Quantum Transport and Dynamics in Nanostructures

The 4th Windsor Summer School on Condensed Matter Theory
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Physics of Nanotubes, Graphite and Graphene

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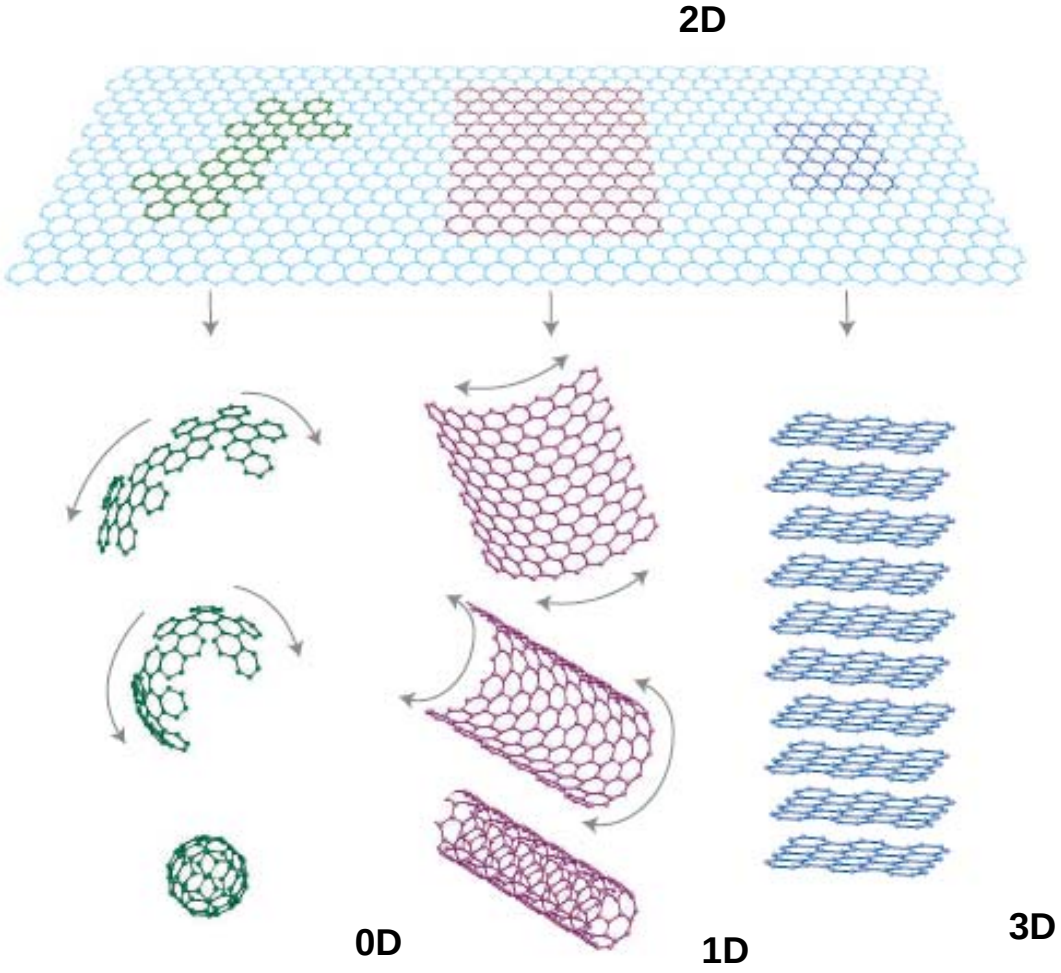
Physics of Nanotubes, Graphite and Graphene

Outline of Lecture 2 - Graphene

- **Introduction to Graphene (2D)**
- **Raman spectra to characterize Graphene**
- **Graphene Ribbons (1D)**
- **Probing Defects**
- **Outlook**

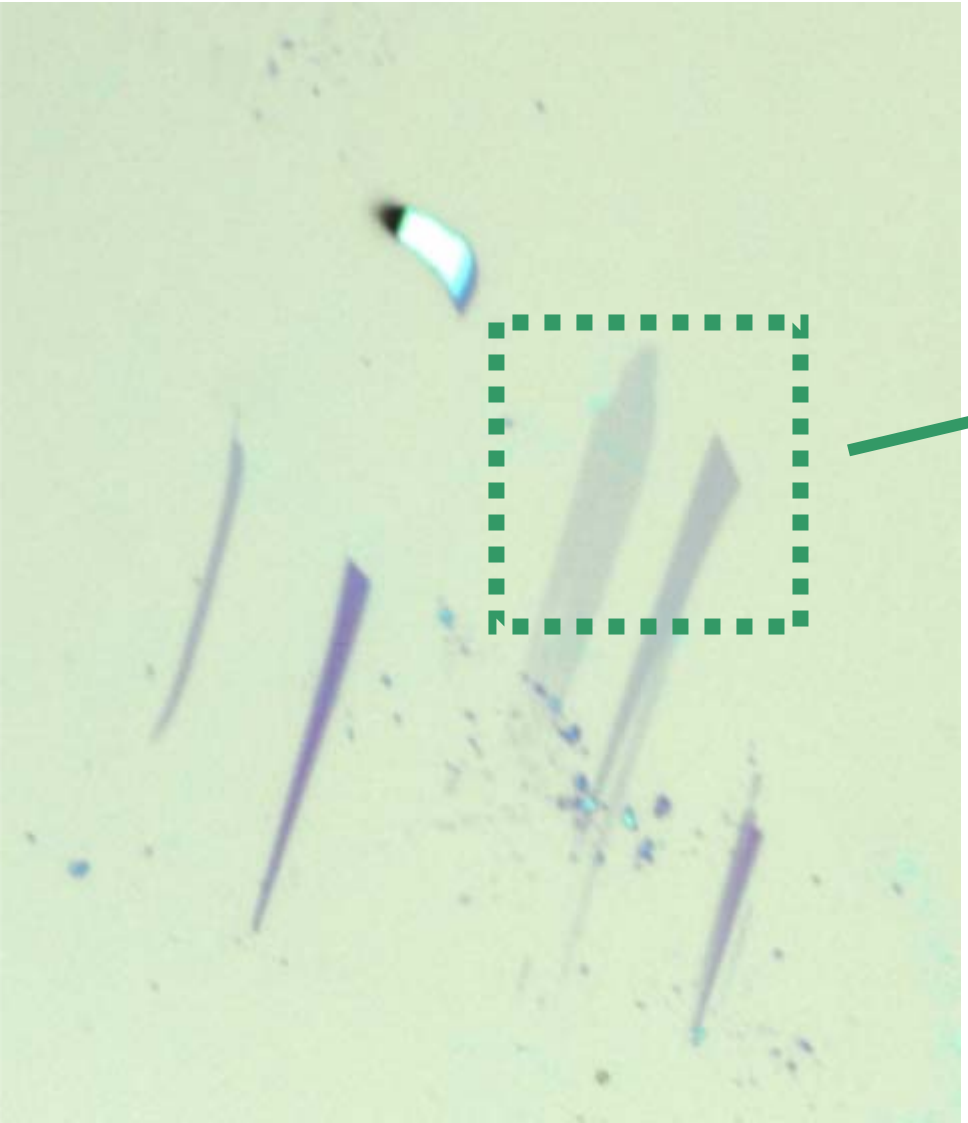
Graphene is the Mother of all Graphitic forms

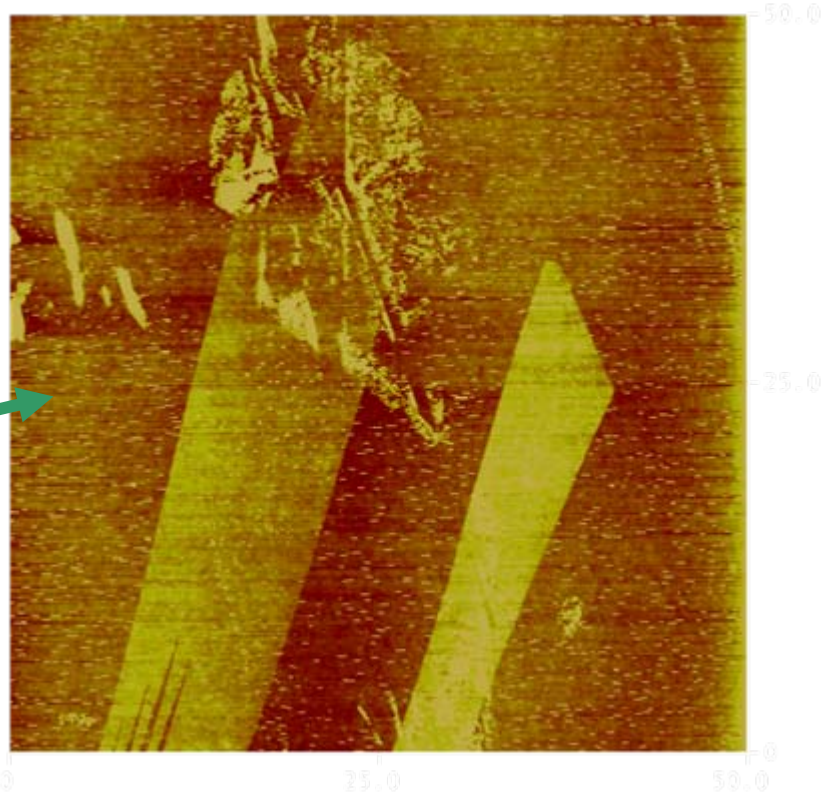


Graphene is a 2D building block material for other sp^2 bonded carbon materials. It can be wrapped up into 0D fullerenes, rolled into 1D nanotubes or stacked into 3D graphite

from A. Geim

Identification of individual graphene sheets





- **1ML (monolayer) left, 2ML lower right**
- **Can be characterized by an optical microscope or by AFM, SEM and Raman**

from Jing Kong, MIT

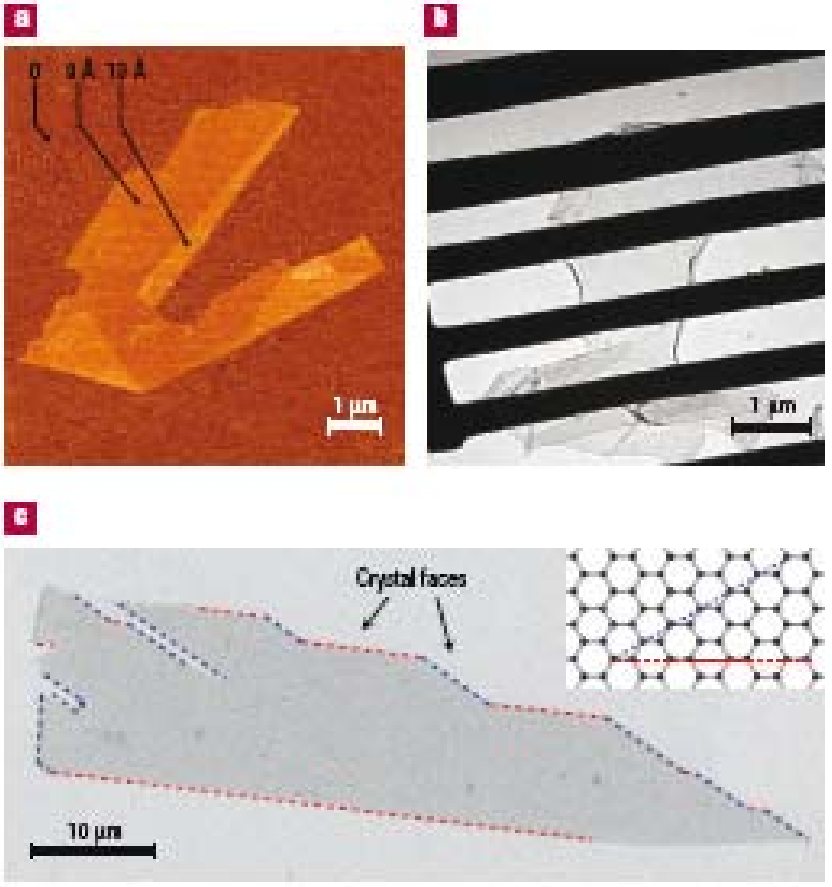
Graphene Crystals

One atom thick single crystals

a) Graphene visualized by atomic force microscope

b) Graphene sheet freely suspended over posts

c) Scanning electron micrograph of a relatively large graphene crystal showing armchair and zigzag edges. The edges of graphene crystals are of special importance because they are unique to few layer graphenes and graphene ribbons



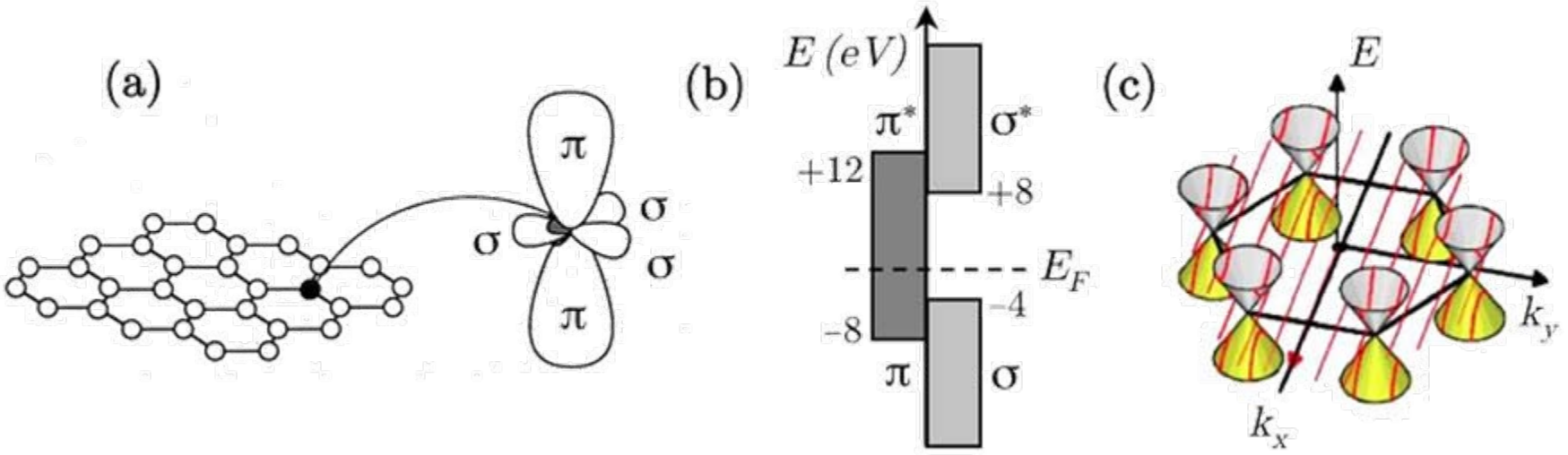
from A. Geim

Graphene devices

- Many graphene devices are similar to nanotube devices
- Current Graphene technology:
  - Mobility (~20000 cm^2/Vs) can be further improved
  - Ballistic transport on submicron scale
  - Gas sensors to detect small gas concentrations
- A band gap can be opened by quantum confinement effects on armchair graphene ribbons
- A band gap can be opened by placement of a graphene sample on a substrate, such as SiC to form a weak surface charge layer
- Spin polarization can be maintained over submicron distances
- Interesting proximity effects are observed in graphene when using superconducting and magnetic electrodes

from Heersche, H. B., *et al.*, Presented at *Nanophysics: from Fundamentals to Applications*, Hanoi, Vietnam, August, 2006

