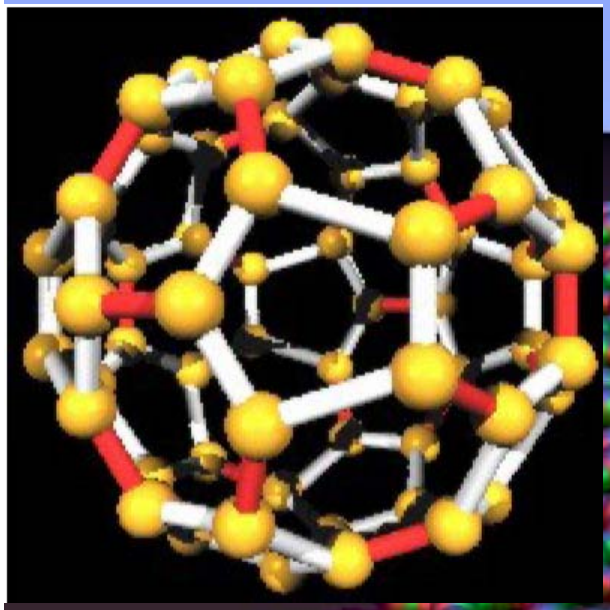
Carbon nanostructures

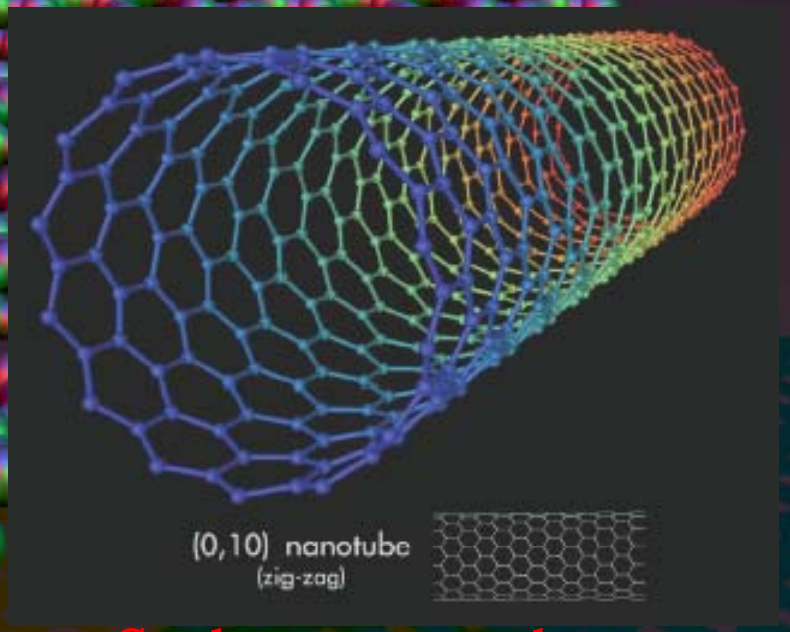
-TIGP course Dec. 2007

Wei-Li Lee, IoP, Academia Sinica



Fullerene

Graphene



Carbon nanotube

Course agenda

-TIGP course on carbon nanostructure

Dec. 15th - Lecture I : 0D system, carbon-based buckyballs (fullerene)

Dec. 22st - Lecture II : 2D system, emerging material : graphene

Dec. 29th - Lecture III : 1D system, carbon nanotube

Jan. 5th at 3 pm : **Study group oral presentation**

Jan. 12th - Final exam

Guideline

-TIGP course on carbon nanostructure

Lecture - Monday 2pm - 5pm

20 minutes break from 3:20pm to 3:40 pm

Study group – 2-3 people a group

each person, 15 minutes oral presentation, 5 for questions

4 topics :

0D system : Practical application of fullerene
1D system : Recent progress of carbon nanotube composites as a space elevator
2 D system : Graphene electronics : advantage and disadvantage
3D system : Quantum information using diamond nanocrystals

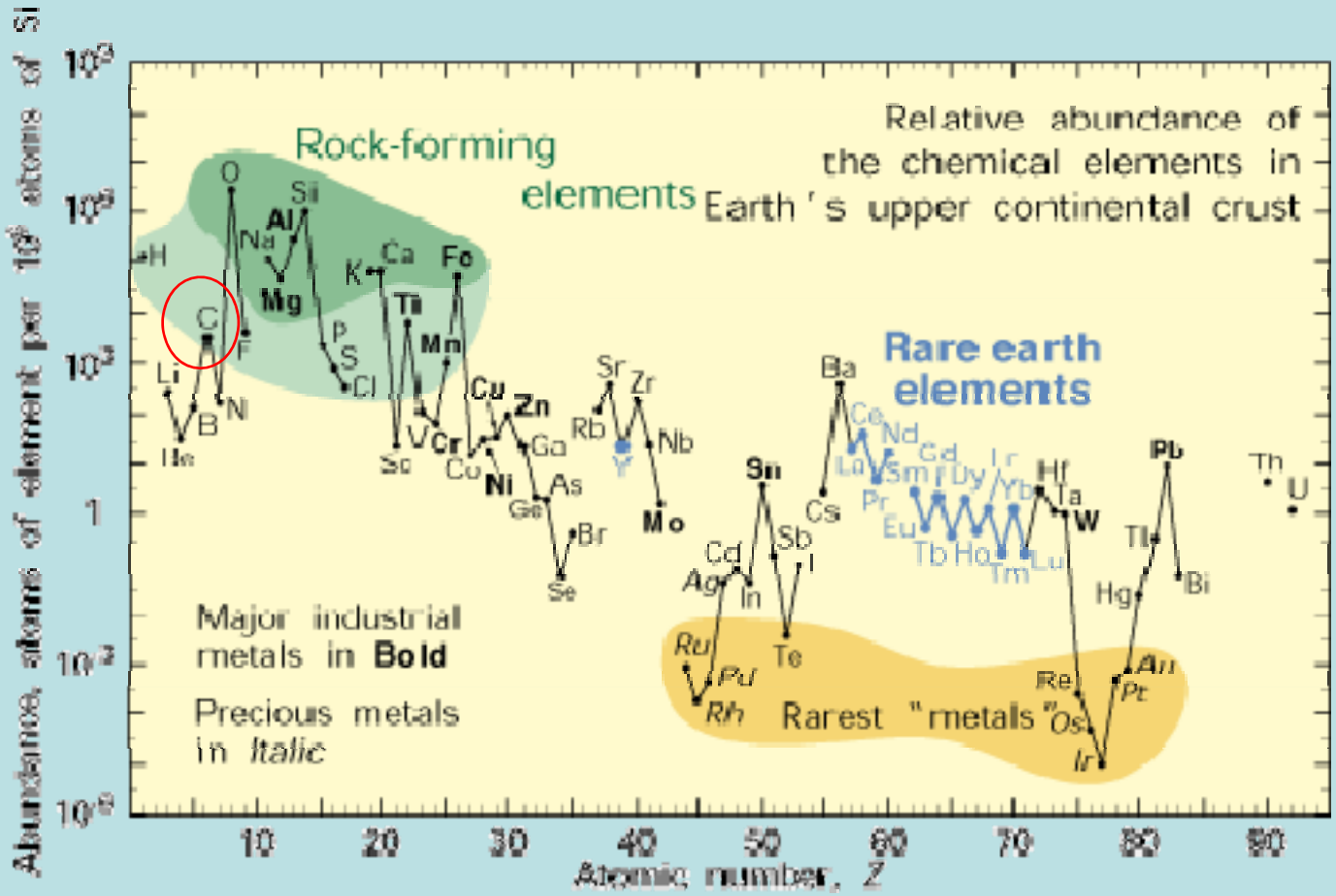
Reference Books:

Introduction to Nanotechnology by Poole and Owens

Science of Fullerenes and carbon nanotubes by Dresselhaus and Eklund

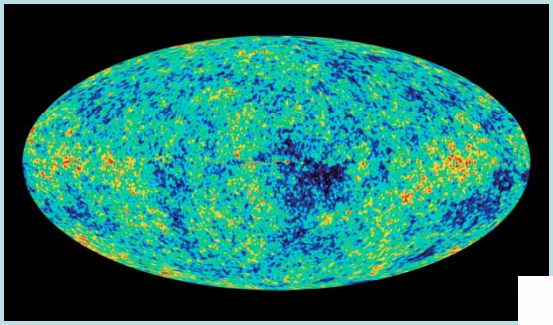
Solid state Physics by Ashcroft/ Mermin

Welcome to Carbon World !!

