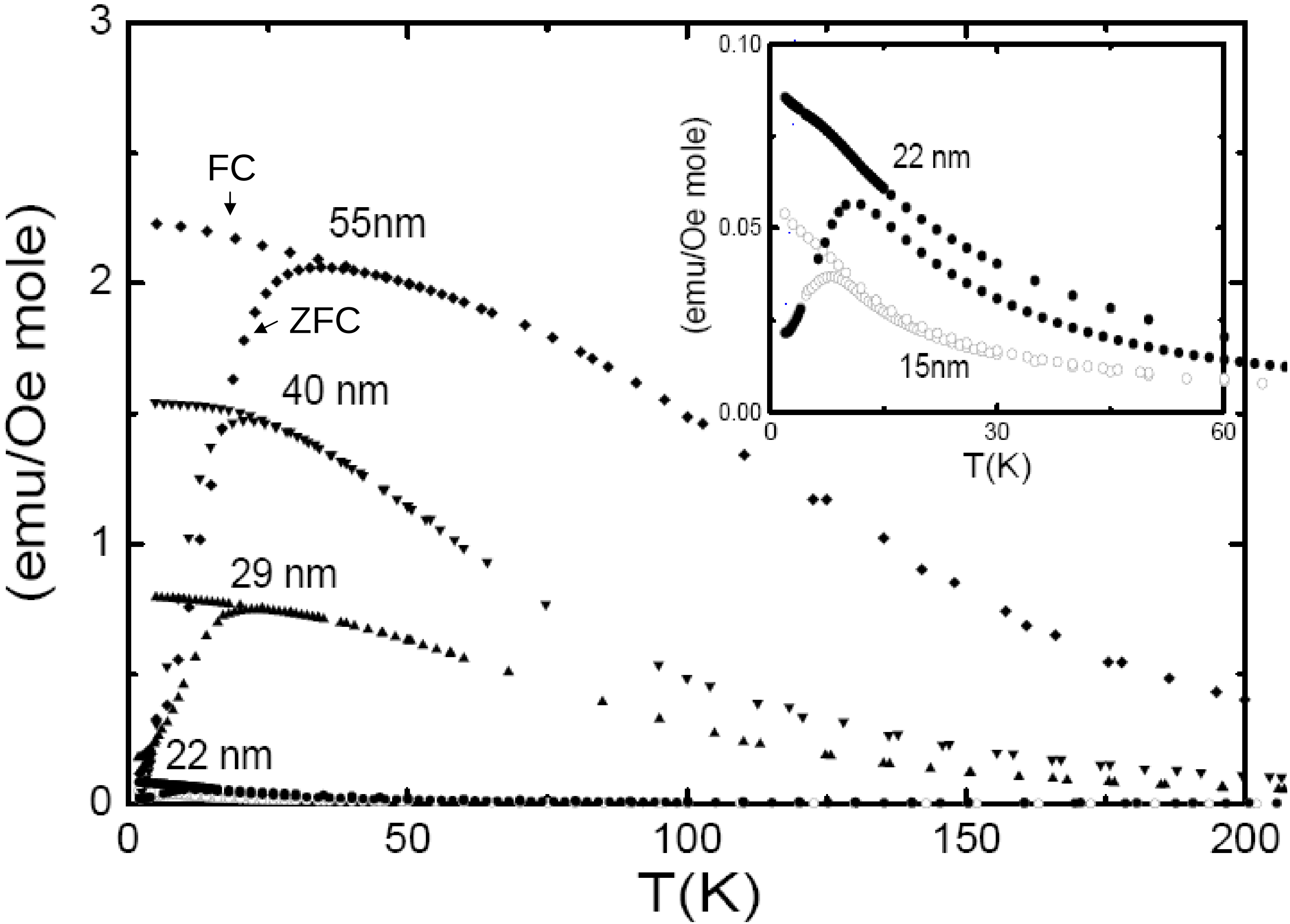
$$\chi = Susceptibility$$





Superparamagnetism

- ⇒Monodomain particles
  - Below 100 nm
- ⇒Fluctuation of the magnetic moment like in a paramagnet
- ⇒Ferromagnetic particles with moment (T_c is high)
- ⇒Moment dependent on particle volume



此圖為$FeSi_2$奈米粉末的DC磁化率-溫度曲線

Temperature dependence of χ

- 1. The temperature of peak value of χ in ZFC is defined as the Blocking temperature T_B。
- 2. χ of ZFC and χ of FC deviate at T_B
- 3. Above T_B, χ of ZFC and χ of FC are overlap.