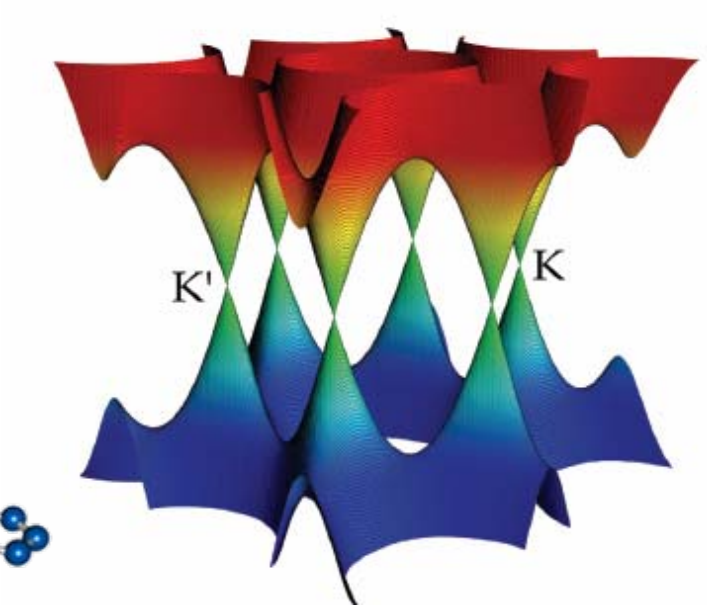
Carbon Valence Orbitals

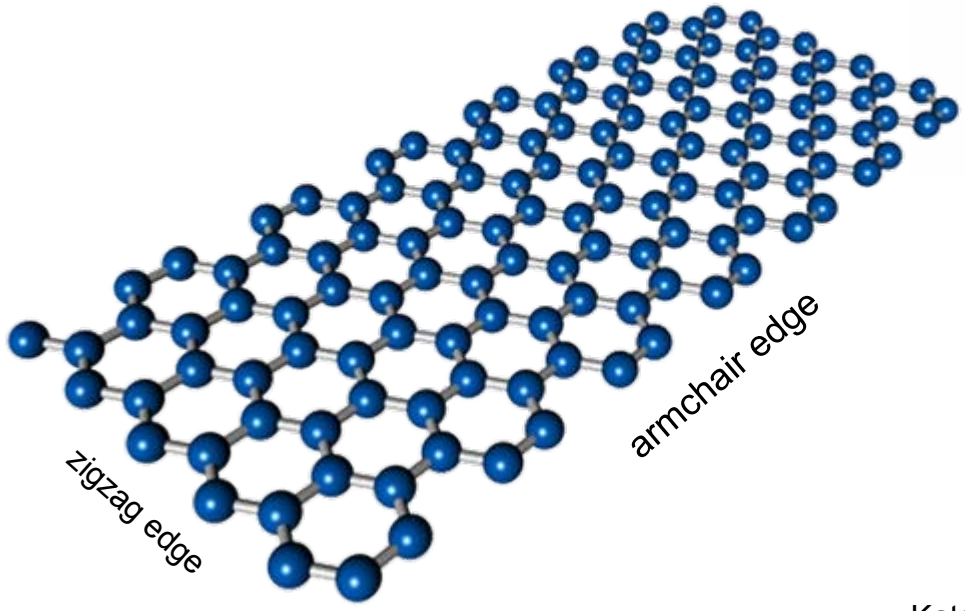


- **Strong in-plane sp^2 (s,p_x,p_y) bonding**
- **p_z electrons form a nearly free electron gas with $E(k)$ linear in k**

Electronic structure of Monolayer Graphene

- E(k) relation is linear in k
- Effective mass vanishes at K and K'
- Different behavior from common metals and semiconductors because of linear instead of parabolic E(k) dispersion relation





Katsnelson, Mikhail I. *MATERIALS TODAY 10 (1-2): Elsevier (2006)*

Electronic Energy dispersion for Graphene

The dispersion relation familiar from the graphene sheet that is used to roll up graphene into a nanotube:

$$E^{\pm}(k_x, k_y) = \pm\gamma_0 \sqrt{1 + 4\cos\frac{\sqrt{3}k_x a}{2}\cos\frac{k_y a}{2} + 4\cos^2\frac{k_y a}{2}}$$

where

$a = \sqrt{3} \cdot a_{\text{c-c}}$ and

γ_0 is the transfer integral between nearest neighbor π-orbitals

(γ_0 values are from 2.9 to 3.1eV)

Near the K point we write $\kappa = k - K$ and

$E^{\pm}(\kappa) = \pm\hbar \mathrm{v}_F \,|\,\kappa\,|$ linear κ relation where $\mathrm{v}_F = \frac{\sqrt{3}\gamma_0 a}{2\hbar}$

and γ_0 is the nearest neighbor overlap integral

Electronic Dispersion for Graphene

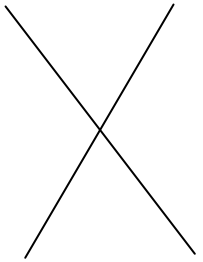
For monolayer graphene the linear dispersion is the solution of the effective Hamiltonian at the K (K') points in the Brillouin zone

$$\hat{\mathrm{H}} = \hbar \mathrm{v}_{\mathrm{F}} (\boldsymbol{\sigma} \cdot \boldsymbol{\kappa})$$

where $\kappa = -i\nabla$ **and** σ Is the Pauli spin matrix

In matrix form

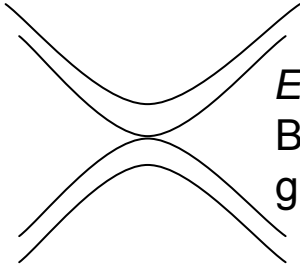
$$\hat{H} = \hbar \mathrm{v}_F \begin{pmatrix} 0 & \kappa_x - i\kappa_y \\ \kappa_x + i\kappa_y & 0 \end{pmatrix}$$



E(κ) Monolayer graphene

For bilayer graphene the Hamiltonian becomes

$$\hat{H} = \hbar \mathrm{v}_F \begin{pmatrix} 0 & (\kappa_x - i\kappa_y)^2 \\ (\kappa_x + i\kappa_y)^2 & 0 \end{pmatrix}$$

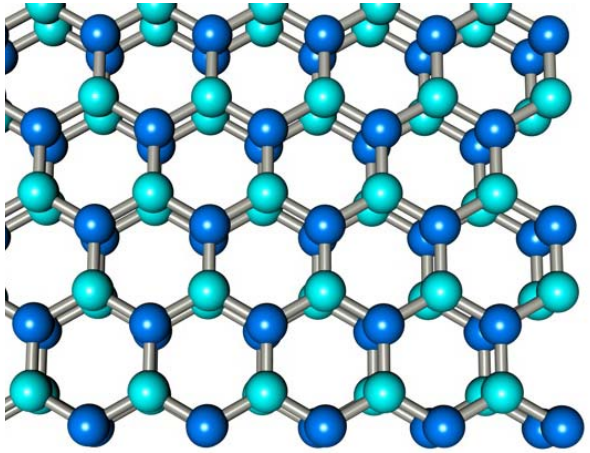


E(κ) Bilayer graphene

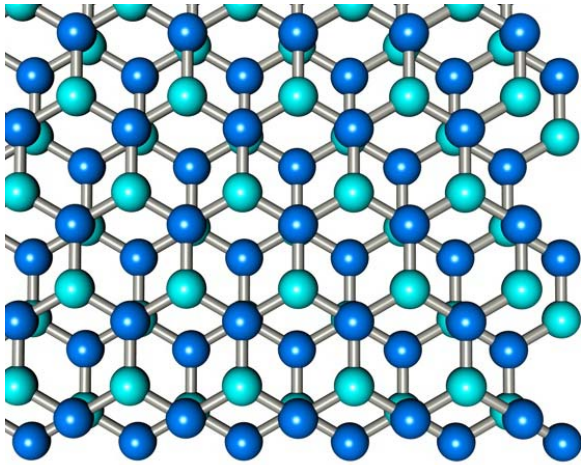
and yields parabolic valence and conduction bands with one set degenerate at the K and K' points in the Brillouin zone

AB stacking in Bilayer Graphene

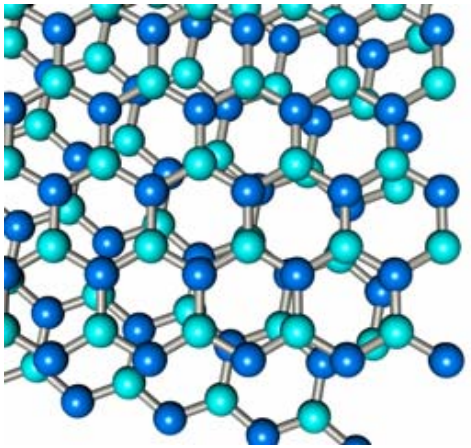
A-A-stacking



A-B-stacking

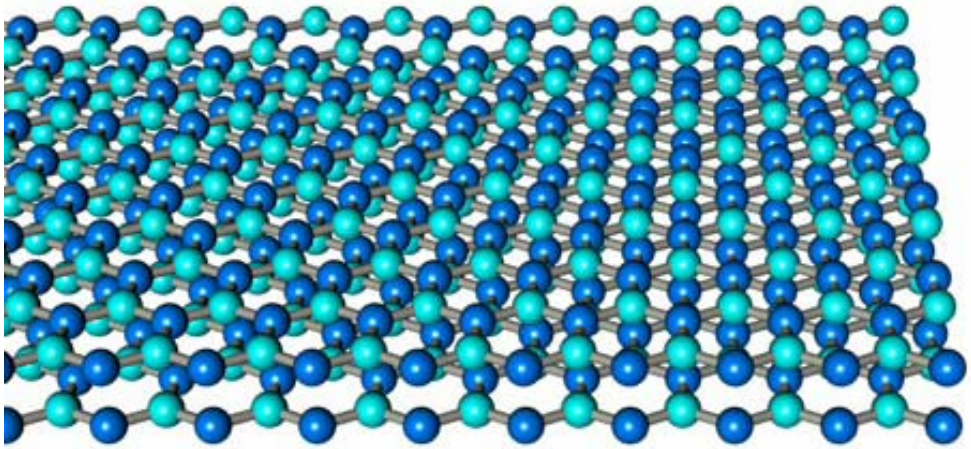


turbostratic

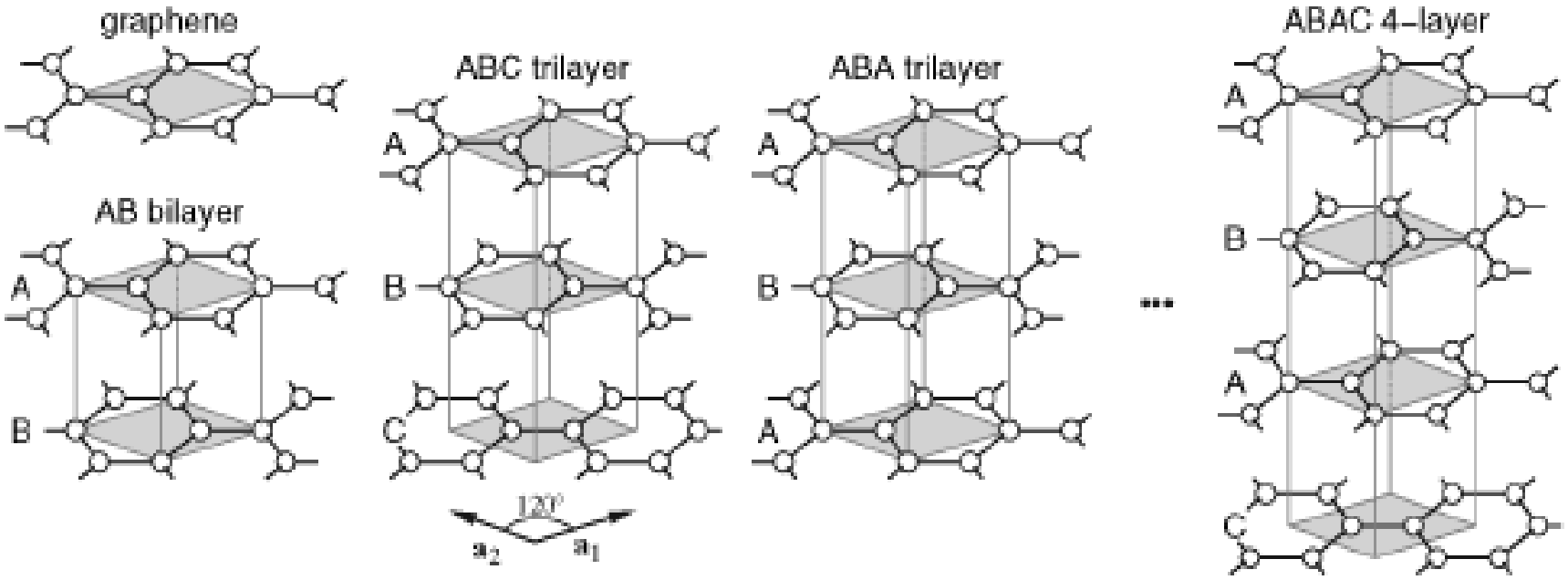


- Theory is usually developed for AB stacking as in graphite.
- For bilayer and multilayer graphene with randomly stacked layers we call the stacking turbostratic.