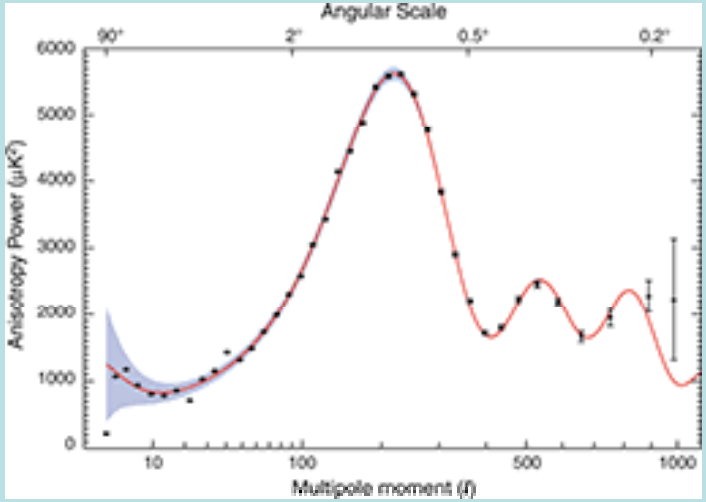


Wilkenson Microwave Anisotropy Probe

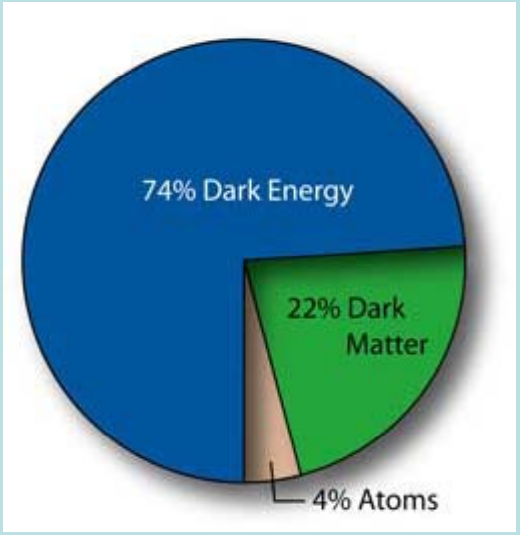
WMAP image of CMB (3 Kelvin)

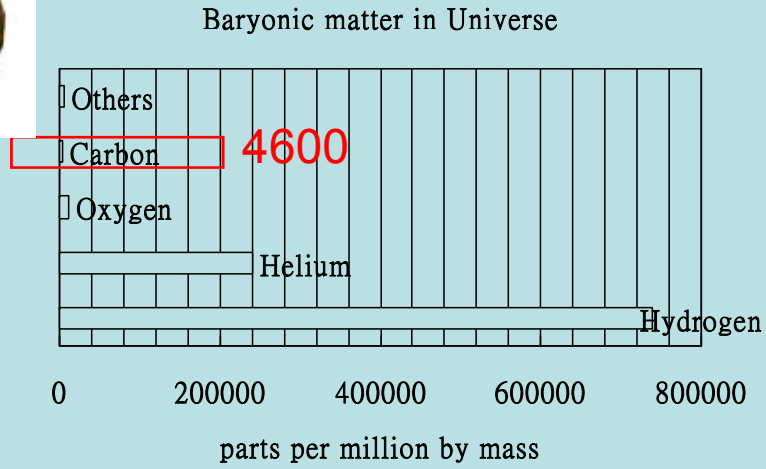


Angular spectrum



WMAP

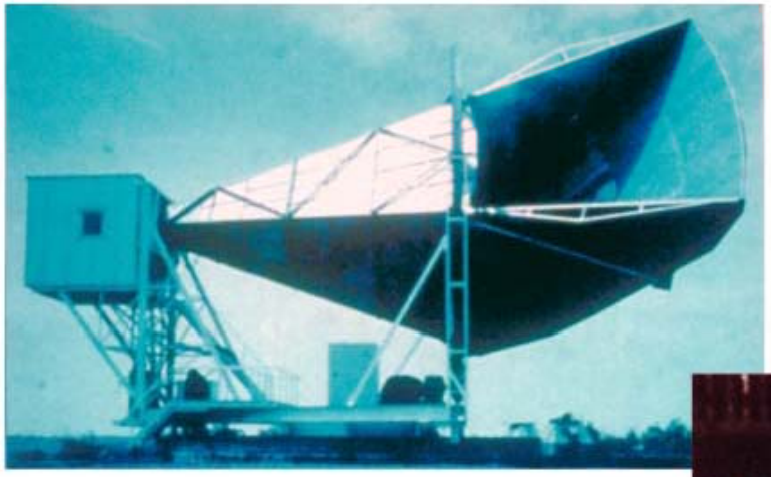




The Nobel Prize in Physics 1978

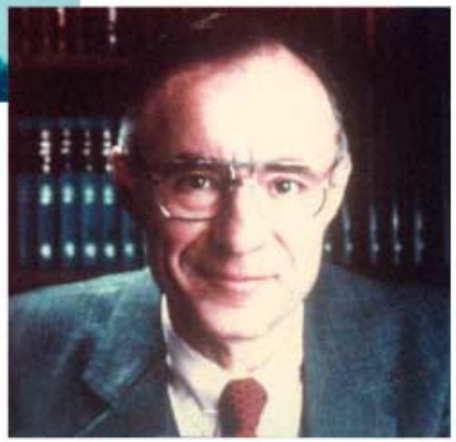
"for their discovery of cosmic microwave background radiation"

Discovery of Cosmic Background



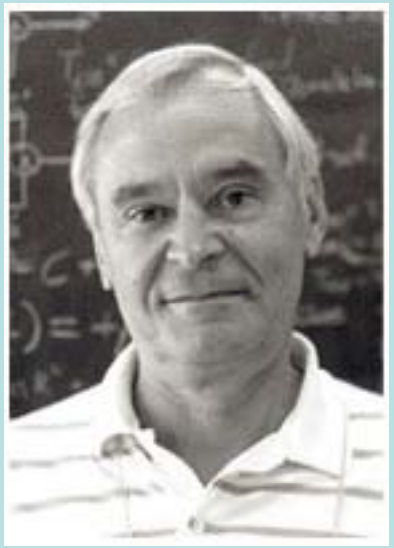
Microwave Receiver

Robert Wilson

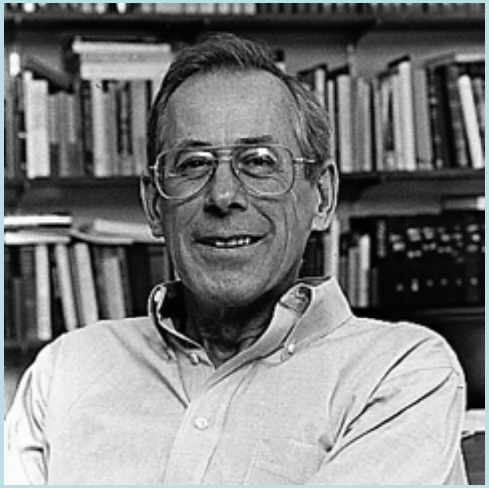


Arno Penzias

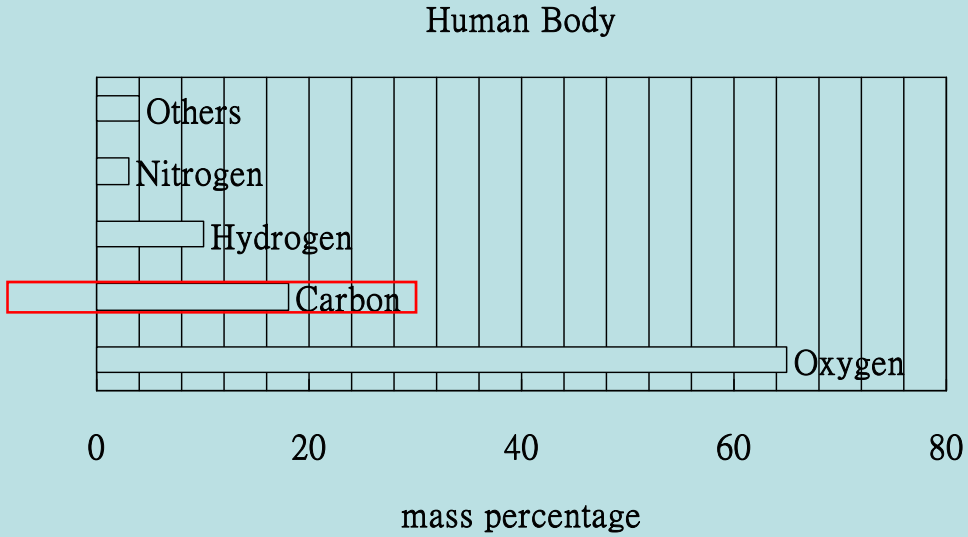
MAP990045

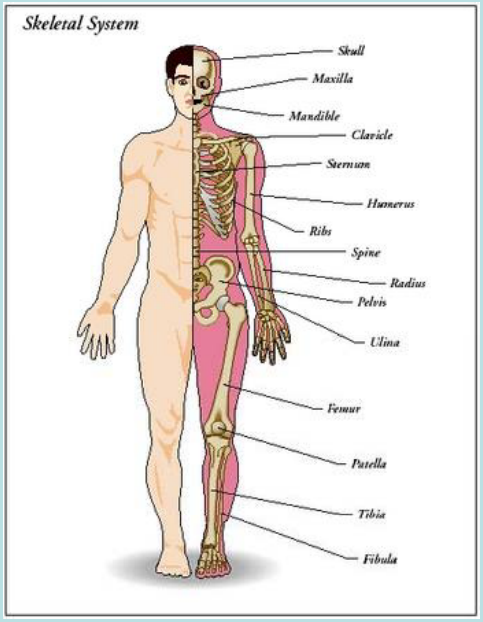


Dave Wilkinson



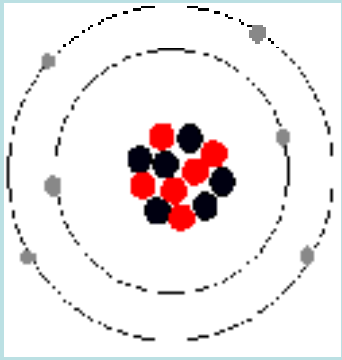
James Peebles


Human Body
Others
Nitrogen
Hydrogen
Carbon
Oxygen
0
20
40
60
80
mass percentage


Skeletal System
Skull
Maxilla
Mandible
Clavicle
Sternum
Humerus
Ribs
Spine
Radius
Pelvis
Ulina
Femur
Patella
Tibia
Fibula