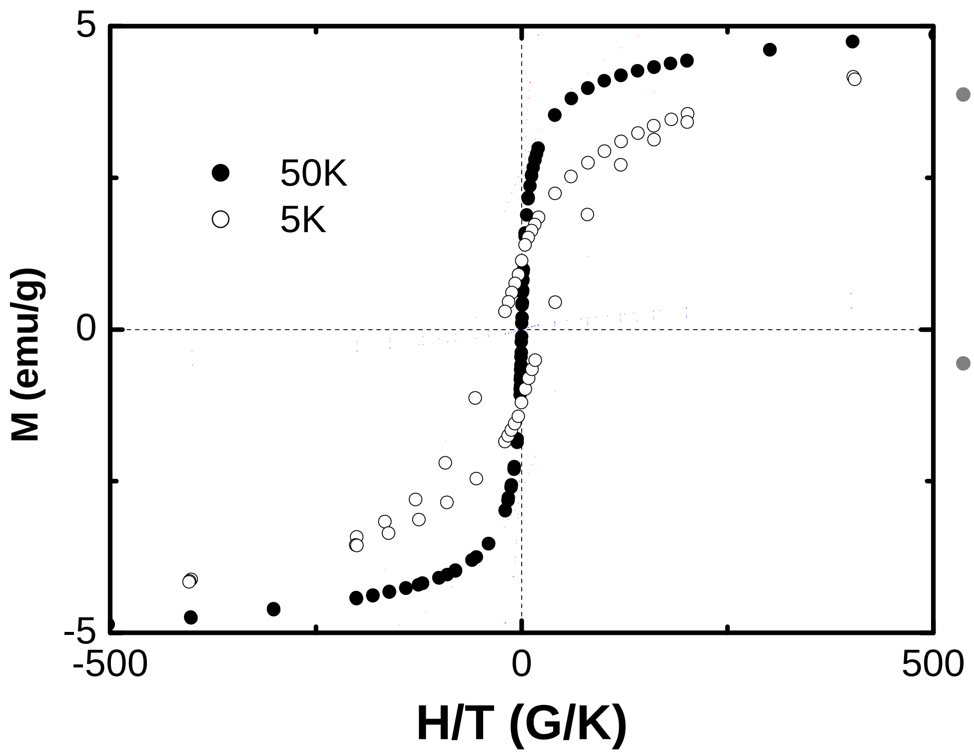
Blocking Temperature

$$T_B = \frac{KV}{25k_B}$$

k_B is the Boltzmann constant
K is the anisotropic constant
V is the volume of nanoparticle

Analysis of size-dependent blocking temperature

M-H曲線

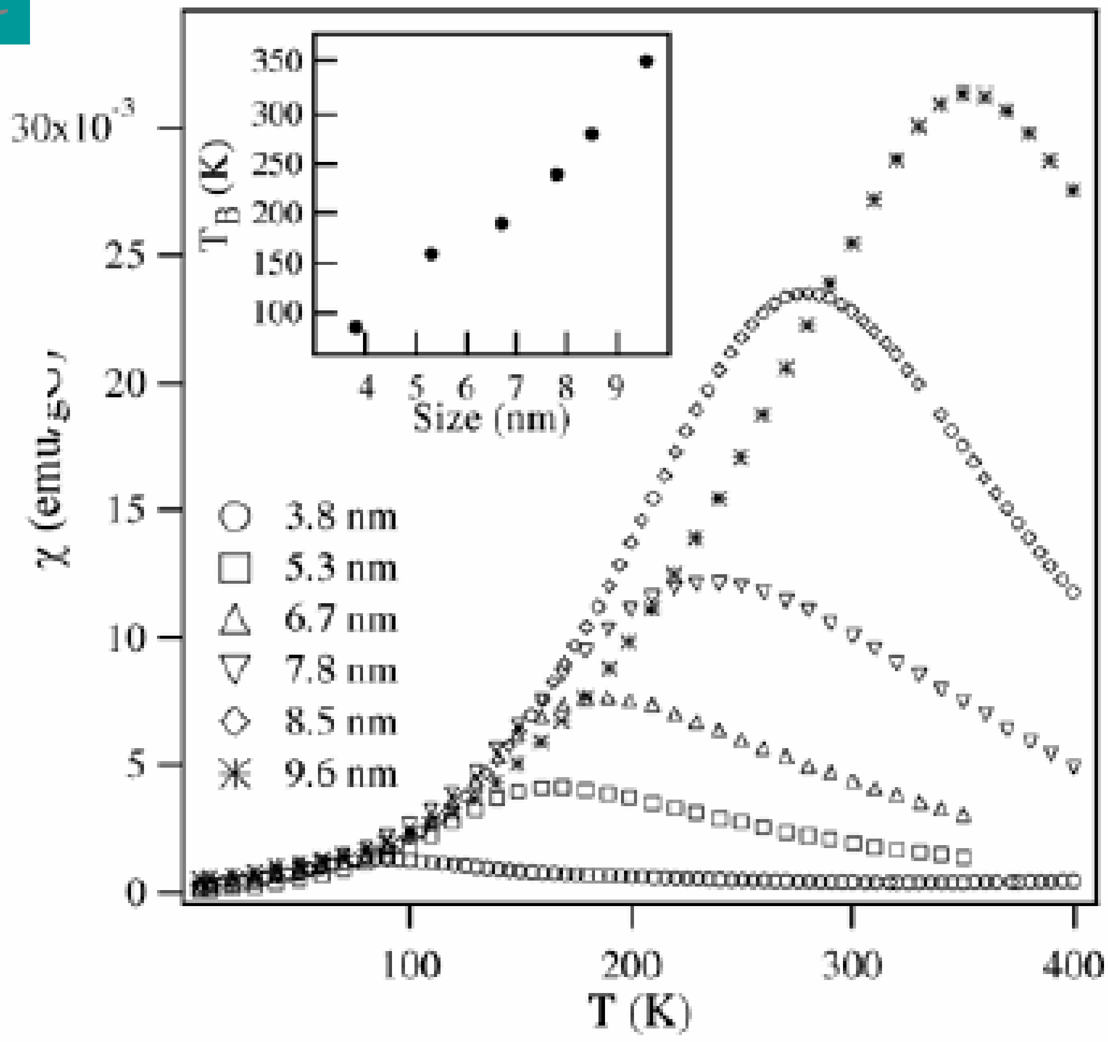


- 1. T< T_B, Hysteresis appears in M-H. Due to thermal energy is less than the interactions among particles
- 2. T> T_B, No hysteresis appears in M-H. Since thermal energy is larger than the interactions among particles