Graphite stacking



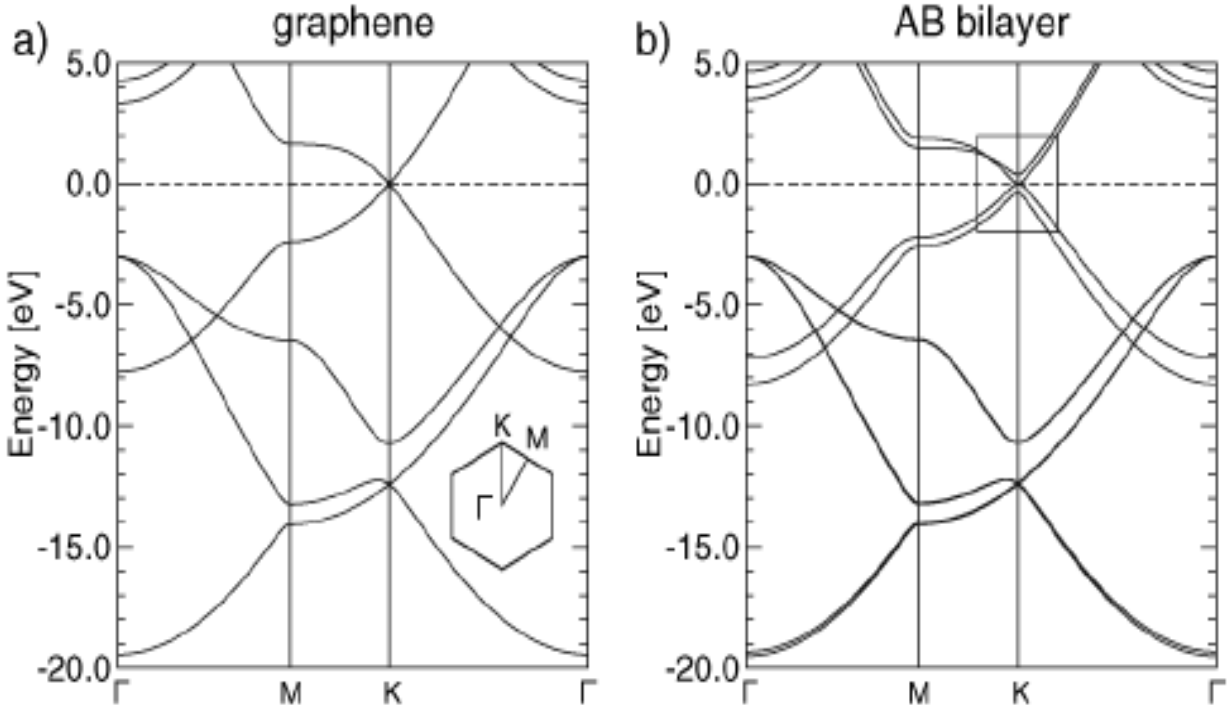
2D primitive cells of some Graphenes



Various stackings up to 4 layer graphene are shown

Latil, Phys. Rev. Lett. ***97****, 036803 (2006)*

Electronic Band Structure of Monolayer and AB-stacked bilayer Graphene

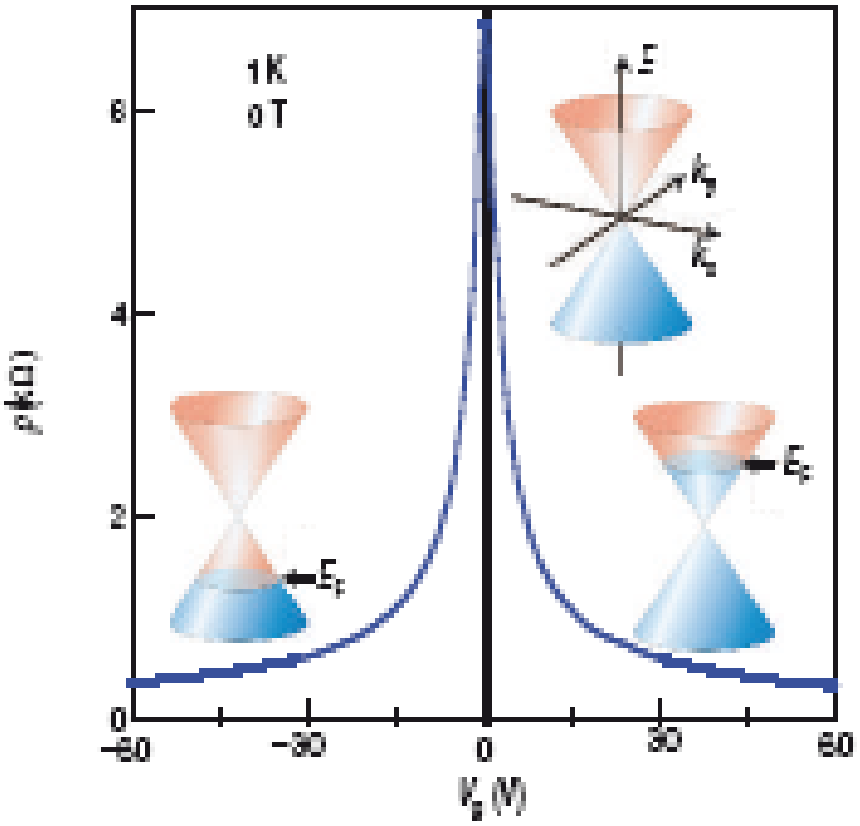


(a) Monolayer graphene with linear E(k) near K point at E_F

(b) Bilayer AB stacked graphene E(k). The weak interaction between layers introduces a minigap at the K point and parabolic bands

Latil, Phys. Rev. Lett. ***97****, 036803 (2006)*
Saito, Phys. Rev. B 33, 7218 (1986)

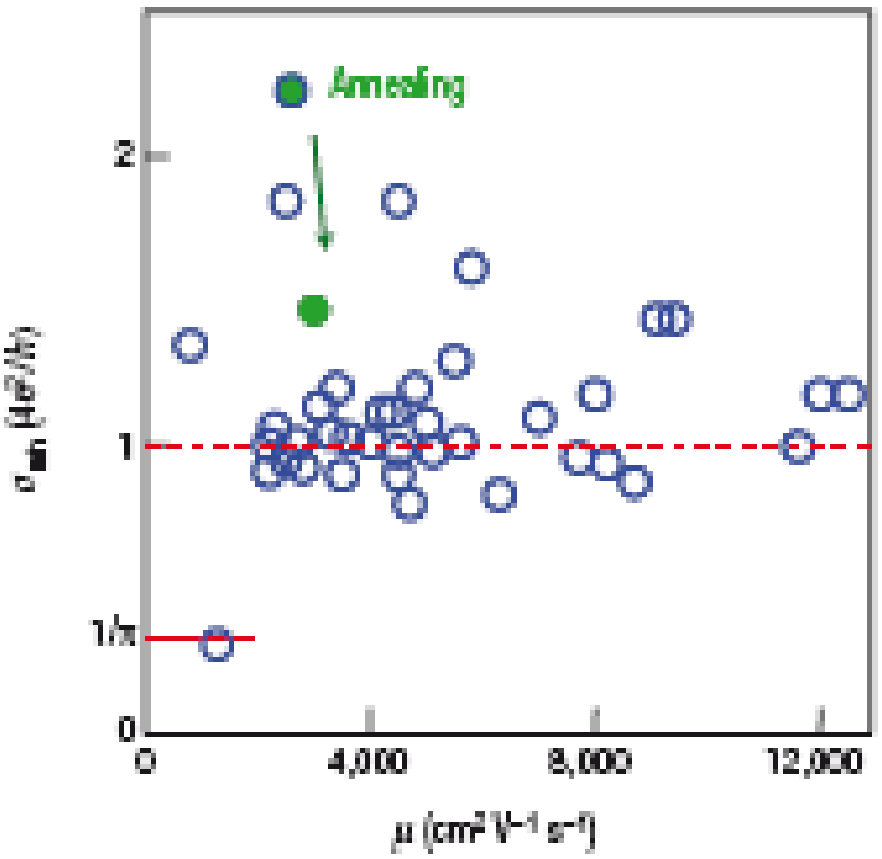
Ambipolar Electric Field Effect



Ambipolar electric field effect in single-layer graphene arising from the symmetry between valence and conduction bands. The insets show the low-energy spectrum *E(k) as the Fermi level is raised by increasing the gate voltage* V_g

from A. Geim

Minimum Conductivity of Graphene



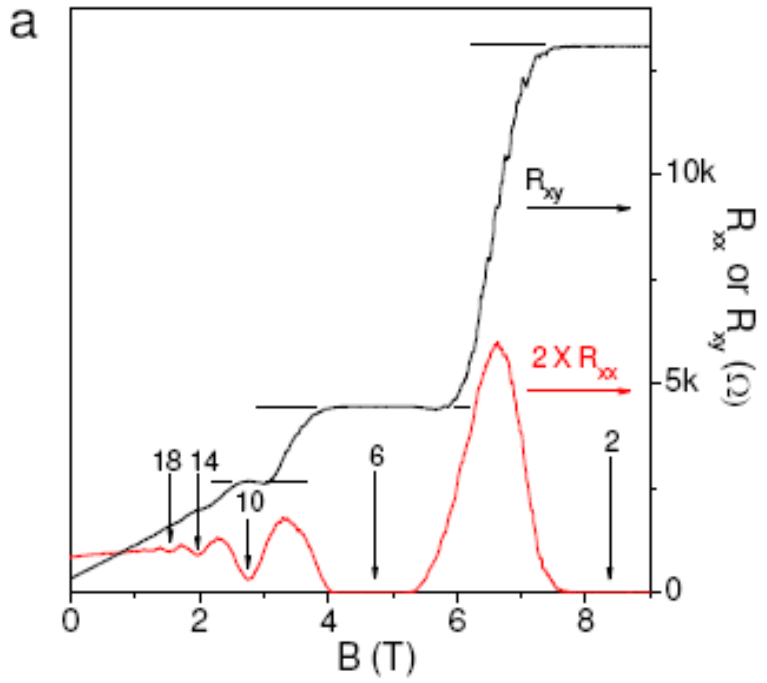
The conductivity for different graphene samples indicates that the minimum conductivity is $4e^2/h$ rather than $2e^2/h$ as in typical semiconductors

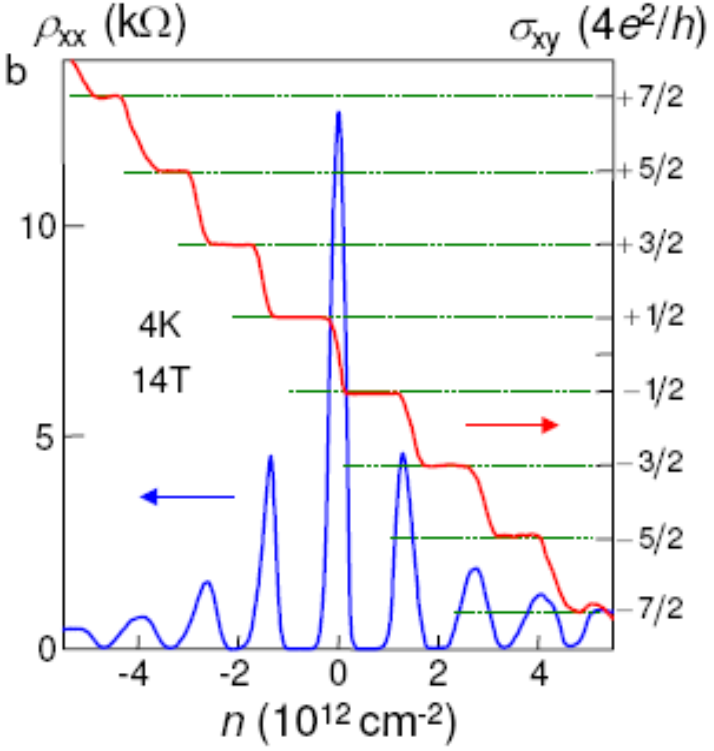
from A. Geim

Anomalous Quantum Hall Effect

Three anomalies:

- Half integer quantum Hall effect,
- Factor of 4 in **$4e^2/h$**
- Berry's phase of π





- This work attracted great attention and interest in graphene

Physics of Nanotubes, Graphite and Graphene

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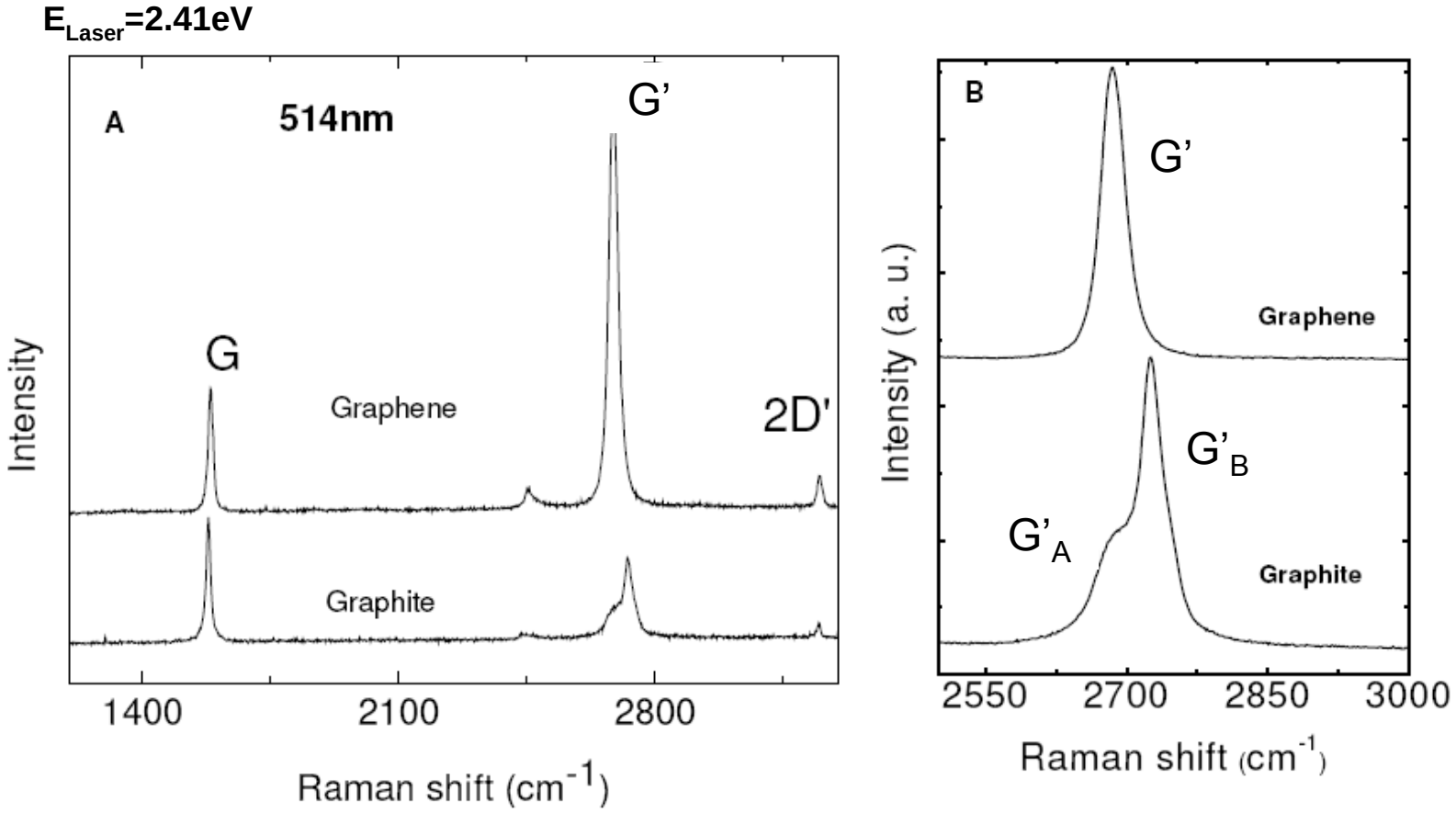
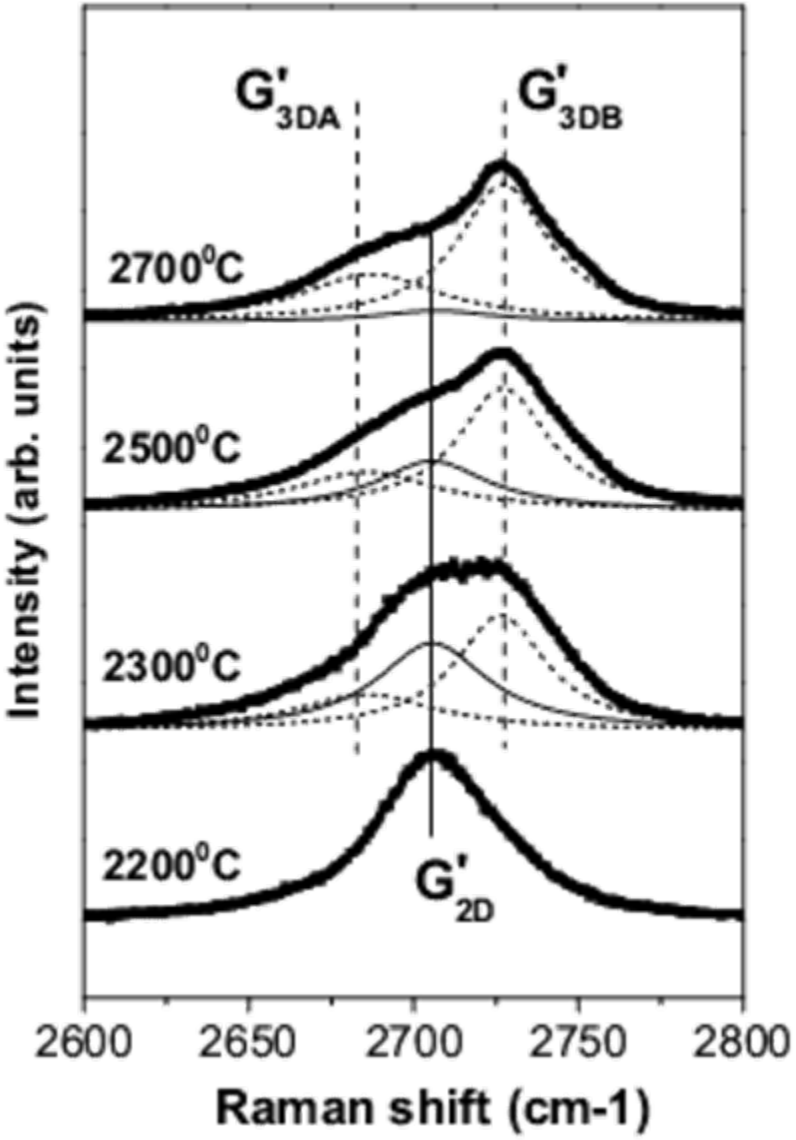
Comparison of the Raman spectra of graphene and graphite