Carbon Bond : hybridized orbitals

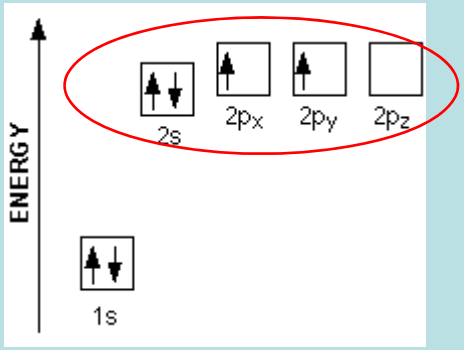
- Carbon : atomic number 6, $1s^2$ [$2s^2$ $2px^1 2py^1$]

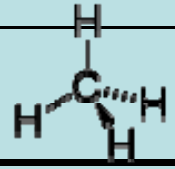


Molecular orbital :

$$\psi_j = \sum_i C_{ij} X_i$$

X_i : atomic orbitals



	Orbitals used for bond	Shape & bond angle	Examples:	
Sp	s, px	Digonal 180°	C_2H_2 Acetylene	H—C≡C—H
Sp^2	s, px, py	Trigonal 120°	Graphite, C_2H_4 Ethylene	
sp^3	s, px, py, pz	Tetrahedra 109°28’	Diamond, CH_4 Methane	

Allotropic forms in solid carbon

- **Many stable and known forms at R.T.**

Examples: diamond, graphite, amorphous carbon, fullerene, carbon nanotube and nanobud…etc

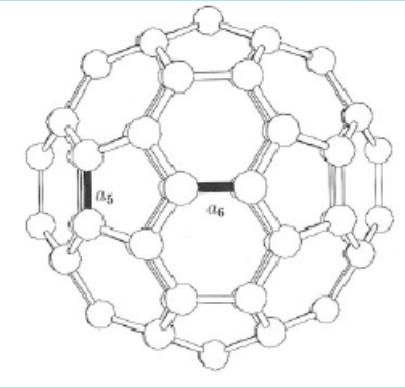
- **Two main structures :** one with sp^3 hybrid bonds (diamond) and the other with sp^2 hybrid bonds (graphite, fullerene, nanotube and nanobud)

- Dramatic different properties between diamond and graphite

	Diamond	**Graphite**
Electric	Insulator	Conductive
Hardness	10 (Mohs scale)	1-2
Appearance	Transparent	Opaque (black)
Value	Expensive	cheap

Structure of C_{60}

- European Football like molecule containing 60 carbons
  - 12 pentagonal and 20 hexagonal faces
  - Double bond length 1.4 Å and single bond 1.46 Å
- Named after architect R. Buckminster Fuller (1895-1983)



Geodesic dome

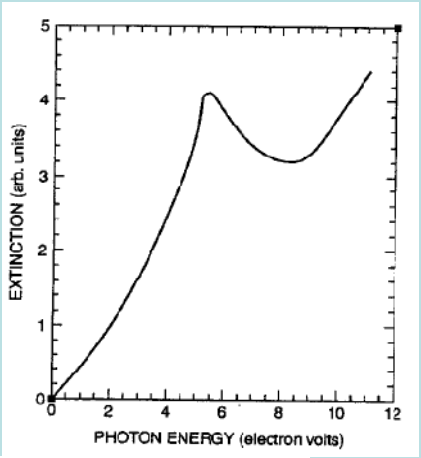
- Geometrically-allowed fullerene C_{20+h*2}

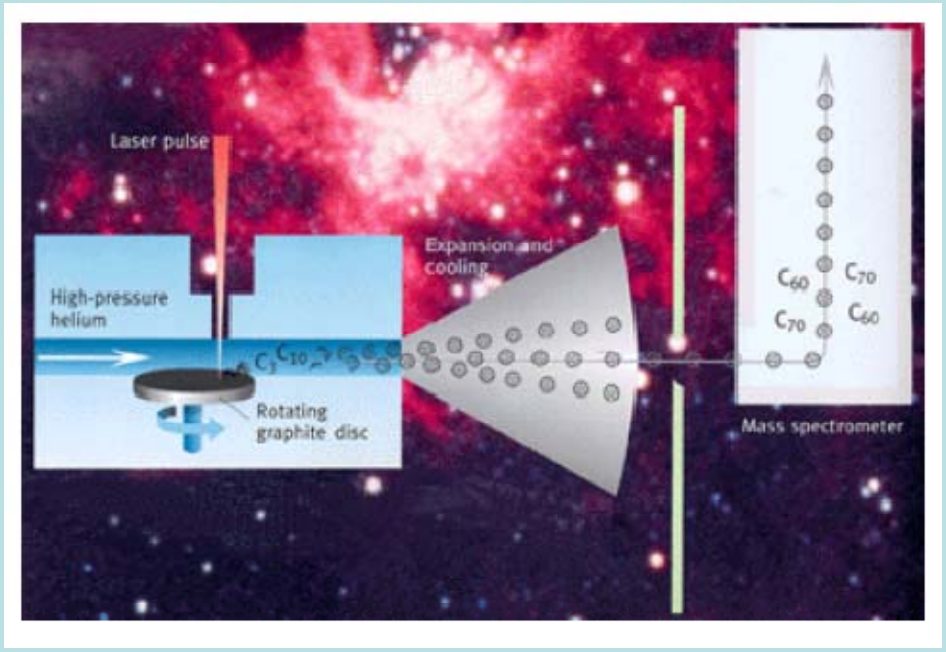
12 pentagonal faces + arbitrary number of hexagonal faces (h)

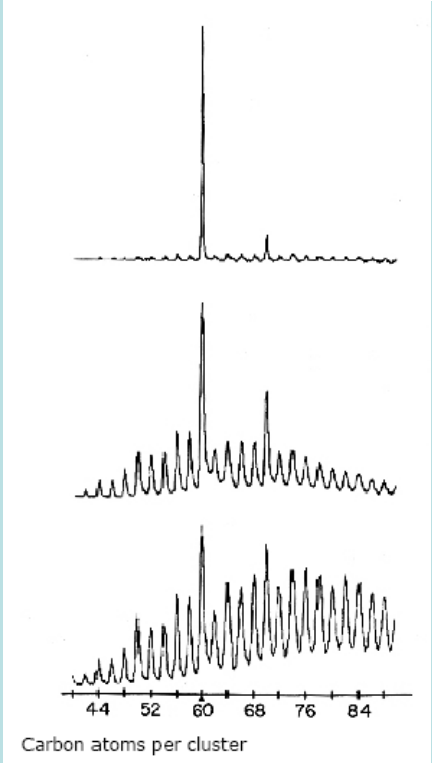
- Smallest Fullerene C_{20}
- Smallest isolated (stable) Fullerene C_{60}

Discovery of Fullerene C_{60}

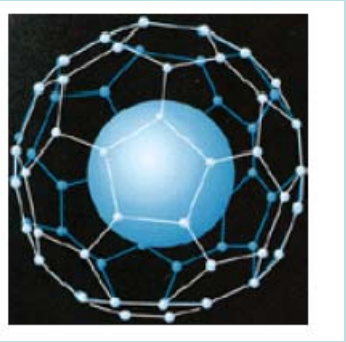
- "An idea from outer space" : 5.6 eV optical extinction
- Robert Kurl, Harold Kroto and Richard Smalley
  -- Nobel Prize laureates in Chemistry 1996