$FeSi_2$ 40nm particles

Example

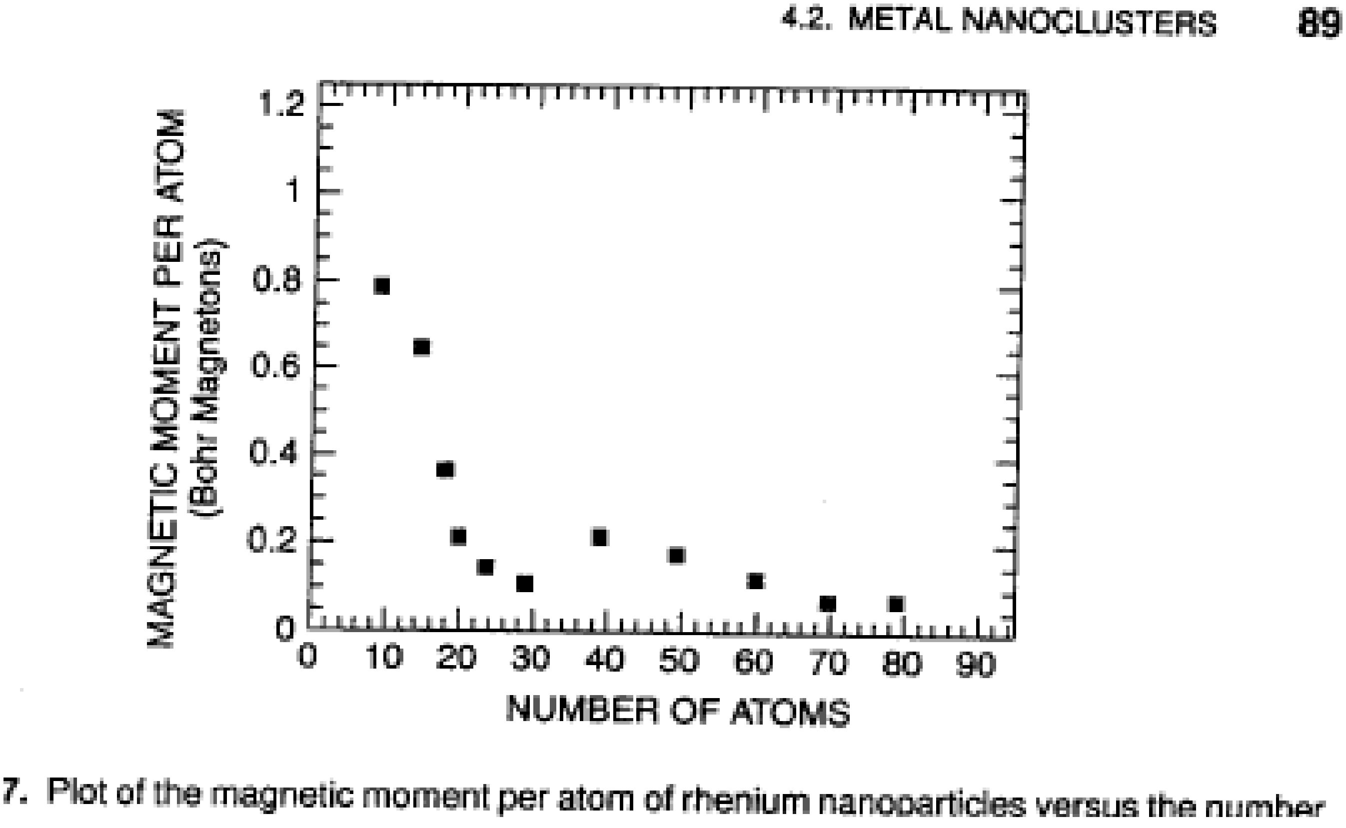
$$T_B = \frac{KV}{25k_B}$$



Magnetic susceptibility vs. Temperature of $CoFe_2O_4$ N.P with various sizes

Pure Appl. Chem., **72**, 37–45 (2000).

Nonmagnetic- magnetic transition



4.2.8 Bulk to Nanotransition

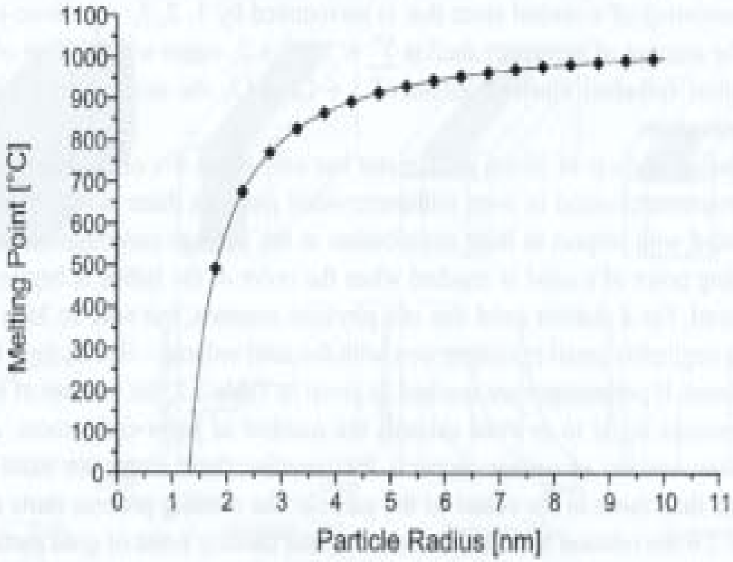
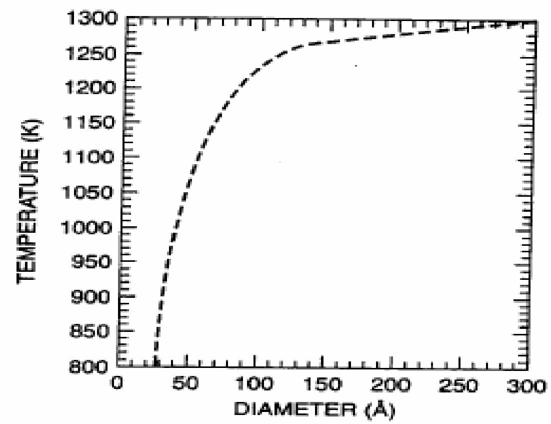


FIGURE 2.6 Relation between the size of gold particles and their melting point.