- Large enhancement of G' band in monolayer graphene relative to graphite
- G' band in monolayer graphene (and SWNTs) is a single peak, but the G' band for graphite has two components

J.C. Charlier, P. C. Eklund, J. Zhu and A. C. Ferrari, vol III, TAP, Springer

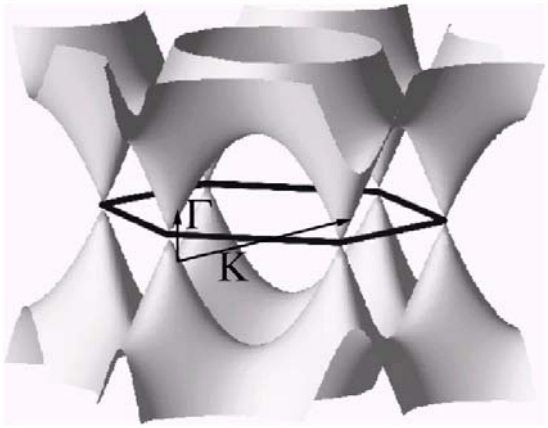
Reason for G'-band Notation
G' band in the Raman spectra of 2D and 3D graphites

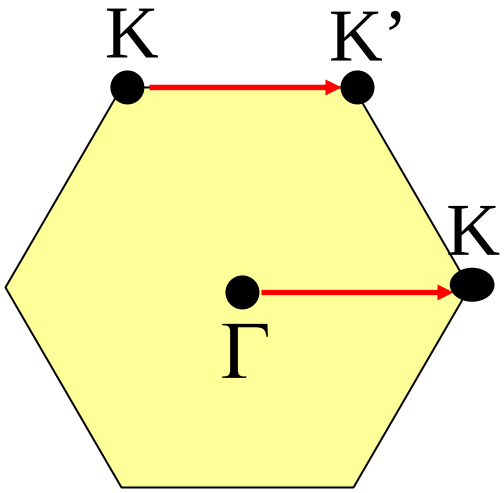


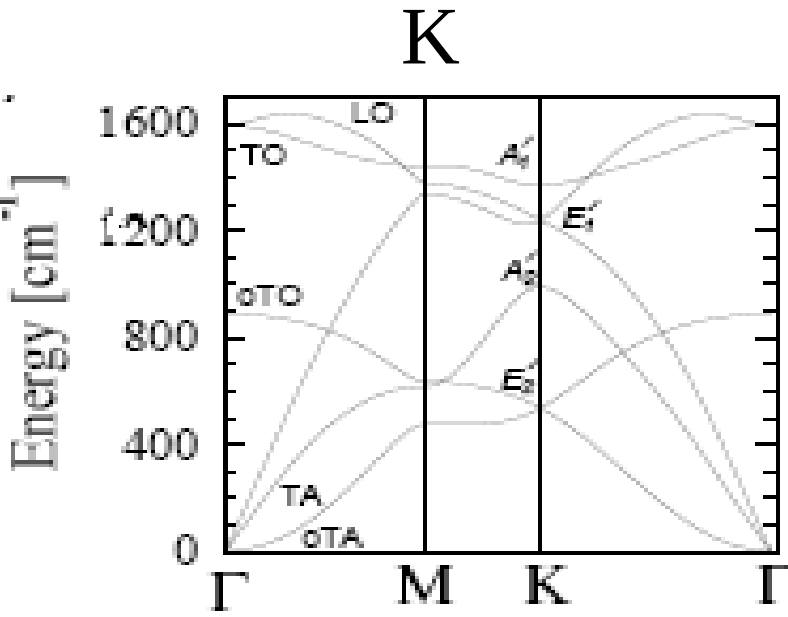
Basis for the notation of the G' band, comes from the graphite and nanographite literature

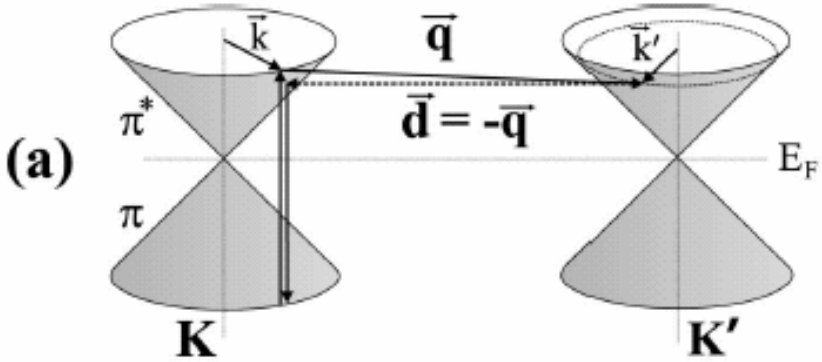
- Lespade *et al.,* Carbon **22**, 375 (1984).
- Wilhelm *et al.,* Journal of Appl. Physics **84**, 6552 (1998).
- Nemanich and Solin, Solid State Comm. **23**, 417 (1977).
- Nemanich and Solin, Phys. Rev. B **20**, 392 (1979).
- Barros *et al.,* Phys. Rev. B **71**, 165422 (2005).

Double resonance Raman scattering







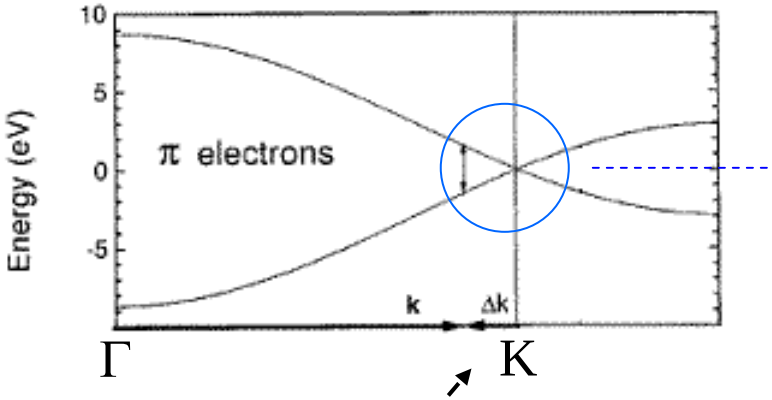


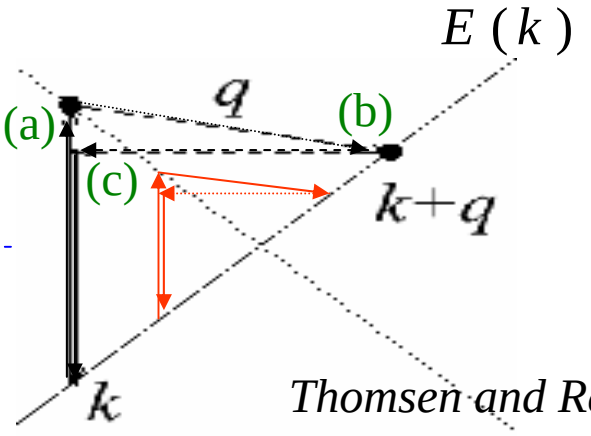
Thomsen and Reich, Phys Rev Letters, 85, 5214 (2000)

Saito et al, Phys Rev. Letters, 88, 027401 (2002)

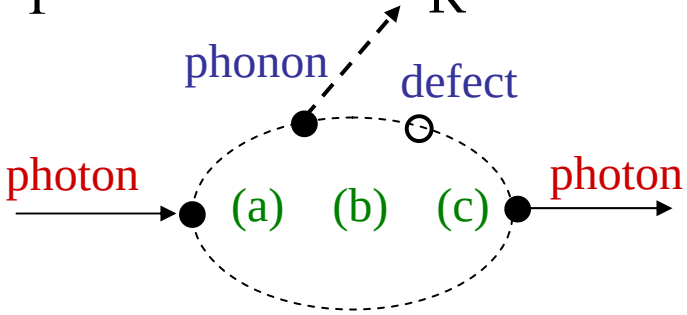
$$I = C \sum_{A,B,C} \frac{M}{(\hbar\omega_i - E_a - i\gamma)(\hbar\omega_i - \hbar\omega_q - E_b - i\gamma)(\hbar\omega_i - \hbar\omega_q - E_c - i\gamma)}$$

Double resonance Raman scattering





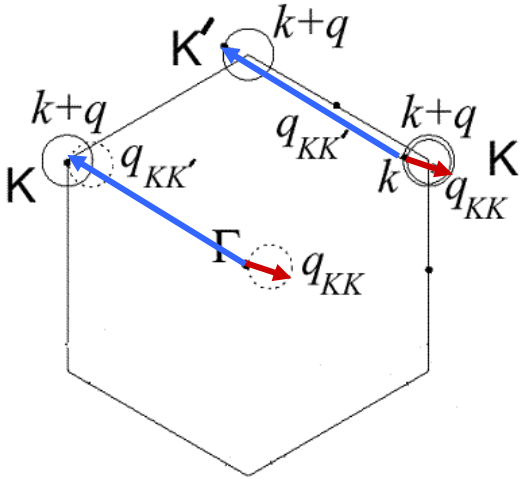
Thomsen and Reich, Phys. Rev. Letters 85, 5214 (2000)



Intra-valley and inter-valley Double resonance

R. Saito, A. Jorio, A. G. Souza Filho, G. Dresselhaus, M.S. Dresselhaus, M.A. Pimenta,

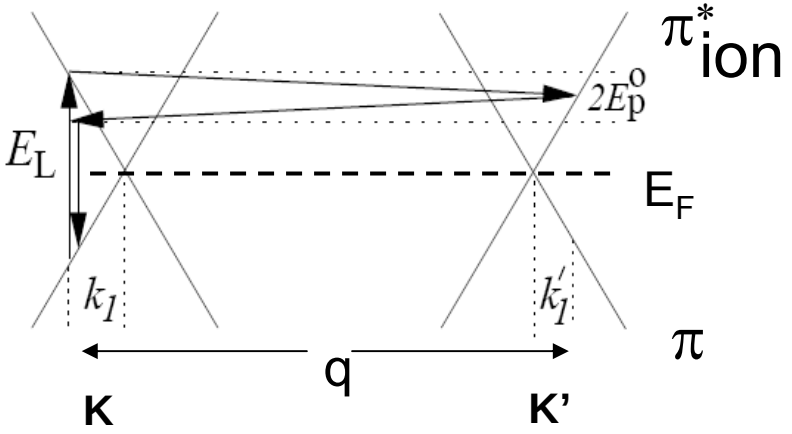
Phys. Rev. Letters, 588, 027401 (2002)



Intra-valley process: probing phonons near the Γ point

Inter-valley process: probing phonons near the K point

Double Resonance Stokes Process for Monolayer Graphene for the G′ feature

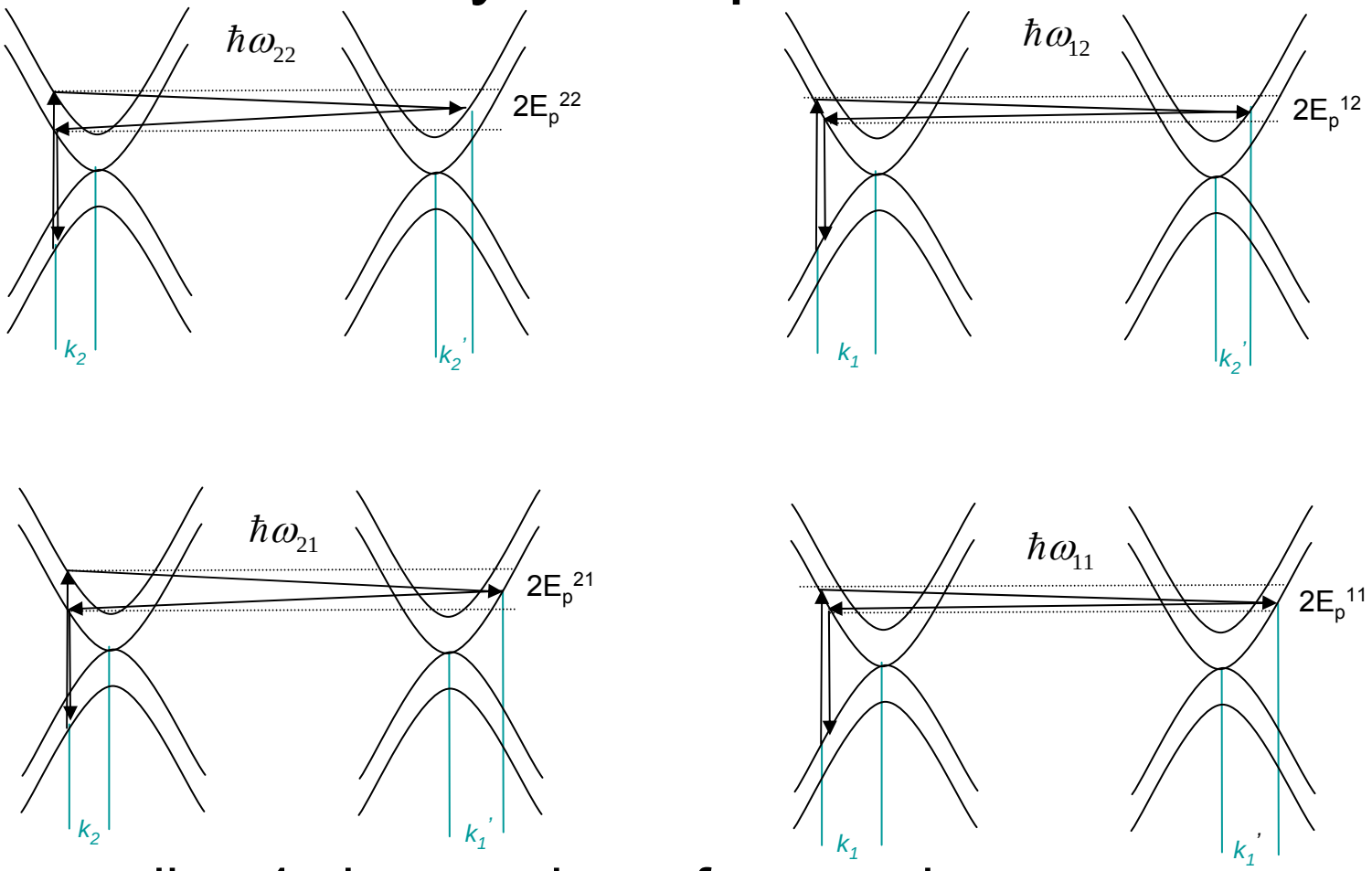


Energy of scattered photon E_{sc} is downshifted by $2E_p{}^0 = \hbar\omega_{G'}$ relative to the incident photon E_{in}