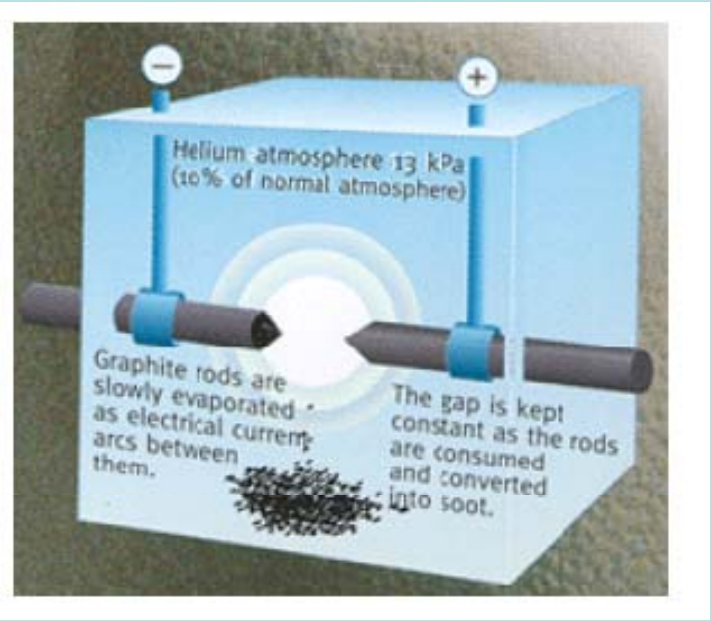


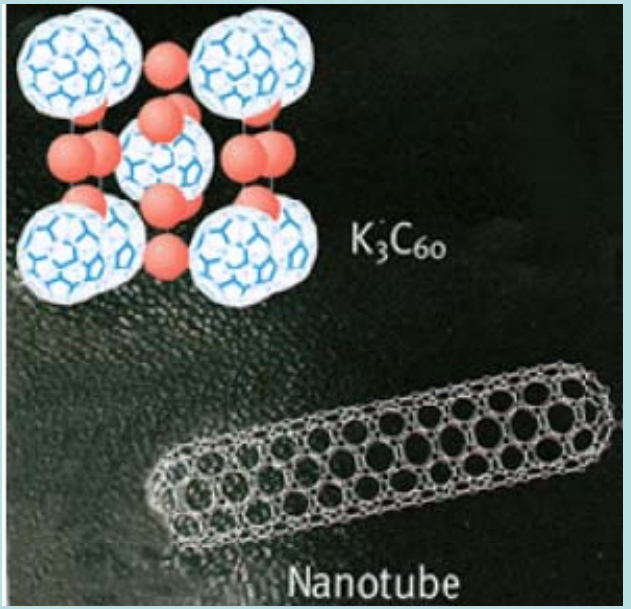


Development of Fullerene

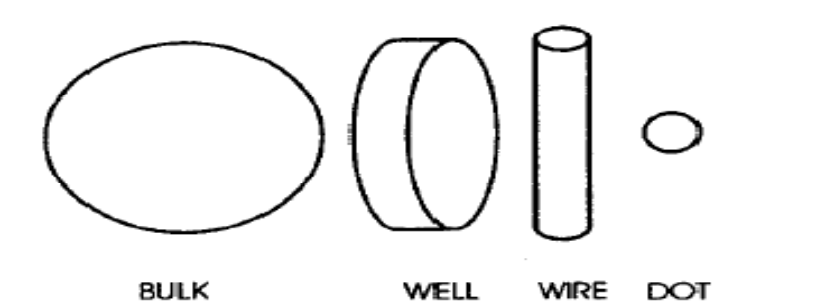


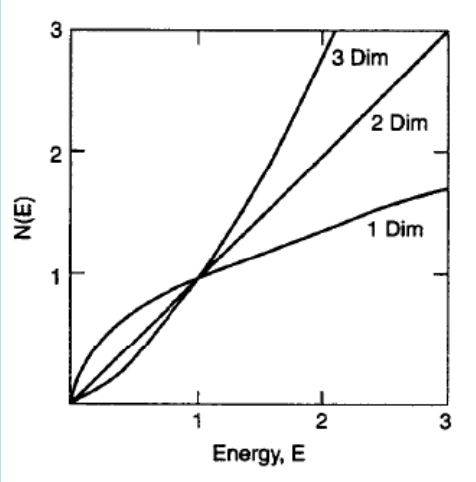
- Carbon ball with a metal core
- Mass production of Fullerene by astrophysicists D. R. Huffmann and W. Krätschmer
- Carbon nanotube – special electric and mechanical properties
- New superconducting crystals M_3C_{60}





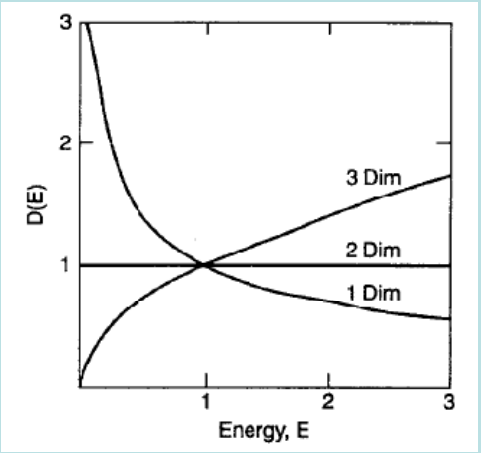
Effect of size and dimensionality on electronic property





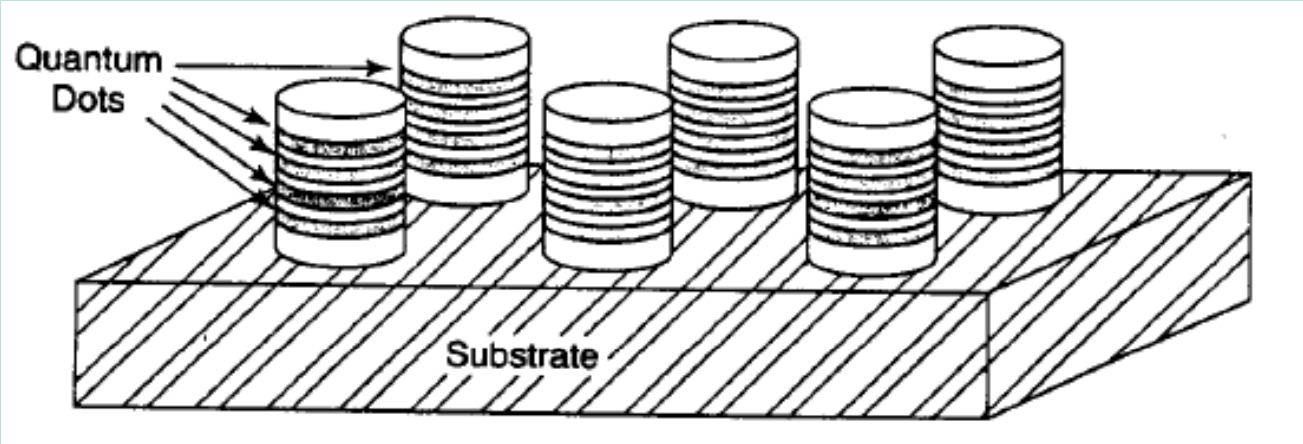
Type	Number of Electrons $N(E)$	Density of States $D(E)$	Dimensions: Delocalized	Dimensions: Confined
Dot	$N(E) = K_0 \sum d_i \Theta(E - E_{iW})$	$D(E) = K_0 \sum d_i \delta(E - E_{iW})^2$	0	3
Wire	$N(E) = K_1 \sum d_i (E - E_{iW})^{1/2}$	$D(E) = \frac{1}{2} K_1 \sum d_i (E - E_{iW})^{-1/2}$	1	2
Well	$N(E) = K_2 \sum d_i (E - E_{iW})$	$D(E) = K_2 \sum d_i$	2	1
Bulk	$N(E) = K_3 (E)^{3/2}$	$D(E) = \frac{3}{2} K_3 (E)^{1/2}$	3	0

[a]The degeneracies d_i of the confined (square or parabolic well) energy levels depend on the particular level. The Heaviside step function $\Theta(x)$ is zero for $x < 0$ and one for $x > 0$; the delta function $\delta(x)$ is zero for $x \neq 0$, infinity for $x = 0$, and integrates to a unit area. The values of the constants K_1, K_2, and K_3 are given in Table A.3 of Appendix A.



0-D quantum dot : an artificial atom

- quasi-0D system : d < ℓ_{mfp}



- Discrete energy level resembles the atomic level of a free atom
  - ex : 3-D infinite rectangular square well

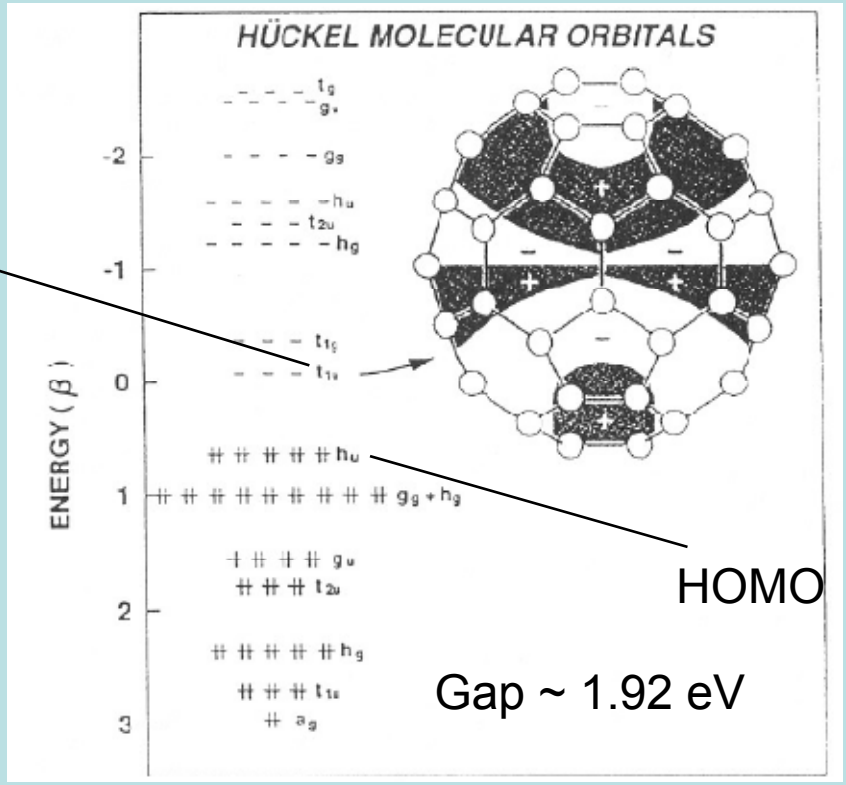
$$E_n = (\frac{\pi^2\hbar^2}{2ma})(n_x^2 + n_y^2 + n_z^2) = E_0 n^2$$

Quantum number = 0,1,2…

6 degeneracy (including spin) at ground state level E_o

Molecular orbital levels of a "free" C_{60}

- Shell model in a free fullerene : symmetry-based model
- 60 πelectrons filling the molecular level



π energy states (in eV) of the C_{60} phenomenological Hamiltonian model.