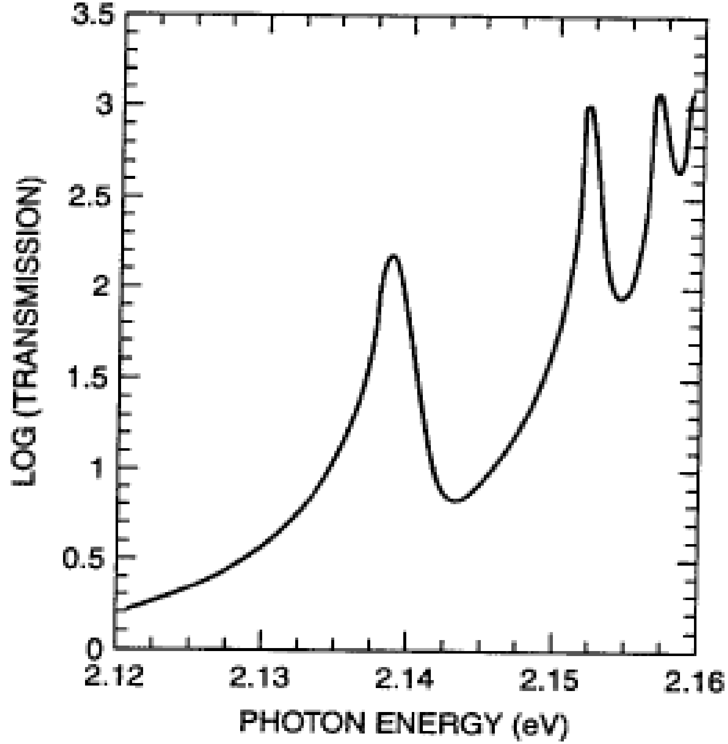


e 4.18. Melting temperature of gold nanoparticles versus particle diameter
ted from J. P. Borel et al., *Surface Sci.* **106**, I (1981).]

4.3 Semiconducting Nanoparticles

- 4.3.1 Optical Properties
- blue shift as size is reduced
- Exciton: bound electron-hole pair,
- Hydrogen-like: energy level spacing
- Light-induced transition

Hydrogen-like: energy level spacing
Light-induced transition

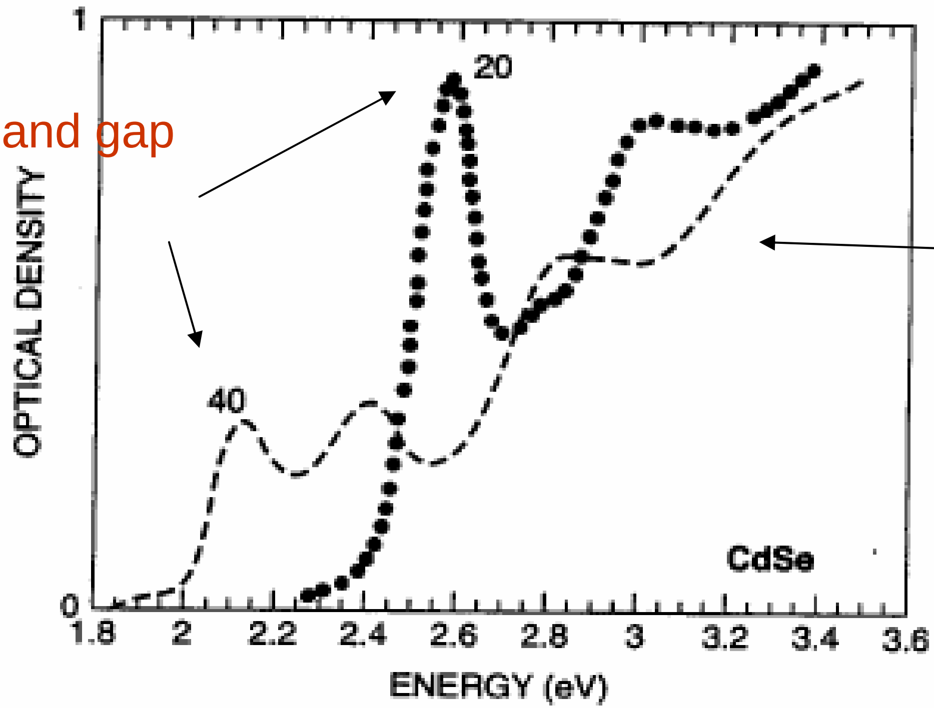


19. Optical absorption spectrum of hydrogen-like transitions of excitons in Cu_2O. 'rom P. W. Baumeister, *Phys. Rev.* **121**, 359 (1961).]

What happens when the size of nanoparticles becomes smaller than to the radius of the orbit of exciton?