$$E_{in} = E_{sc} + \hbar\omega_{G'}$$

J.C. Charlier, P. C. Eklund, J. Zhu and A. C. Ferrari, vol III, TAP, Springer

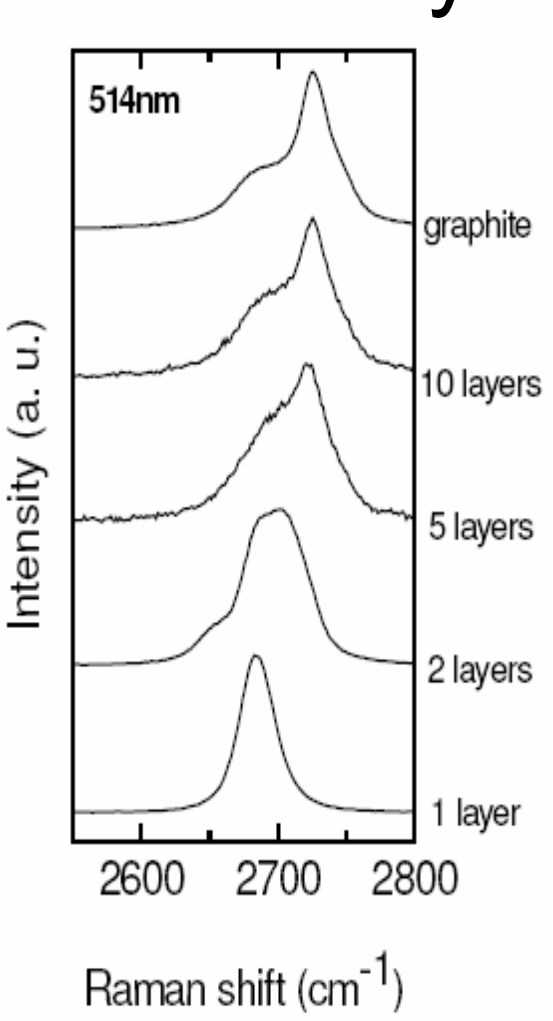
Double Resonance Raman process for Bilayer Graphene

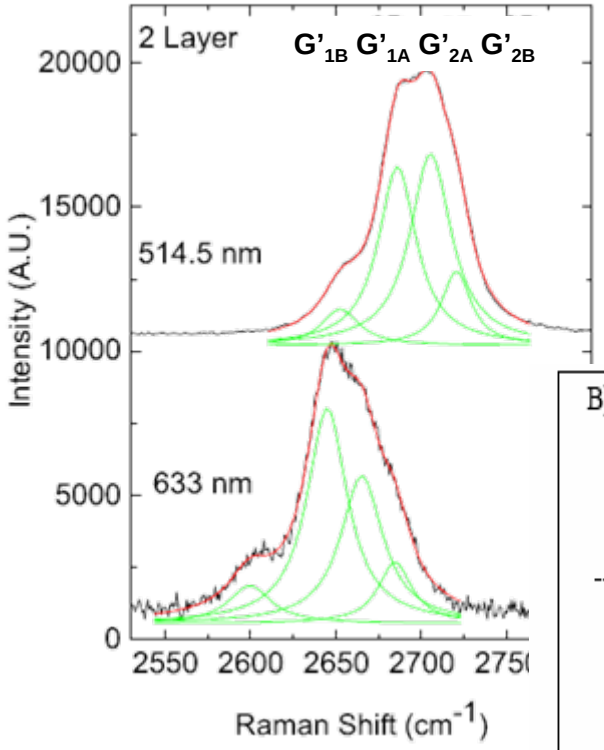


Corresponding 4 phonons have frequencies:

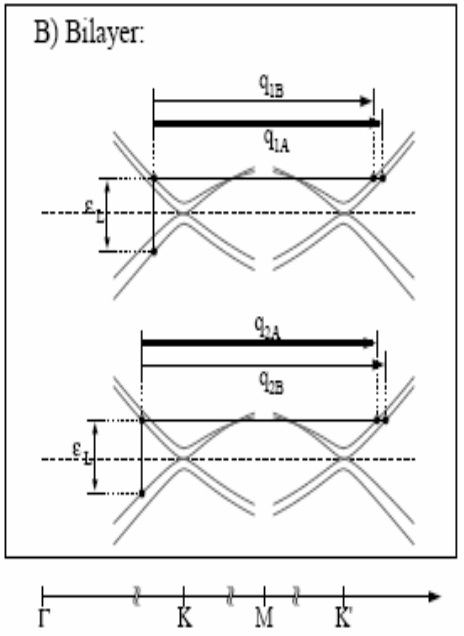
$\hbar\omega_{22}$, $\hbar\omega_{21}$, $\hbar\omega_{12}$ and $\hbar\omega_{11}$

The four components of the G' peak in bilayer graphene





Lineshape is sensitive to both E_{Laser} and number of layers

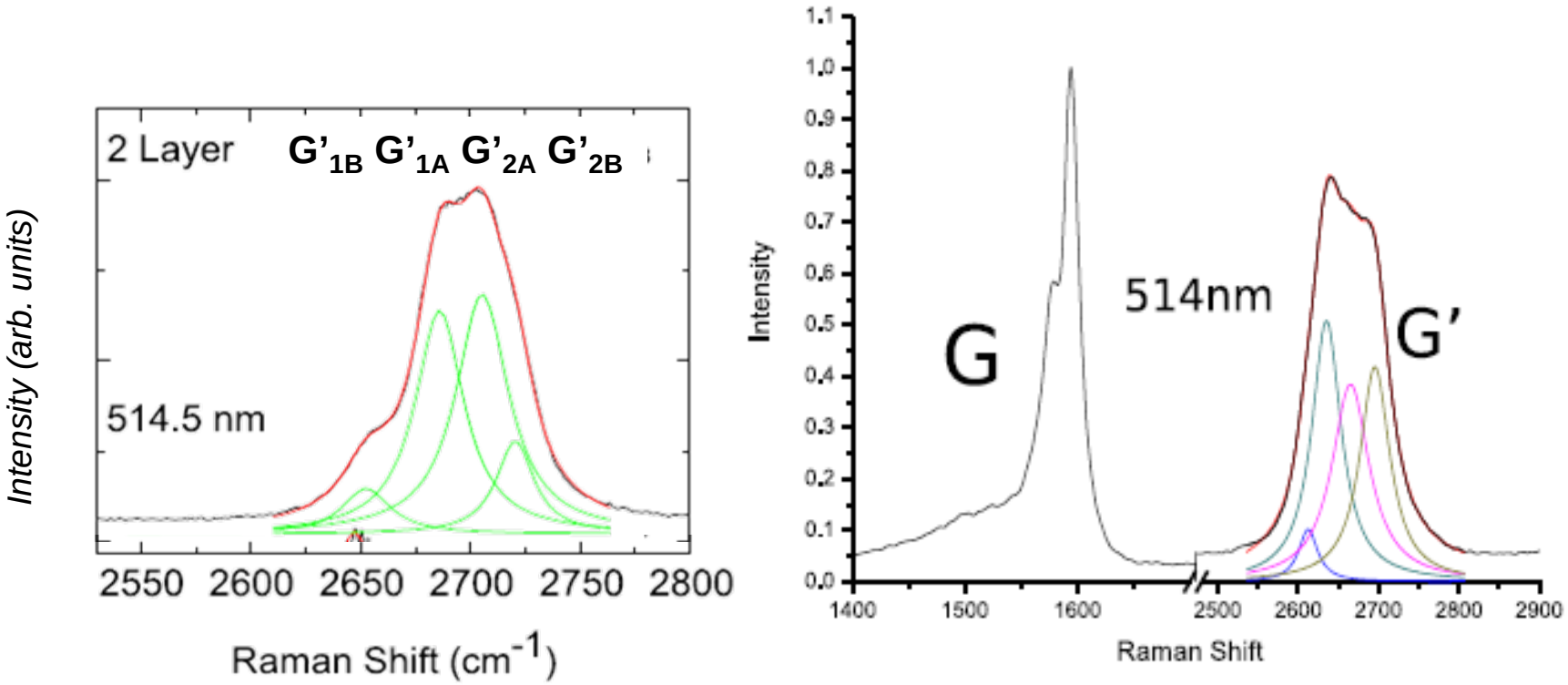


The lineshape of G' band identifies the number of layers

The relative intensities of the 4 peaks distinguishes bilayer graphene from DWNTs

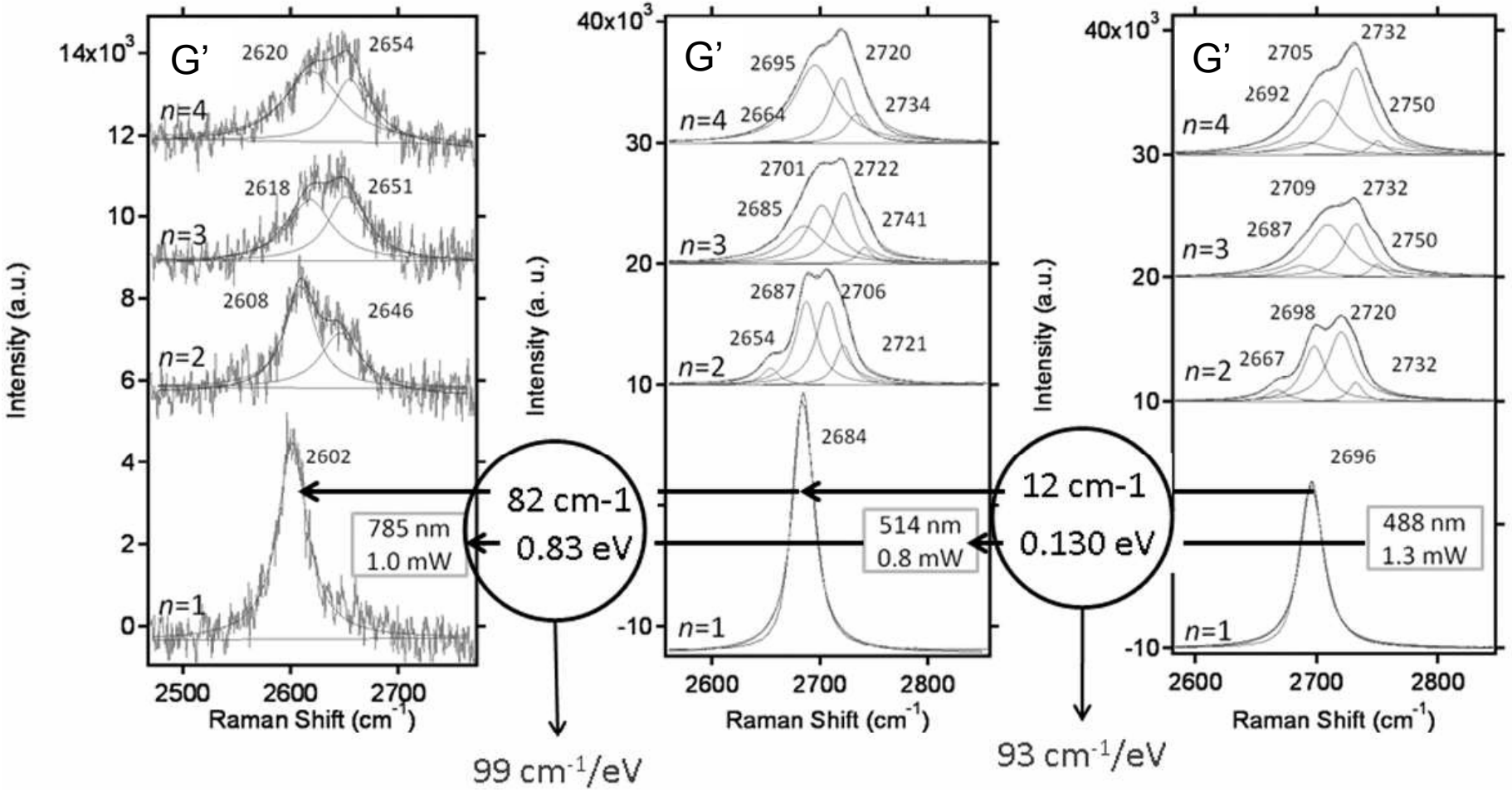
J.C. Charlier, P. C. Eklund, J. Zhu and A. C. Ferrari, vol III, TAP, Springer

Contrast G' band in bilayer graphene and DWNTs at 2.41 eV excitation



- Both bilayer graphene (left) and double wall carbon nanotubes (right) have 4 peaks but the relative intensity of the peaks is different
- Curvature effects and incommensurate interlayer structure strongly affect DWNTs but are absent in bilayer graphene.

G' band for *n*=1-4. *n*LG supported on SiO_2:Si for three laser excitation energies



- Because of the linear *E(k)* dispersion, $\omega_{G'}$ increases linearly with laser excitation energy
- Relative intensity of peaks change with E_{laser}

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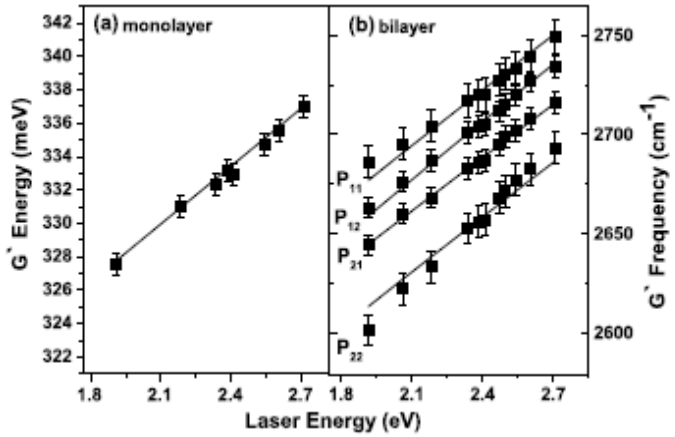
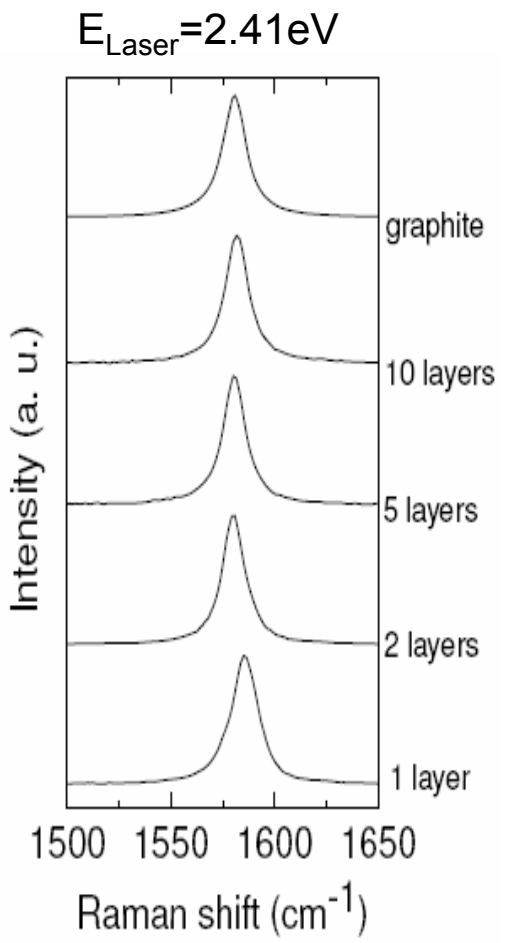
Dispersion of $\omega_{G'}$ with E_{laser} for 1LG and 2LG