ℓ	Symmetry	Model[a]	*Ab initio*[b]
0	a_g	−7.41	−7.41
1	f_{1u}	−6.87	−6.87
2	h_g	−5.87	−5.82
3	f_{2u}	−4.40	−4.52
	g_u	−4.13	−3.99
4	h_g	−2.21	−2.44
	g_g	−2.12	−2.37
5	h_u	−0.20	−1.27
	f_{1u}	0.88	0.62
	f_{2u}	1.82	2.71
6	f_{1g}	3.38	1.59
	h_g	3.43	2.78
	g_g	4.92	4.60
⋮	⋮	⋮	⋮

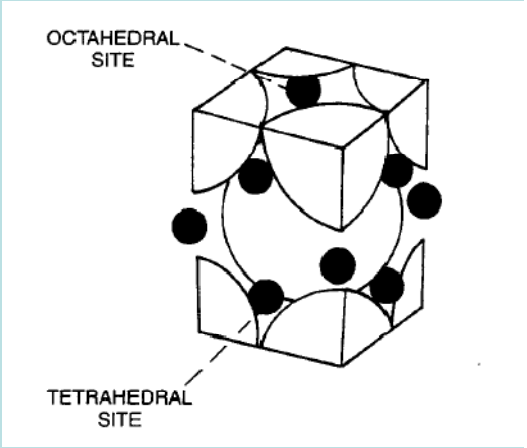
- Free C60 molecule should be a good insulator

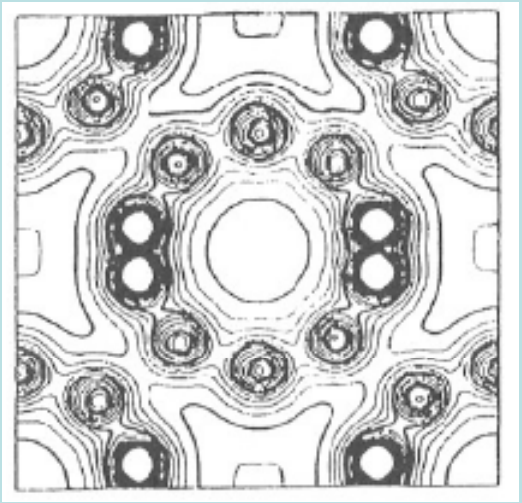
Band structure of solid C_{60}

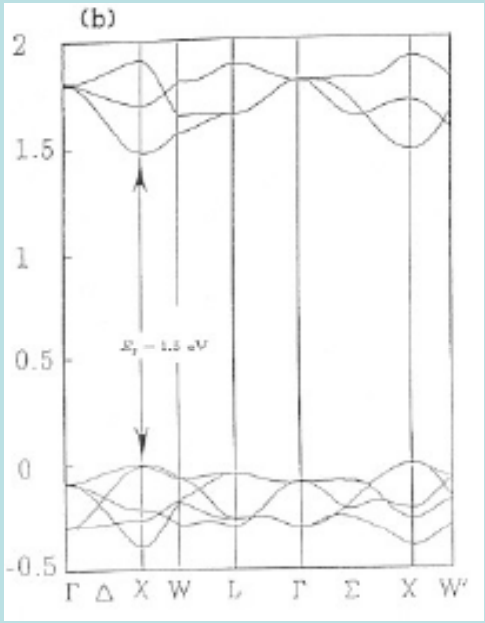
- Molecular crystal : BCC stacking structure
- Grown by slow evaporation from benzene solution

  filled with C60 molecules
- Band calculation :

  LDA + Gaussian orbital basis set
- Useful information :
  - ➢ Insulator with direct band gap ~ 1.5 eV band width ~ 0.4 eV
  - ➢ charge density map suggest weak coupling b/w fullerene molecule

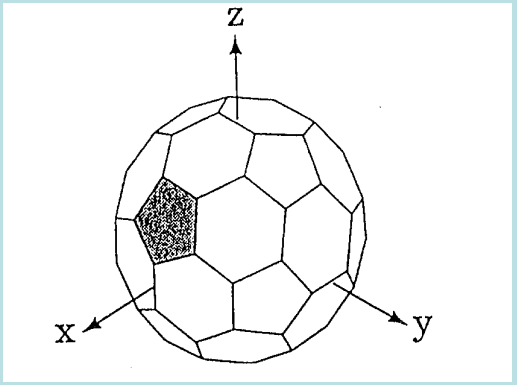




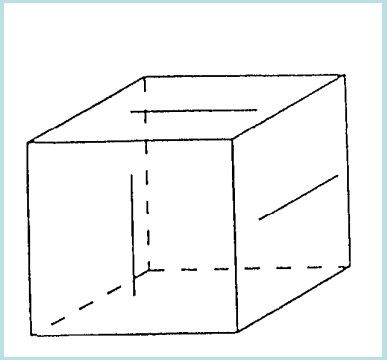


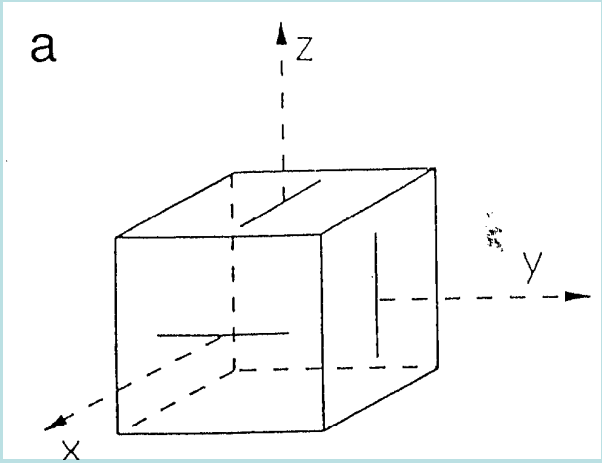
Symmetry consideration and Merohedral disorder in C_{60}

- Two standard orientations of fullerene molecule



Two fold sym. axis

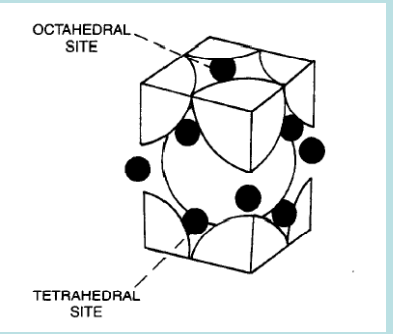




Two standard orientations

- Merohedral disorder : random choice b/w one of the two possible standard orientations (lack of four fold symmetry point)
  - ➢ relative orientation b/w adjacent C_{60} can affect its physical properties.

Doping Buckyball solid : M_xC_{60}



- Transport charges from doping alkali metal element M
- Two competing process due to doping effect:
  - decrease of C_{60} wave func. overlap
  - increase of the D.O.S
- Best conductivity occurs at x ~ 3 (half filled band)

-available sites (octahedral and tetrahedral) all filled

- undoped fullerene ρ_{300K}~ 10^8 Ωcm
- Single crystal K_3C_{60} ρ_{300K} ~ 5 mΩcm
- Strongly correlated electronics system
  - $k_F\ell$ <1 , one electron model may fail
  - from photo emission, large Hubbard U (1-2 eV)

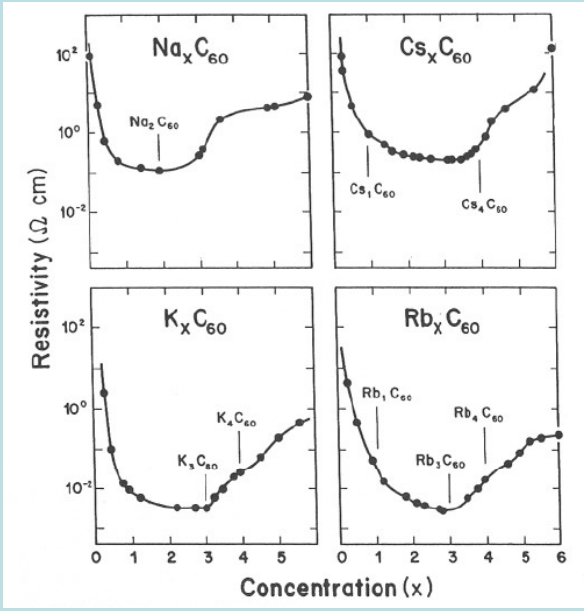


Table 14.1

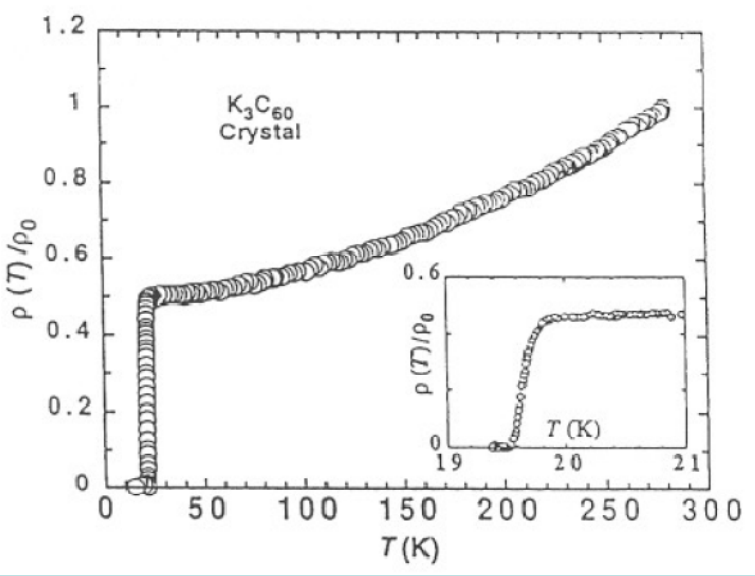
Physical constants for M_3C_{60} (M = K, Rb).