- **Weak-confinement**
- size d> radius of electron-hole pair:
- blue shift
- **Strong-confinement**
- size d< radius of electron-hole pair:
- Motion of the electron and the hole become independent, the exciton does not exist

Absorption edge, band gap

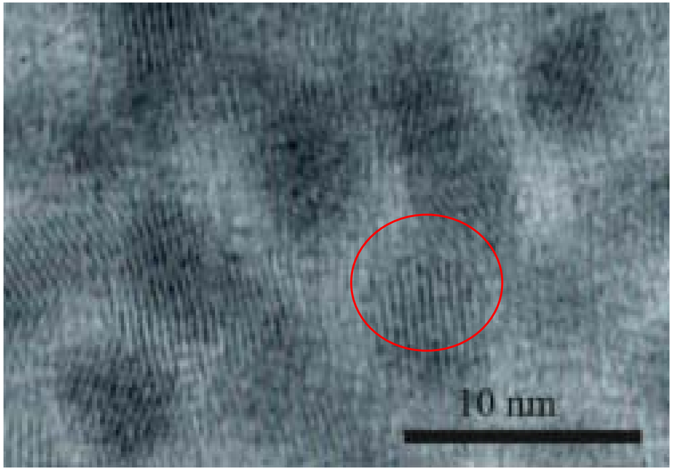


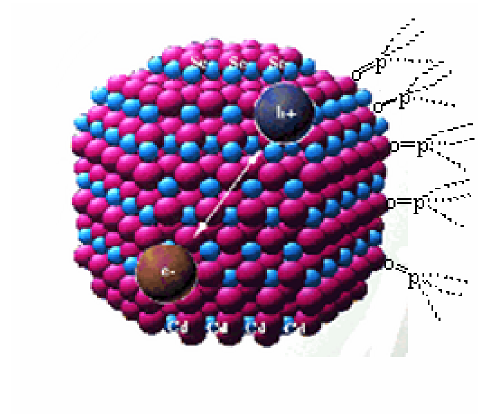
exciton

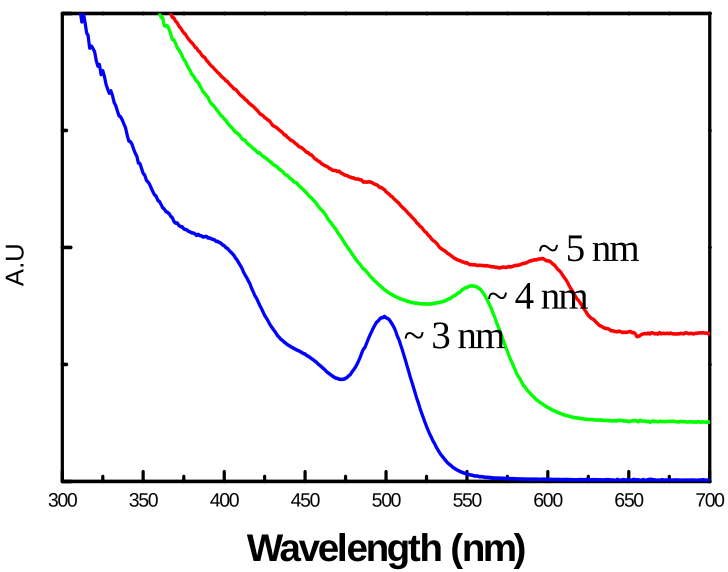
Figure 4.20. Optical absorption spectrum of CdSe for two nanoparticles having sizes 20 Å and 40 Å, respectively. [Adapted from D. M. Mittleman, *Phys. Rev.* **B49**, 14435 (1994).]

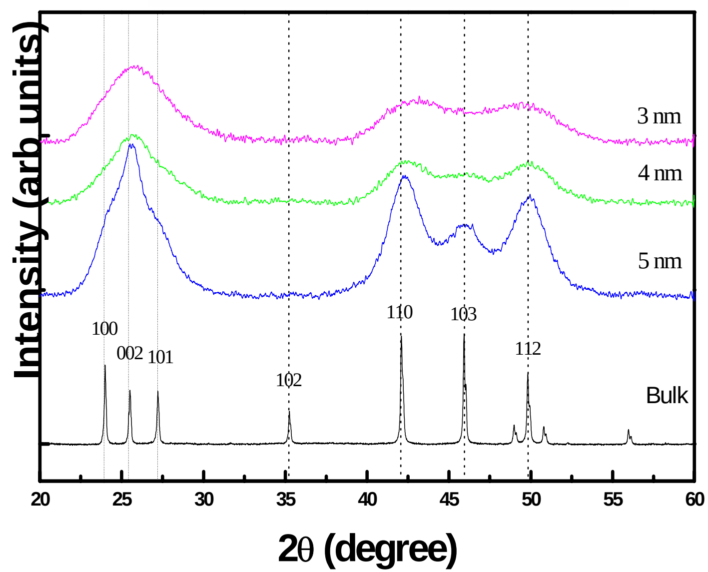
5. Size dependence properties of quantum dots CdSe –surface charge density

absorbance









4.3.2 Photofragmentation

- Si or Ge can undergo fragmentation under laser light

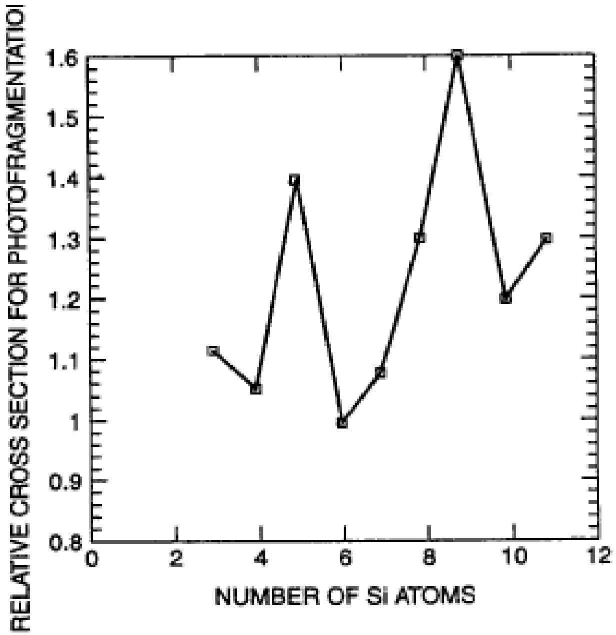


Figure 4.21. Photodissociation cross section of silicon nanoparticles versus number of atoms in particle. [Adapted from L. Bloomfield et al., *Phys. Rev. Lett.* **54**, 2266 (1985).]