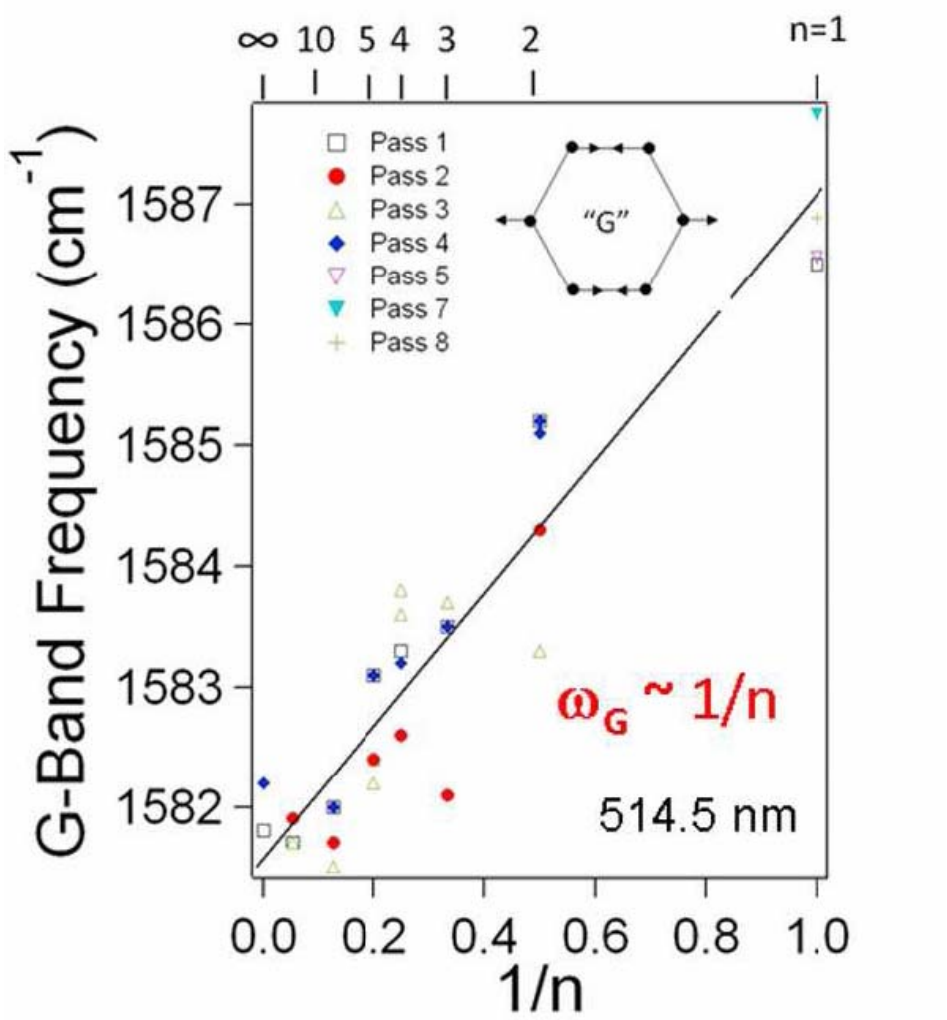


- $d\omega_{G'}/dE_{laser}$ ~ 100 cm^{-1}/eV in general
- The slope for p_{22} (or $\omega_{22'}$) is steeper than for the others because of departures of E(k) from a linear k relation

L. Malard, M. Pimenta (NT07)

G-band frequency vs. 1/*n*

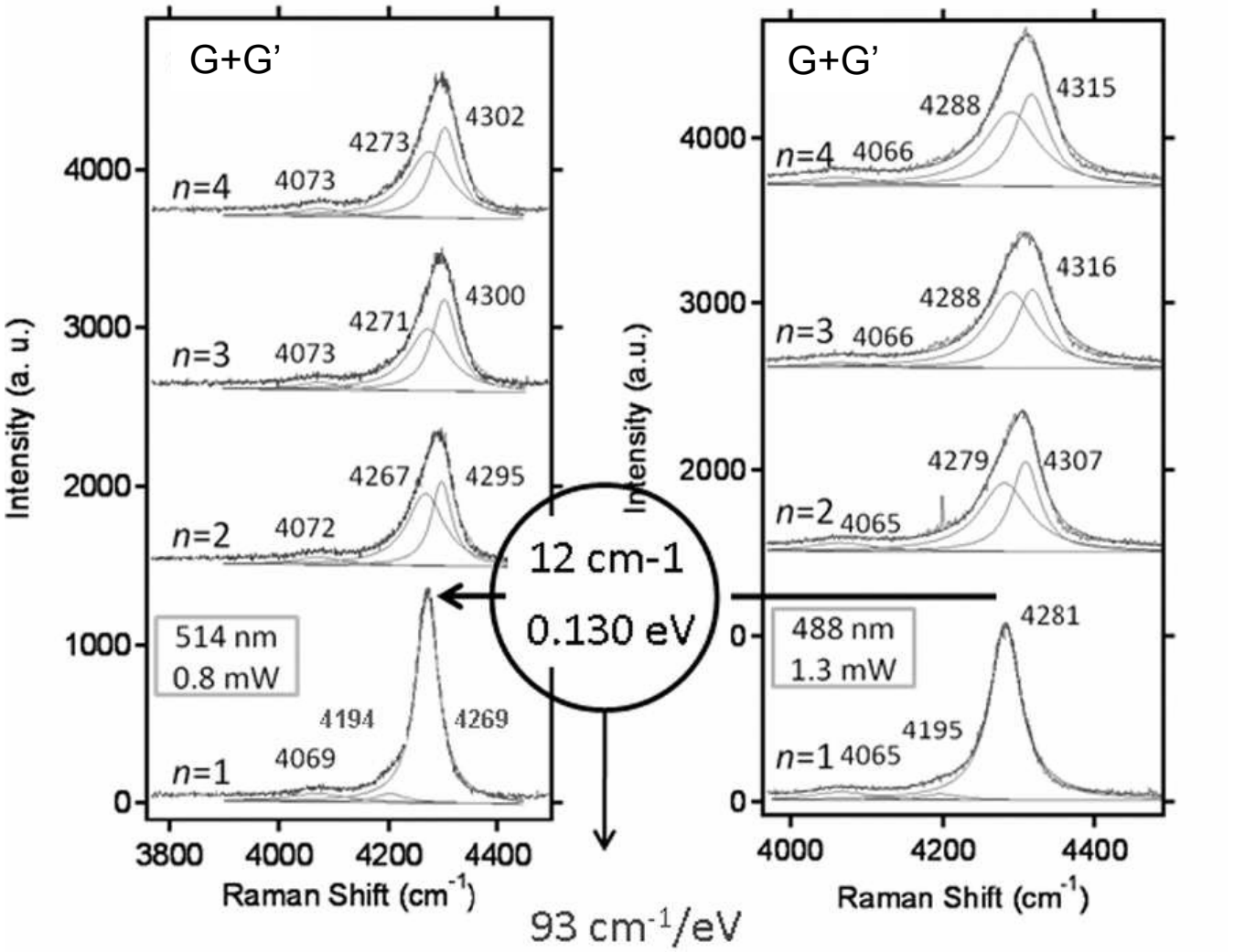




-Spectra excited with 514.5 nm (2.41 eV) light and collected from *n*LGs supported on a single SiO_2:Si substrate show small upshift of 1LG graphene (5 cm^{-1}) results

J.C. Charlier, P. C. Eklund, J. Zhu and A. C. Ferrari, vol III, TAP, Springer

G+G' band for *n*=1-4. *n*LGs on SiO_2:Si for two laser excitation energies



G+G' feature is also sensitive to the number of graphene layers and also to E_{laser}

J.C. Charlier, P. C. Eklund, J. Zhu and A. C. Ferrari, vol III, TAP, Springer

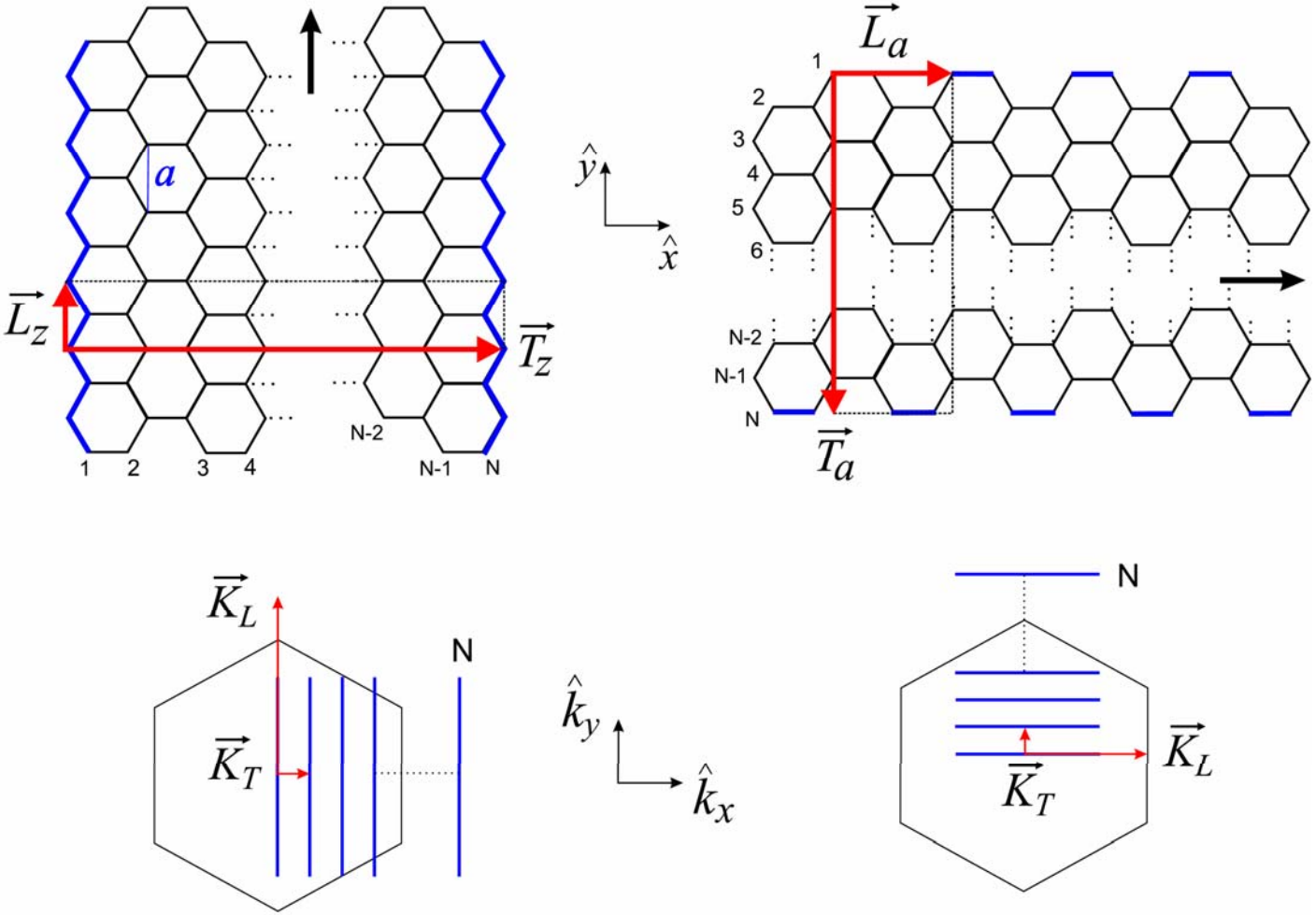
Physics of Nanotubes, Graphite and Graphene

Outline of Lecture 2 - Graphene

- **Introduction to Graphene (2D)**
- **Raman spectra to characterize Graphene**
- **Graphene Ribbons (1D)**
- **Probing Defects**
- **Outlook**

Graphene Ribbons

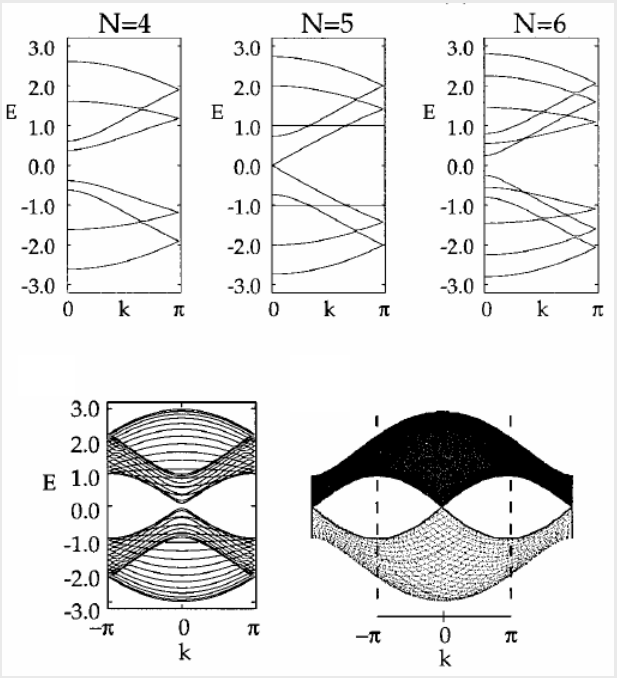
Zigzag **Armchair**



•Special feature of graphene ribbons is that they have edges and few rows of atoms

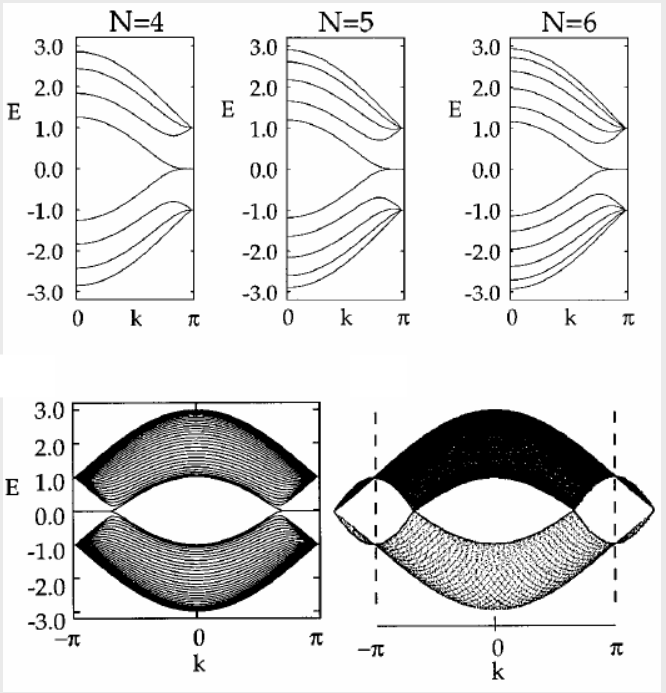
Electronic structure of graphene ribbons

Armchair



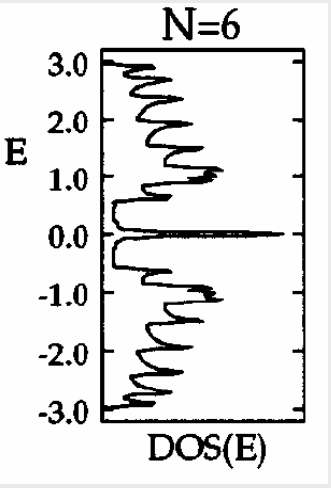
Metallic for N=3M-1 (M integer)

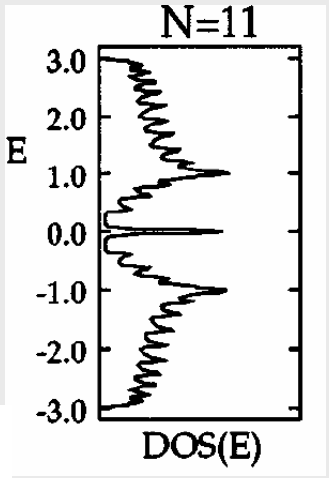
Zigzag



- **Always metallic**
- **Presence of localized edge states at the Fermi level**

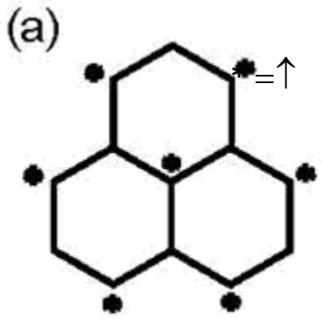
Van Hove singularities in the DOS





Nakada *et al.*, Phys. Rev. B **54**, 17954 (1996).