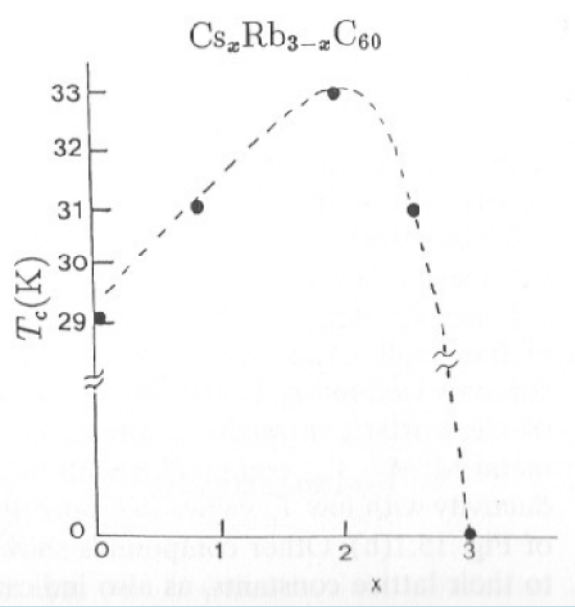
Quantity	K_3C_{60}	Rb_3C_{60}	Reference
Space group	$Fm\bar{3}$	$Fm\bar{3}$	[14.10]
C_{60}—C_{60} distance (Å)	10.06	10.20	[14.10]
M-C_{60} closest distance (Å)	3.27	3.33	[14.10]
Volume per C_{60} (cm^3)	7.22×10^{-22}	7.50×10^{-22}	[14.10]
fcc lattice constant a (Å)	14.253	14.436	[14.11]
$(-d \ln a/dP)$ (GPa^{-1})	1.20×10^{-2}	1.52×10^{-2}	[14.12]
Bulk modulus (GPa)	28	22	[14.13]
Thermal expansion coefficient (Å/K)	2×10^{-5}	—	[14.10]
Cohesive energy (eV)	24.2	—	[14.13]
Heat of formation (eV)	4.9	—	[14.13]
Density of states[a] [states/(eV/C_{60})]	25	35	[14.14]
Carrier density[a] ($10^{21}/cm^3$)	4.155	4.200	[14.10]
Electron effective mass (m_e)	1.3	—	[14.13]
Hole effective mass (m_e)	1.5, 3.4	—	[14.13]

[a] Assumes 3 electrons per C_{60}.

Superconductivity in M_3C_{60}

- Discovered in K_3C_{60} by Hebard (Bell lab, 1991) $T_c \sim 19.8$ K
- Highest Tc ~ 33K in Cs_2RbC_{60}
- The larger the radius of the dopant alkali atom the higher the T_c



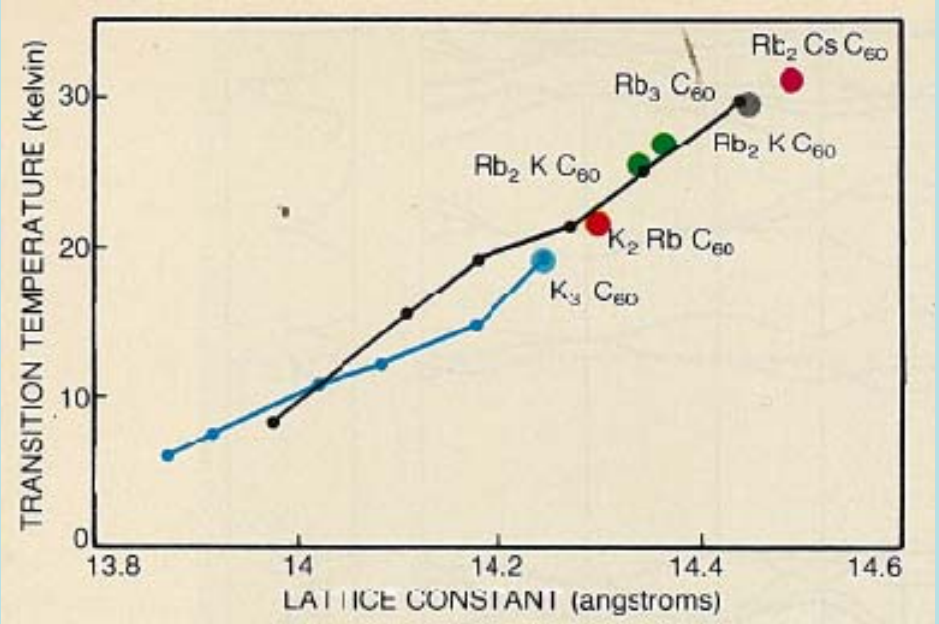


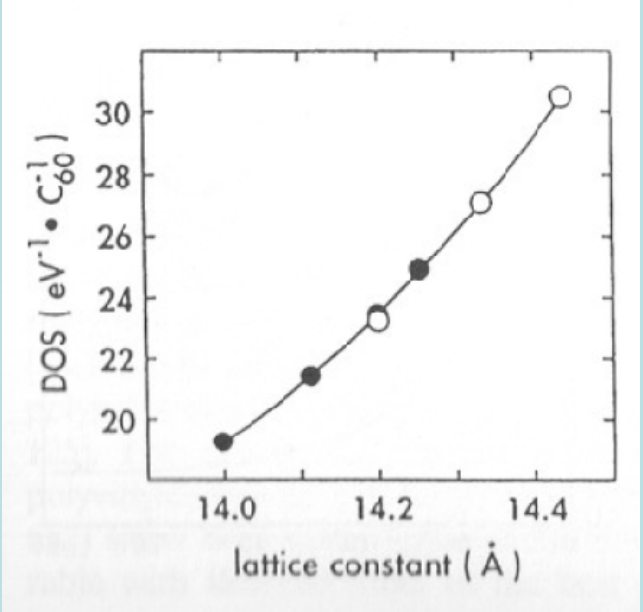
Bardeen-Cooper-Schrieffer Theory

- In weak-coupling limit (ʎ <<1)