Dissociate!

$$Si_{12} + h\nu \rightarrow Si_6 + Si_6 \quad (4.4)$$

$$Si_{20} + h\nu \rightarrow Si_{10} + Si_{10} \quad (4.5)$$

4.3.3 Coulombic Explosion

Multiple ionization of clusters causes them to become unstable, resulting in very rapid high-energy dissociation or explosion. The fragment velocities from this process are very high. The phenomena is called *Coulombic explosion*. Multiple ioniza-

Table 4.2. Some examples of the smallest obtainable multiply charged clusters of different kinds (smaller clusters will explode)

	Charge		
Atom	+2	+3	+4
Kr	Kr_{73}		
Xe	Xe_{52}	Xe_{114}	Xe_{206}
CO_2	$(CO_2)_{44}$	$(CO_2)_{106}$	$(CO_2)_{216}$
Si	Si_3		
Au	Au_3		
Pb	Pb_7		

The attractive forces between the atoms of the cluster can be overcome by the electrostatic repulsion between the atoms when they become positively charged as a result of photoionization. One of the most dramatic manifestations of Coulombic explosion reported in the journal *Nature* is the observation of nuclear fusion in deuterium clusters subjected to femtosecond laser pulses. A femtosecond is 10^{-15} seconds. The clusters were made in the usual way described above, and then subjected to a high-intensity femtosecond laser pulse. The fragments of the dissociation have energies up to one million electron volts (MeV). When the deuterium fragments collide, they have sufficient energy to undergo nuclear fusion by the following reaction:

$$D + D \Rightarrow {}^{3}He + \text{neutron} \tag{4.6}$$

This reaction releases a neutron of 2.54 MeV energy. Evidence for the occurrence of

4.4 Rare Gas and Molecular Clusters

- 4.4.1
- Xenon clusters are formed by adiabatic expansion of a supersonic jet of the gas through a small capillary into a vacuum.

Xenon having 13, 19, 25, 55, 71, 87, and 147 atoms.

$$U(R) = \frac{B}{R^{12}} - \frac{C}{R^6}$$

Repulsion of electronic core

Dipole attractive potential

4.4.2 Superfluid Clusters

- By supersonic free-jet expansion
- He4 : N=7,10,14,23,30
- He3: N+ 7,10,14,21,30

- Superfluidity:
- He N=64,128
- Fermion has half-integer spin

  Boson has integer spin

difference. The case where all the bosons are in the lowest level is referred to as *Bose–Einstein condensation*. When this occurs the wavelength of each boson is the same as every other, and all of the waves are in phase.

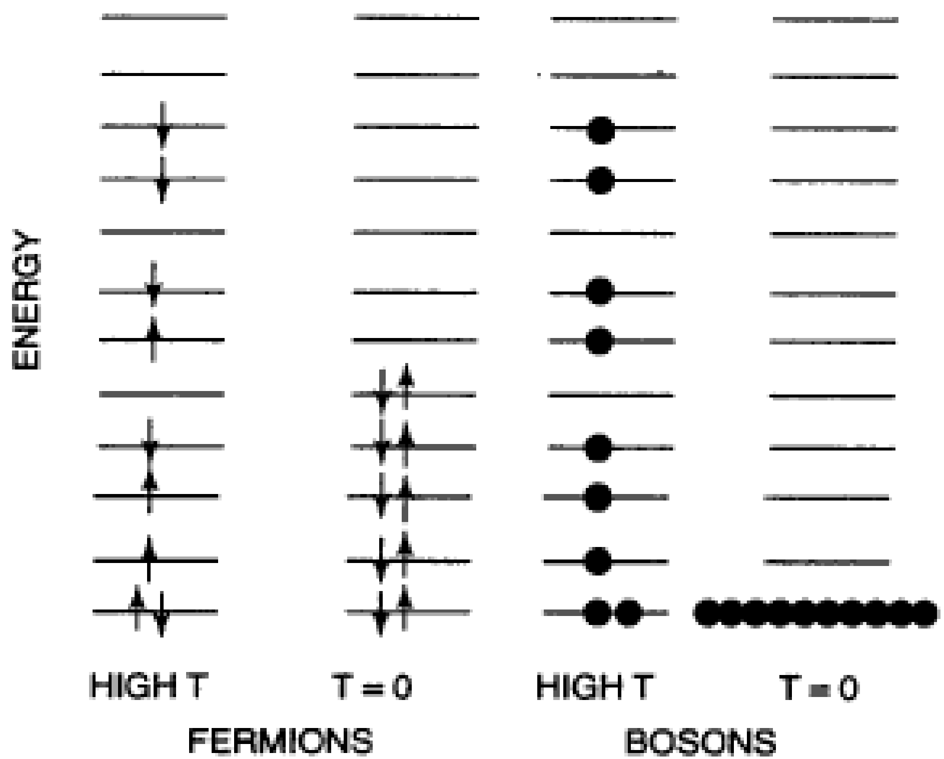


Figure 4.22. Illustration of how fermions and bosons distribute over the energy levels of a system at high and low temperature.

superfluid

- When T= 2.2 K lambda point
- He4 becomes a superfluid, its viscosit drops to zero

When boson condensation occurs in liquid He^4 at the temperature 2.2 K, called the *lambda point* (λ point), the liquid helium becomes a superfluid, and its viscosity drops to zero. Normally when a liquid is forced though a small thin tube, it moves