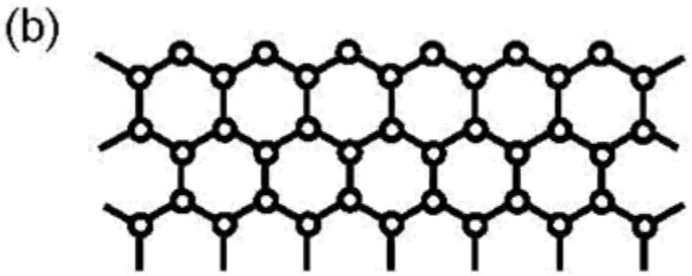
Types of Graphene ribbons



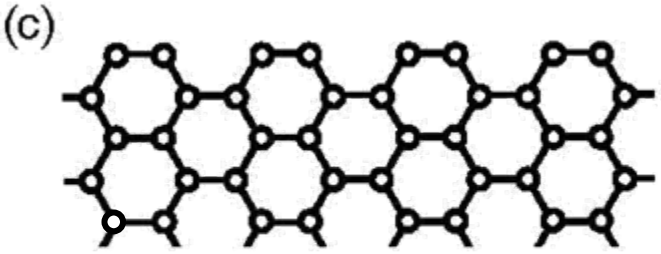
sites

free radicals

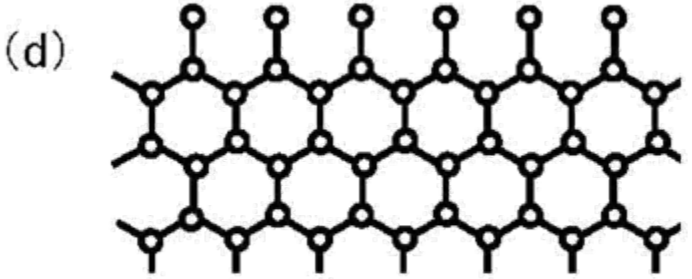
itinerant magnetism



zigzag-edge of Fujita type



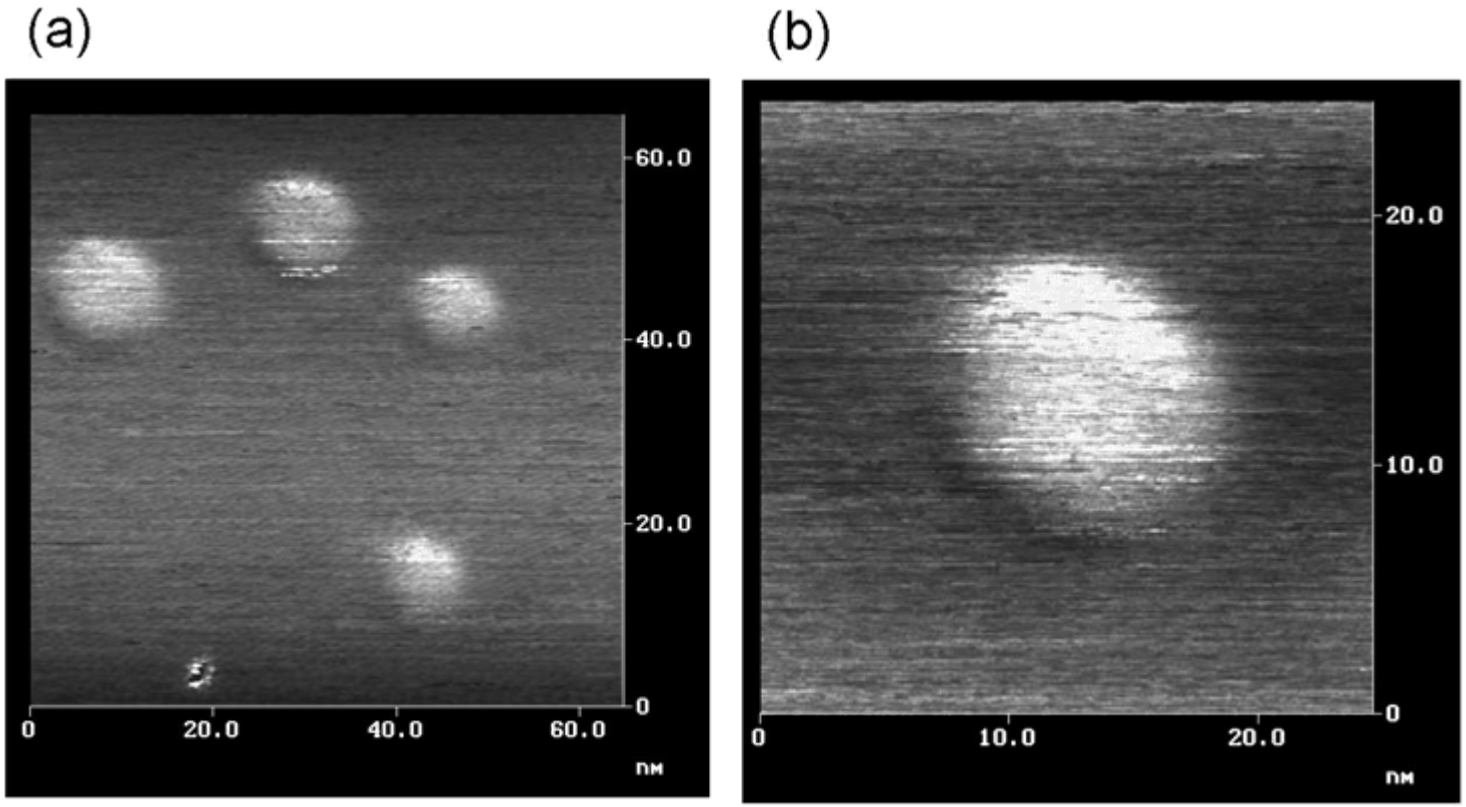
armchair-edge



zigzag-edge of Klein type

ferromagnetism

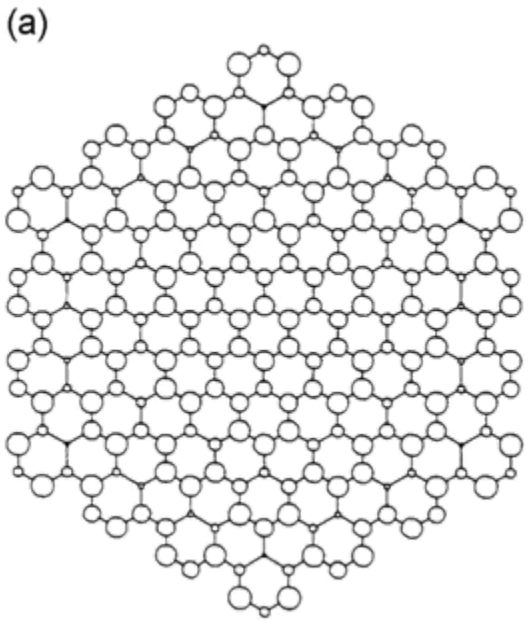
Enoki *et al.*, (2007).



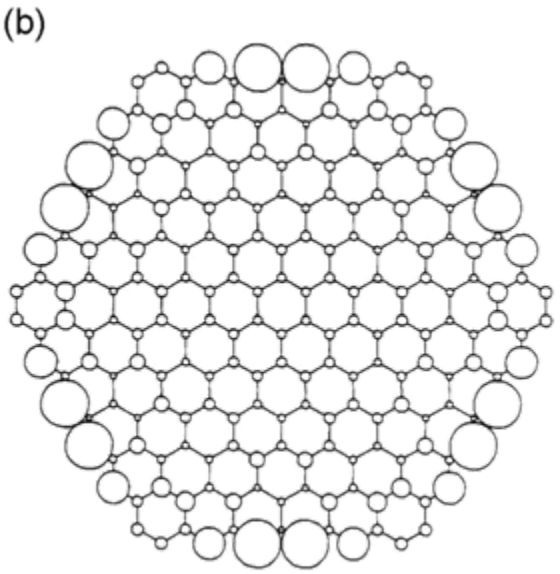
- STM images of nanographenes after heat treatment of nano-diamond particles at 1600°C. Magnified image on right

Affoune et al., Chem. Phys. Lett. **348**, 17 (2001), Langmuir **17**, 547 (2001) .

Spatial distribution of Population of HOMO level for nano-graphene



armchair edges

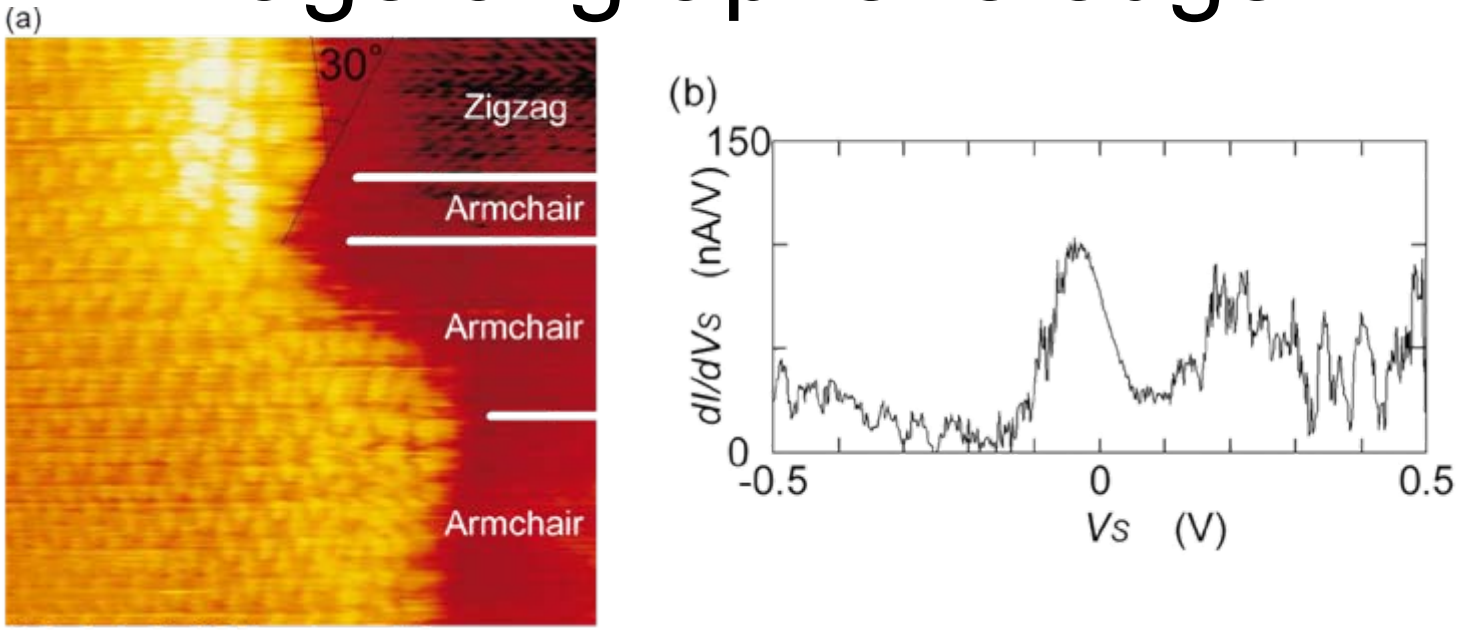


zigzag edges

- Large Density of states is predicted at center of zigzag edges

Enoki *et al.*, (2007).

Atomically-resolved UHV STM image of graphene edge

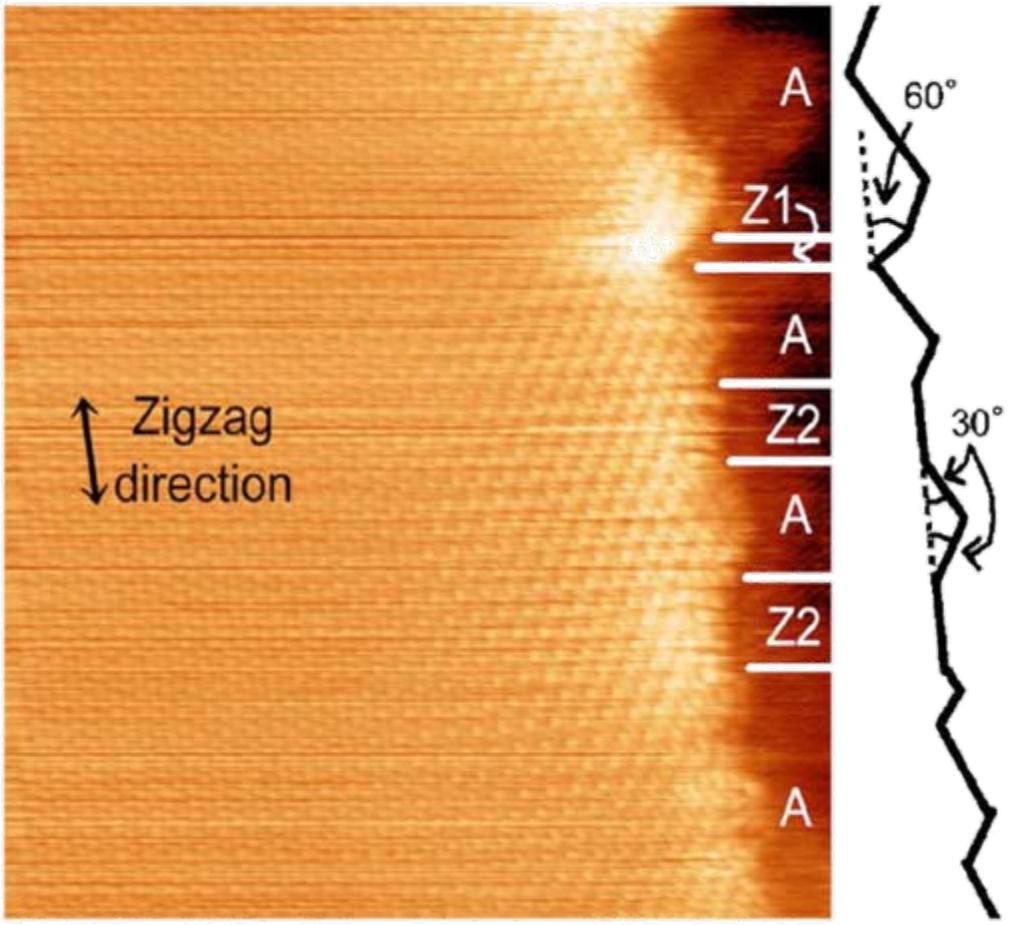


- constant height mode STM image

  (Bias voltage 0.02V, I=0.1nA on 9x9nm^2 sample)
- dI/dV$_s$ curve shows experimental evidence for high density of states for zigzag tubes