$$k_B T_c = 1.13\hbar\omega_D \exp[-1/\lambda],\ \lambda \equiv N(E_F)V$$

$$\lambda : \text{dimentionless e-phonon coupling parameter}$$

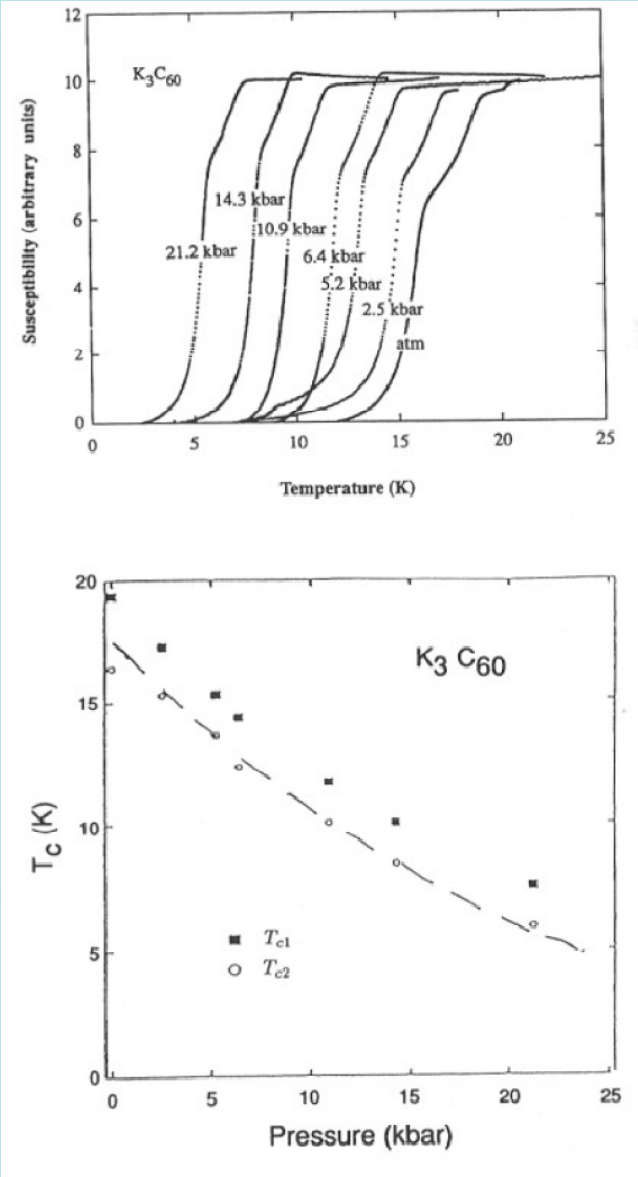




- Increase in lattice spacing reduced overlap of molecular orbital

⇨ reduced band width and increased D.O.S. $N(E_F)$

Pressure dependence of Tc



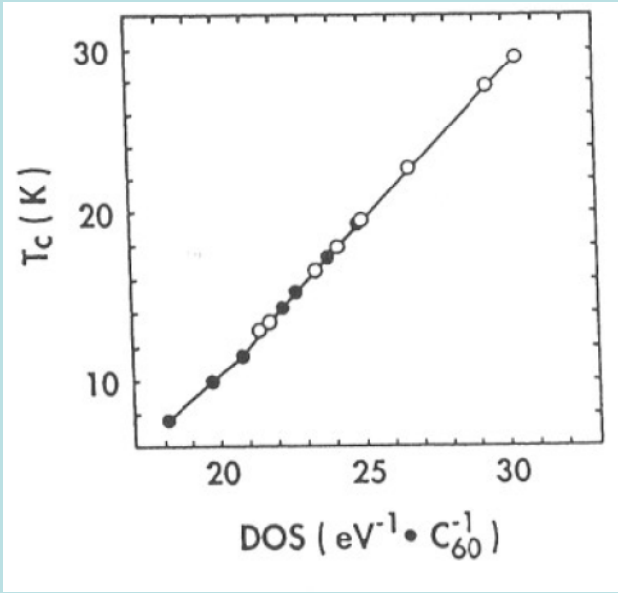
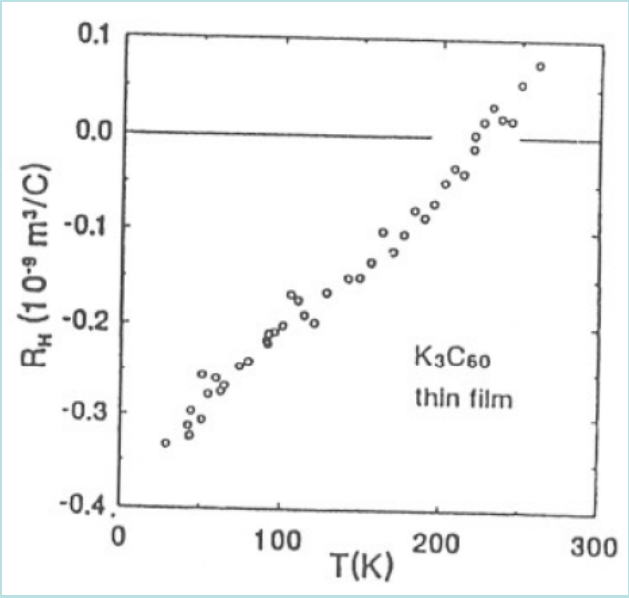
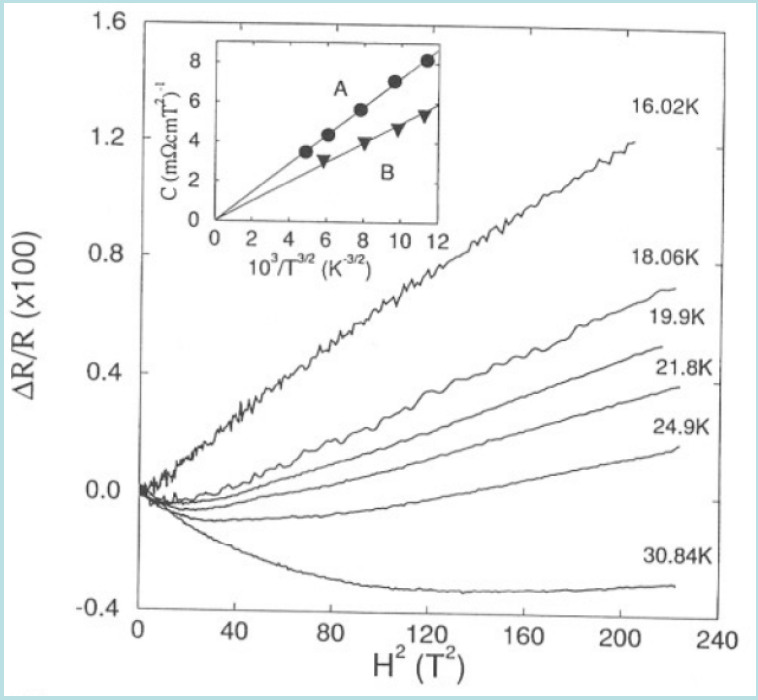


Fig. 15.3. Dependence of T_c on the density of states at the Fermi level for K_3C_{60} (closed circles) and Rb_3C_{60} (open circles) [15.22] using pressure-dependent measurements of T_c on these compounds [15.17, 23].

Other properties in K_3C_{60}

- Hall coefficient : $R_H = 1/ne$
  - ✓Sign change at 200K
  - ✓Both electron and hole like pockets





- Transverse magnetoresistance :

$$\frac{\Delta\rho}{\rho_0} = \frac{\Delta\rho_C}{\rho_0} + \frac{\Delta\rho_{L,I}}{\rho_0}$$

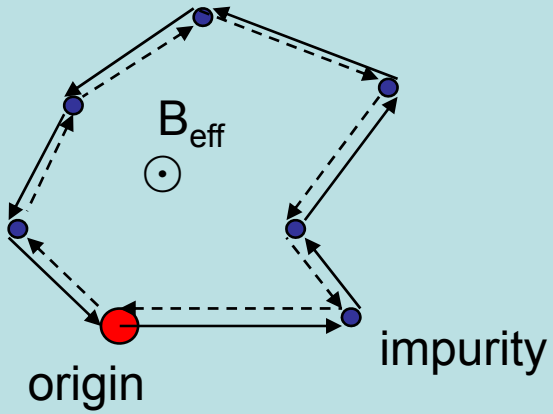
Classical orbital contribution : positive and quadratic in H

Weak localization and e-e interaction:

Negative, H^2 at low H and $H^{1/2}$ in high H

Weak localization in disordered system

- Appeared In disordered and time reversal symmetric system
- Negative MR : Strongly suppressed by applying magnetic field
- Merohedral disorder and also missing alkali ion at the tetrahedral and octahedral sites

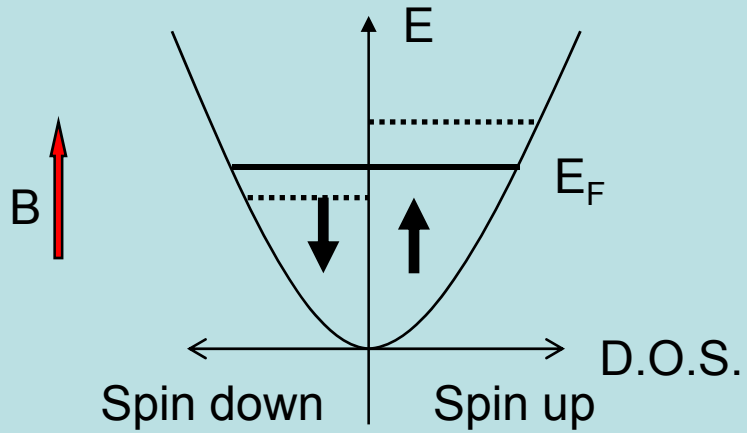


Constructive $|2A|^2$ ⇨ localization

$$\int B \cdot dA = \oint A \cdot d\ell : \text{additional phase change}$$

Experimental determination of D.O.S.

(I) Pauli susceptibility



$$n_{\uparrow} = \int d\varepsilon \frac{1}{2} N(\varepsilon + \mu_B H) f(\varepsilon)$$

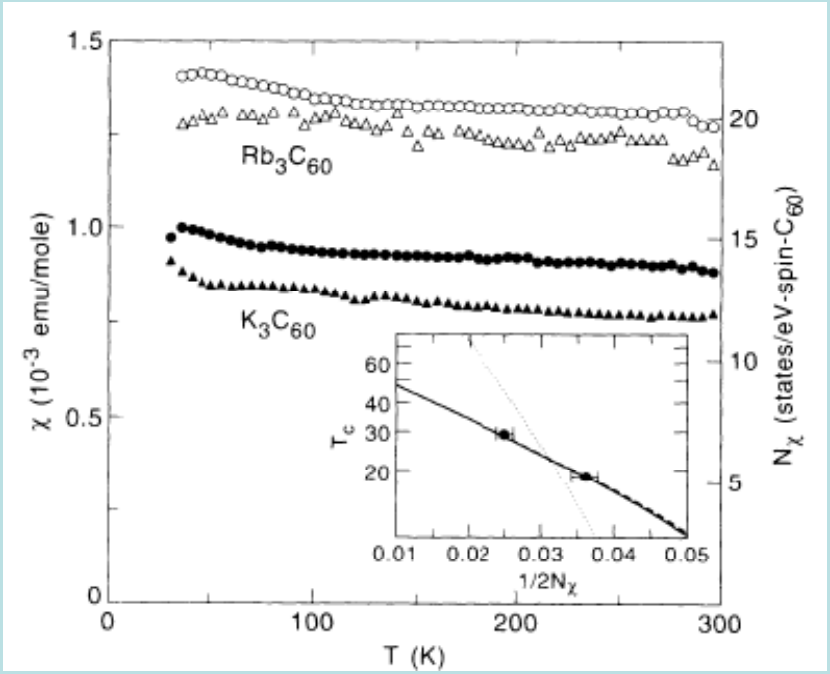
$$M = \mu_B (n_{\uparrow} - n_{\downarrow})$$

$$\chi_P = \mu_B^2 N(E_F)$$

- D.O.S. :

  K_3C_{60} : 28 states/eV-C60

  Rb_3C_{60} : 38 states/eV-C60



(II) Specific Heat

- In crystals with free electron gas model at low T

$$C = C_e + C_p$$

$$C_e = \left[\frac{\pi^2}{3} k_B^2 N(\varepsilon_F)\right] T\,, \quad C_p = \frac{12\pi^4}{5} n_i k_B \left(\frac{T}{\theta_D}\right)^3$$