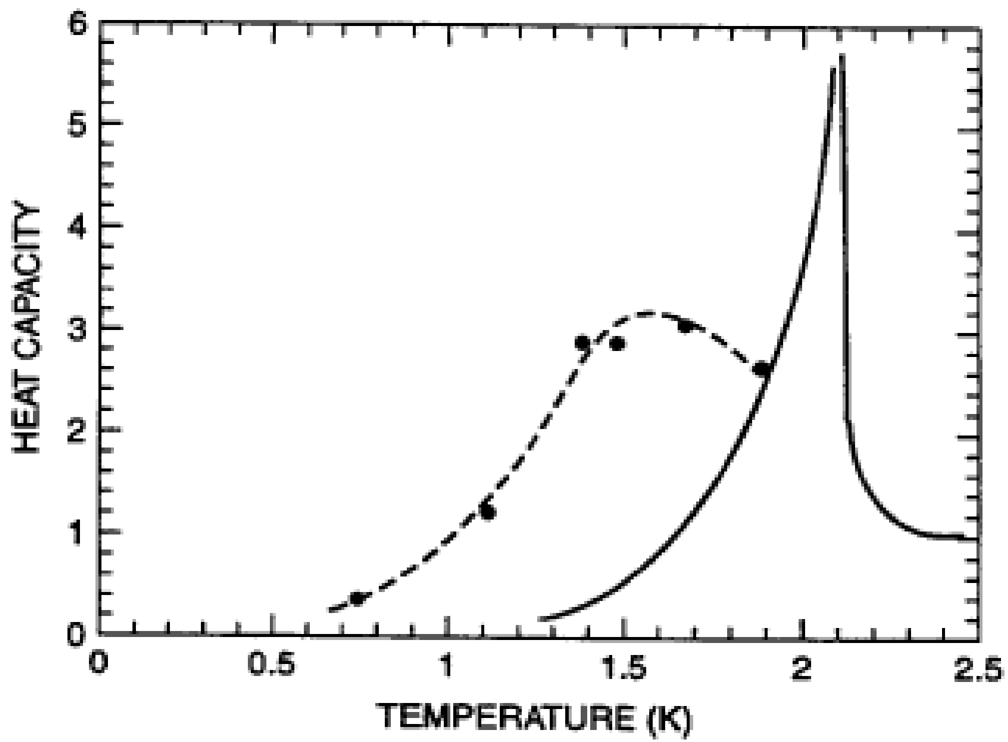


Figure 4.23. Specific heat versus temperature for liquid helium (solid line) and a liquid consisting of clusters of 64 helium atoms (dark circles). The peak corresponds to the transition to the superfluid state. [Adapted from P. Sindzingre, *Phys. Rev. Lett.* 63, 1601 (1989).]

4.4.3. Molecular Clusters

Individual molecules can form clusters. One of the most common examples of this is the water molecule. It has been known since the early 1970s, long before the invention of the word *nanoparticle*, that water does not consist of isolated H_2O molecules. The broad Raman spectra of the O–H stretch of the water molecule in the liquid phase at 3200–3600 cm^{-1} has been shown to be due to a number of overlapping peaks arising from both isolated water molecules and water molecules hydrogen-bonded into clusters. The H atom of one molecule forms a bond with the

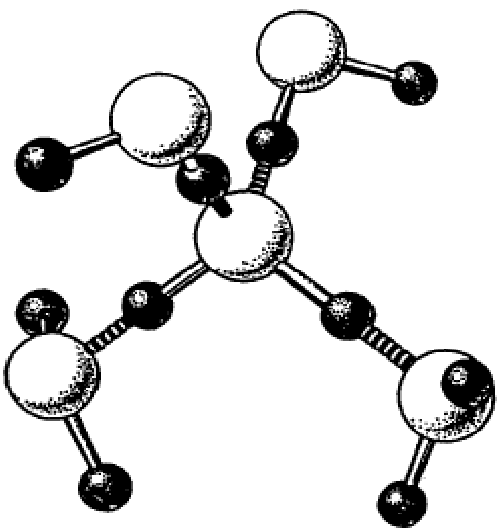


Figure 4.24. A hydrogen-bonded cluster of five water molecules. The large spheres are oxygen, and the small spheres are hydrogen atoms.

4.5 Method of Synthesis

- 1. RF Plasma
- 2. Chemical Methods
- 3. Thermolysis
- 4. Pulsed Laser Methods

4.5.1 RF Plasma

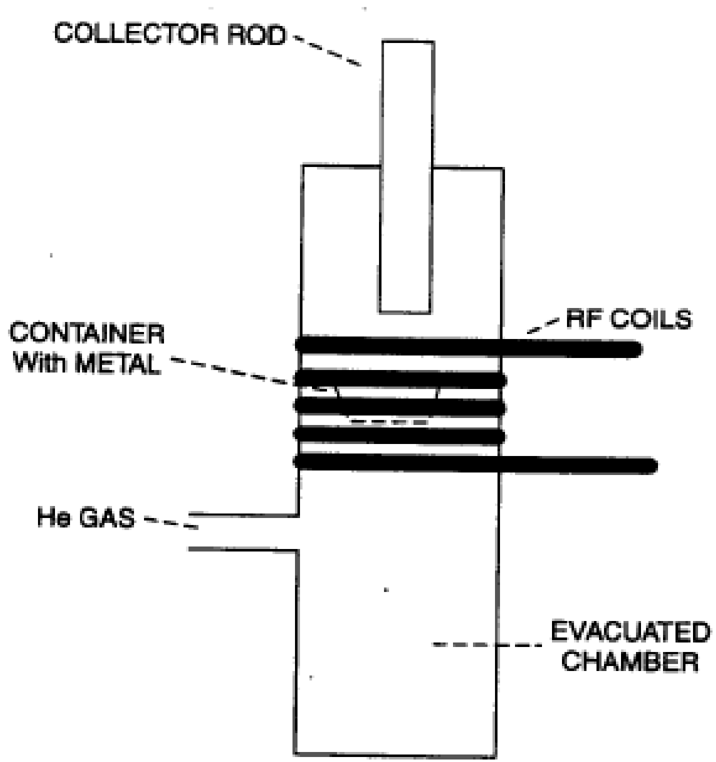


Figure 4.25. Illustration of apparatus for the synthesis of nanoparticles using an RF-produced plasma.