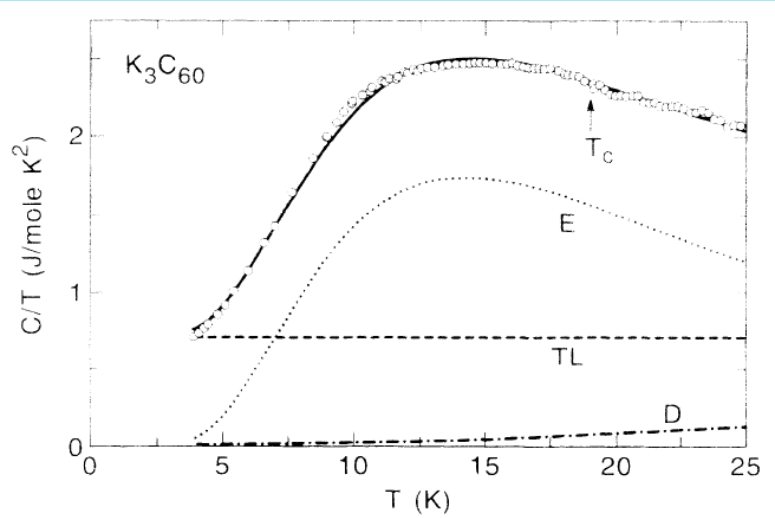
- In amorphous system and also fullerene solids at low T

  ⇨ Einstein mode (1907) plays an important role

$$C = C_e + C_p + C_E$$

$$C_E = p n_i k_B \frac{(\hbar\omega_E / k_B T)^2 e^{\hbar\omega_E / k_B T}}{(e^{\hbar\omega_E / k_B T} - 1)^2}$$

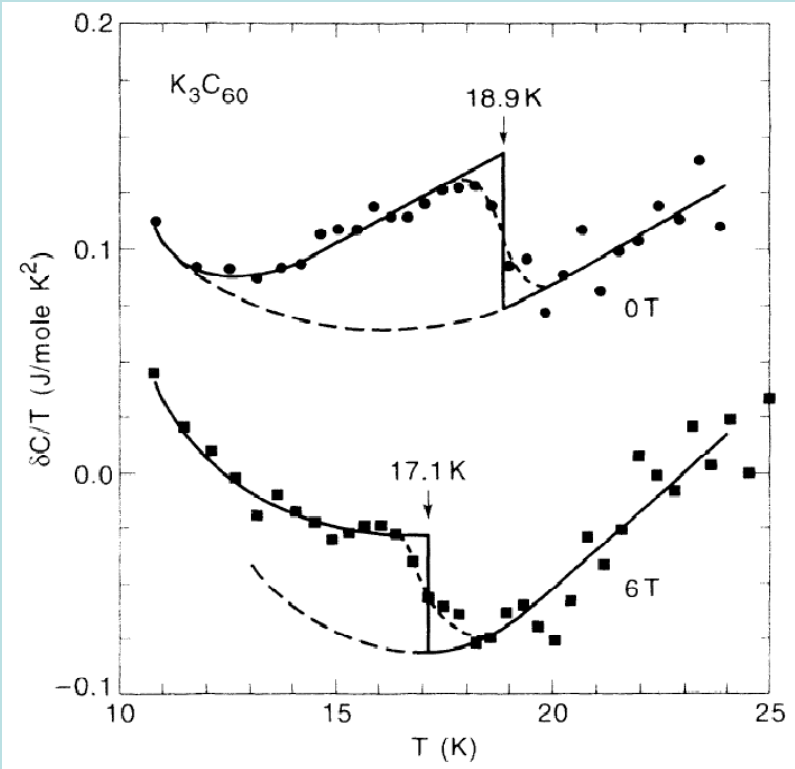
(II) Specific Heat



E : Einstein term ⇨ inter(intra)-molecule vibration modes with θ_E~ 34K

D : Debye term gives θ_D ~70K

TL : electronic term



• From BCS theory :

$$\left[\frac{C_{\text{sup.}} - C_{norm.}}{C_{norm}}\right]_{T_C} = 1.43$$

$N(E_F)$ ~ 12 states /eV-C_{60}

⇨ 3 fold smaller than that from Pauli susceptibility measurement

Many-body effect and spin fluctuation enhancement in χ_{pauli} measurement

(III) Thermopower

- Current density

$$\vec{J}_e = \sigma \vec{E} + \vec{\vec{\alpha}}(-\nabla T)\ ,\ \alpha : \text{peltier cond. tensor,}$$

turn on $-\nabla_x T$, and in steady state $J_x = J_y = 0$, $-\nabla_y T = 0$,

assume isotropic ,

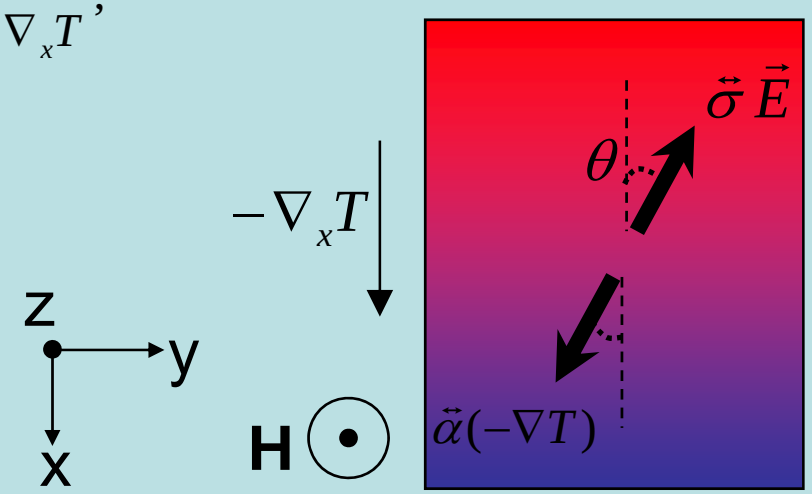
$$\Rightarrow \quad \text{Thermopower } S \equiv \frac{E_x}{\nabla_x T} = \frac{\alpha_{xx}}{\sigma},$$

$$e_N = \rho\alpha_{xy} - \rho S\sigma_{xy}, \quad \text{Nernst signal } e_N \equiv \frac{E_y}{-\nabla_x T},$$

- Sign convention of S

  Positive for hole like carrier

  Negative for electron-like



(III) Thermopower

• Semiclassical theory

$$S_d = -\frac{\pi^2}{2}\frac{k_B}{e}\left(\frac{k_B T}{\varepsilon_F}\right), \text{ linear in T}$$

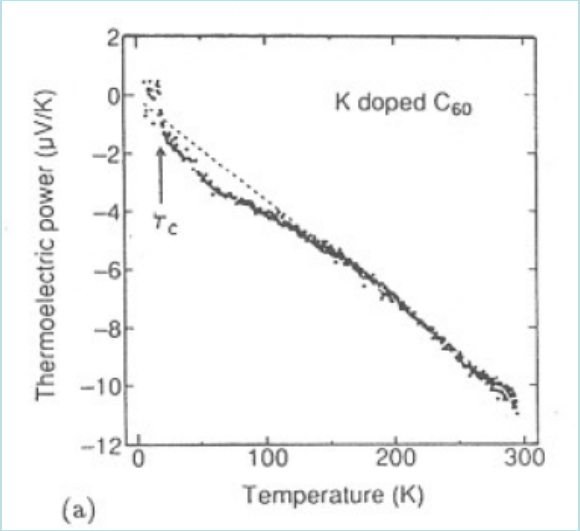
• Determination of E_F from the slope dS/dT

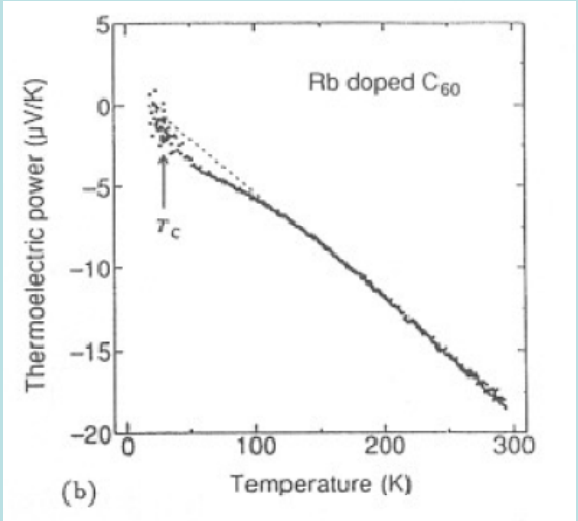
K_3C_{60} : E_F ~ 0.32 eV ⇨ 5 states/eV-C_{60}-spin

Rb_3C_{60} : E_F ~ 0.2 eV ⇨ 9 states/eV-C60-spin

• In K_3C_{60}, $S = S_d + S_p$

S_p : phonon drag effect contribution





Concluding Remarks

- Fullerene structure : C_{20+h*2}
- An example of strongly correlated electronic system
  - Insulator – undoped C_{60}
  - Metallic – Alkali-doped C_{60}
  - Superconductivity – A_3C_{60} (A=K, Rb,CsK,RbCs)
- T_c increase linearly with lattice constant : BCS theory prediction
- Reduced Hall coefficient and sign change at 200K : both electron and hole pocket
- Weak localization effect associated with Merohedral disorder and missing alkali ions.
- D.O.S. at Fermi Level in K_3C_{60}:
  - Pauli susceptibility : 28 states/eV-C60(spin fluctuation enhancement
  - Thermopower S : 11 states/eV-C60
  - Specific heat : 12 states/eV-C60