4.5.2 Chemical Method

Reducing agents

$$MoCl_3 + 3NaBEt_3H \Rightarrow Mo + 3NaCl + 3BEt_3 + (3/2)H_2 \qquad (4.9)$$

4.5.3. Thermolysis(Thermal decomposition)

LiN_3-> Li

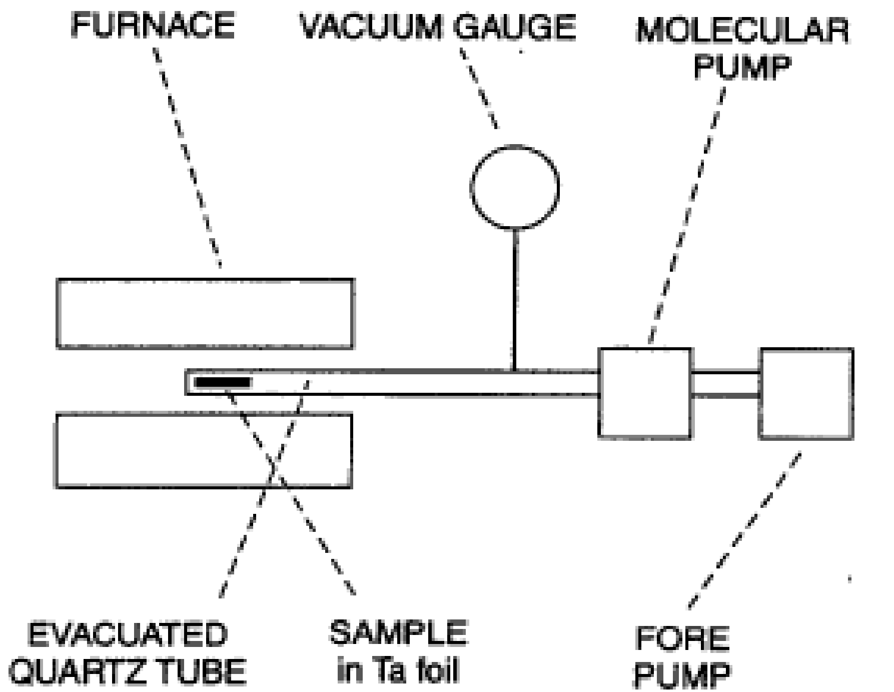


Figure 4.26. Apparatus used to make metal nanoparticles by thermally decomposing solids consisting of metal cations and molecular anions, or metal organic solids. (F. J. Owens, unpublished.)

Electron paramagnetic resorance (EPR)

- EPR measures the energy absorbed when electromagnetic radiation such as microwave induces a transition between the spin states m_s split by a DC magnetic field.

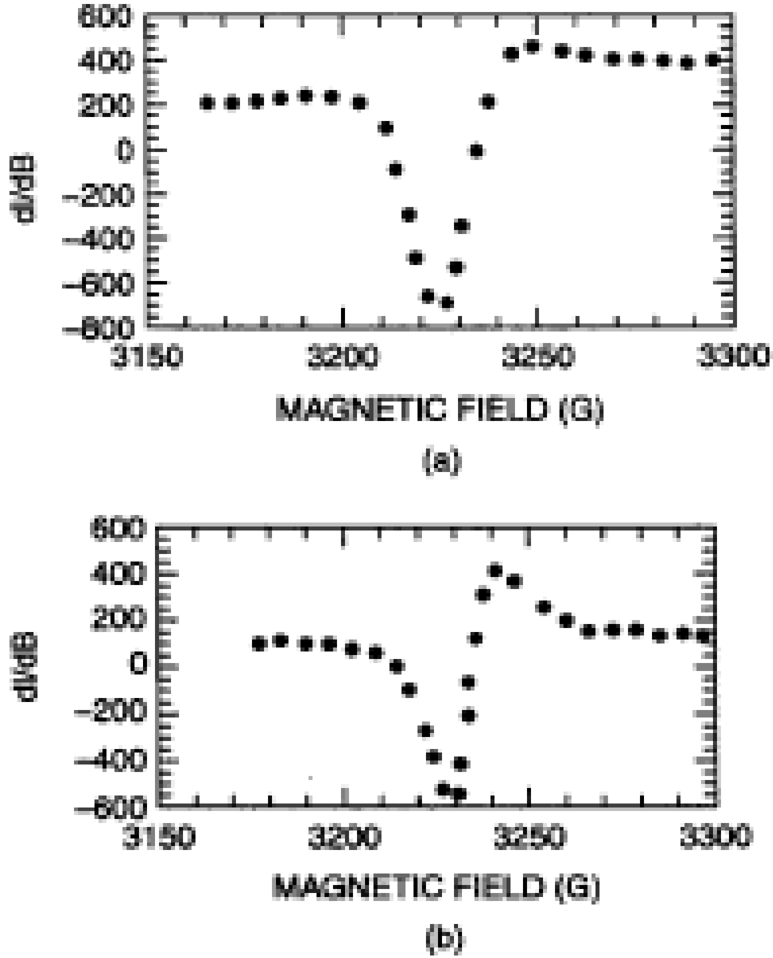


Figure 4.27. Electron paramagnetic resonance spectra at 300 K (a) and 77 K (b) arising from conduction electrons in lithium nanoparticles formed from the thermal decomposition of LiN_3. (F. J. Owens, unpublished.)