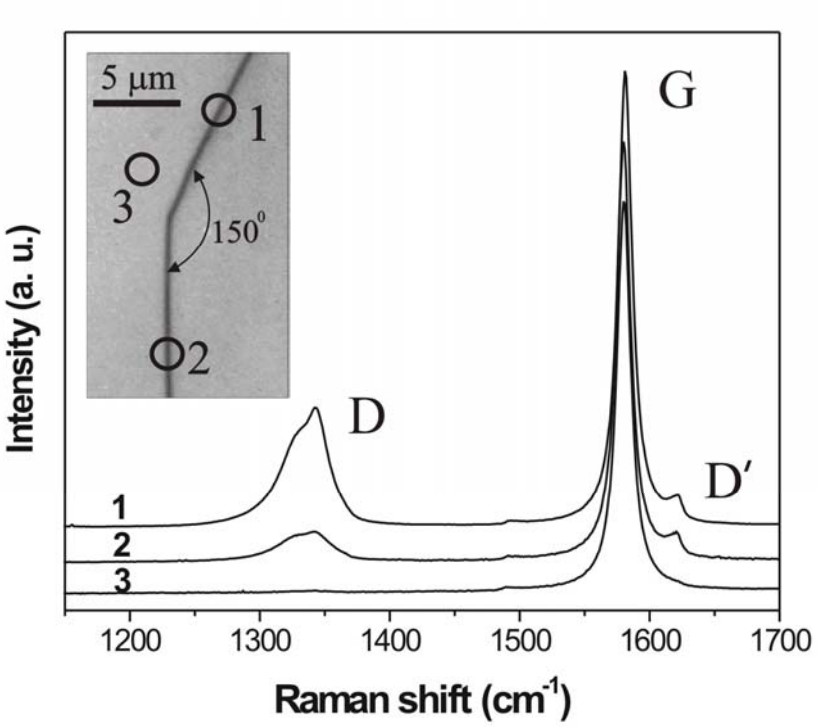
Enoki *et al.*, (2007).

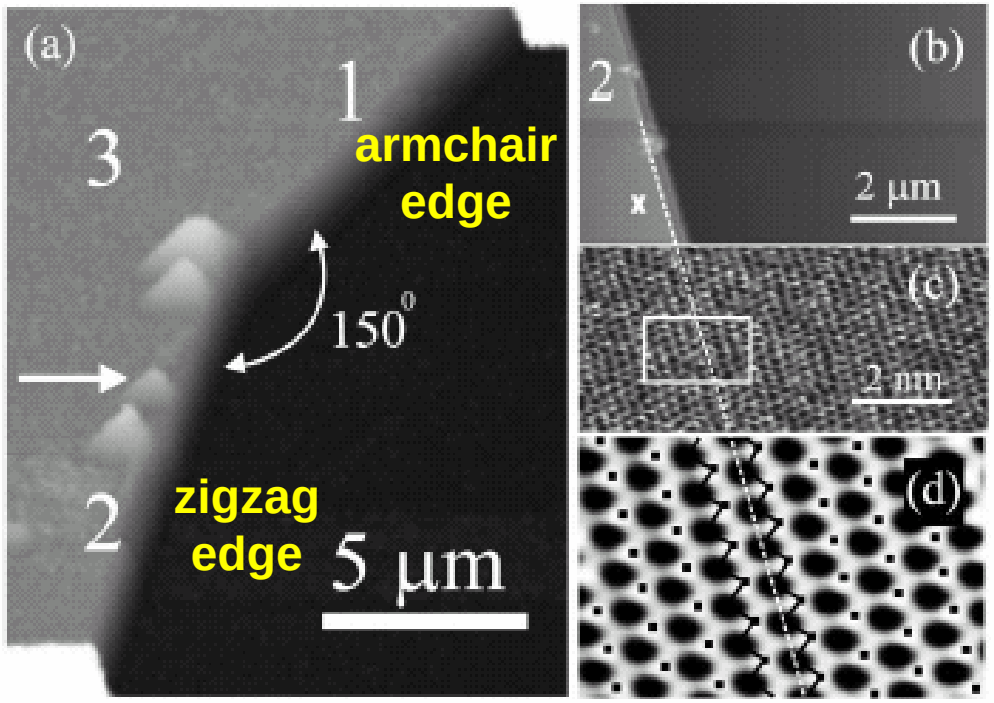
Graphene edge are armchair and zigzag edges



- armchair edges are favored (more stable)

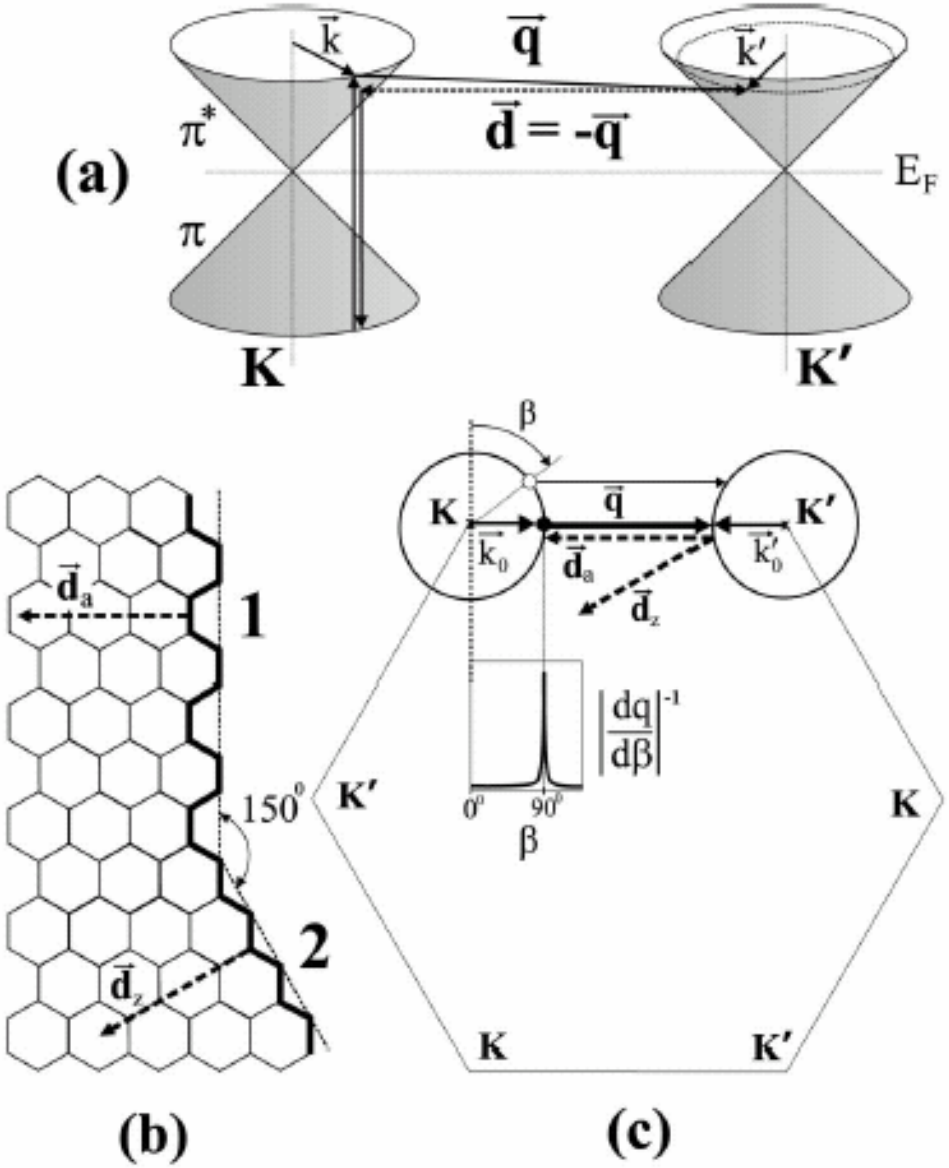
Raman and Scanning Probe Microscope studies in graphene edges





- The D-band intensity depends on the edge type
- The D-band is more intense in armchair edges

Double resonance Raman scattering in graphite edges

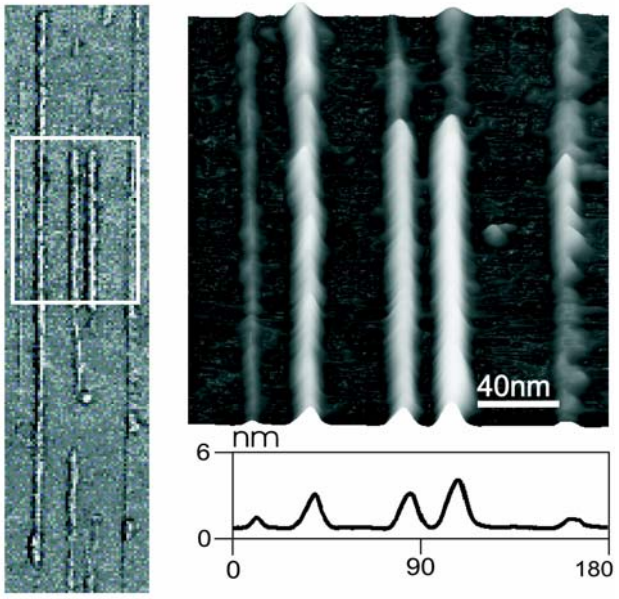


- The defect associated with the step edge is only able to transfer momentum in the direction perpendicular to the edge.
- Raman spectroscopy can be used to distinguish between armchair and zig-zag edges.

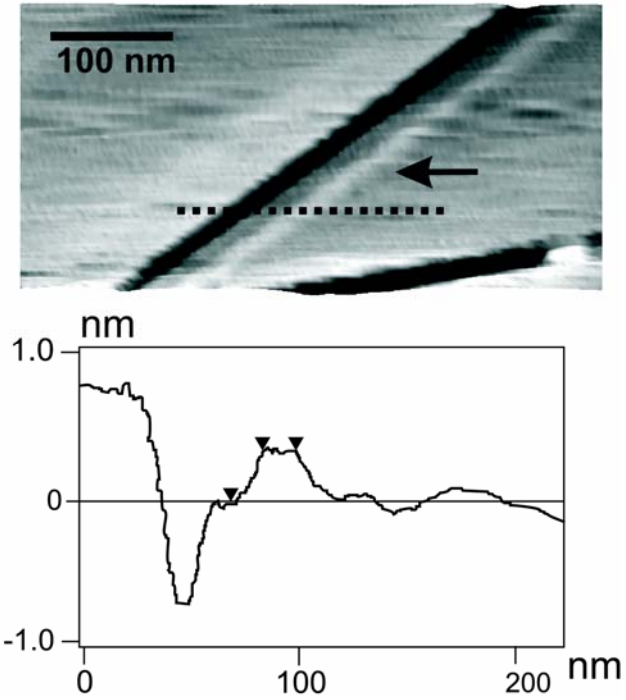
L. G. Cançado, et al. Phys. Rev. Letters, vol. 93, 247401 (2004)

Graphene ribbons for Raman study

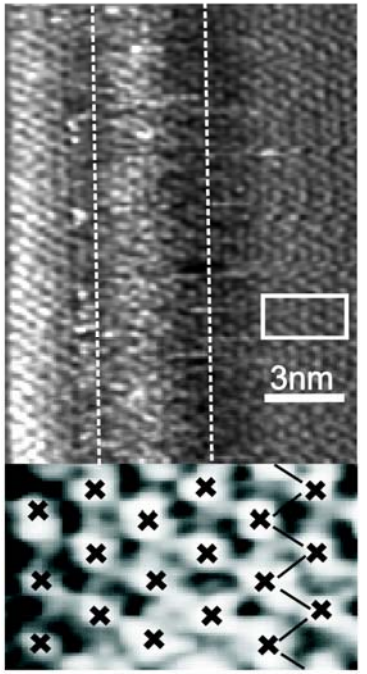
AFM image of many nanographite ribbons parallel to each other:



AFM image of a monolayer graphene ribbon:



STM image of a zigzag ribbon:



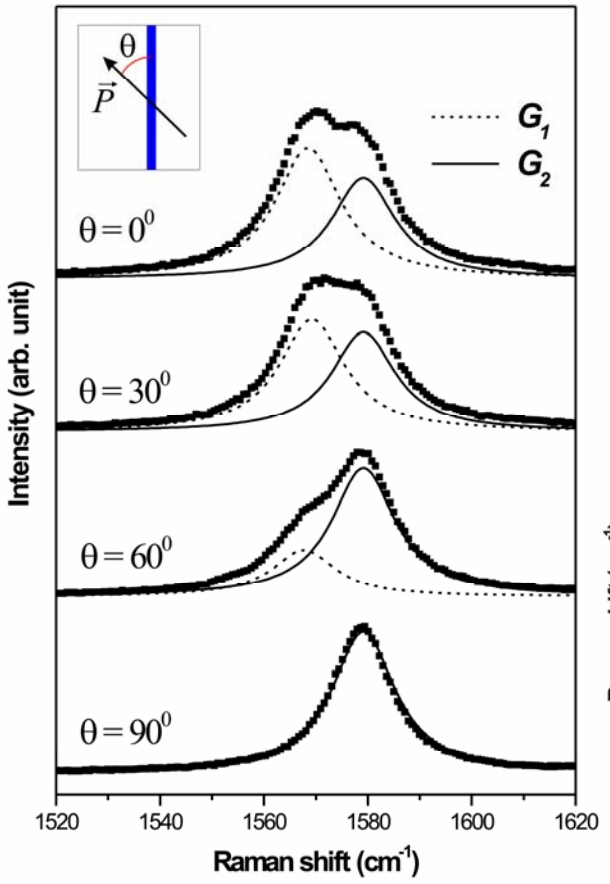
Cançado *et al.*, Phys. Rev. Lett. 93, 047403 (2004).

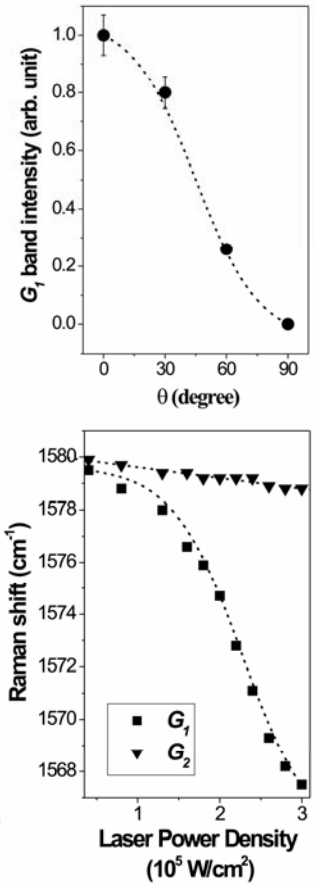
Synthesis:

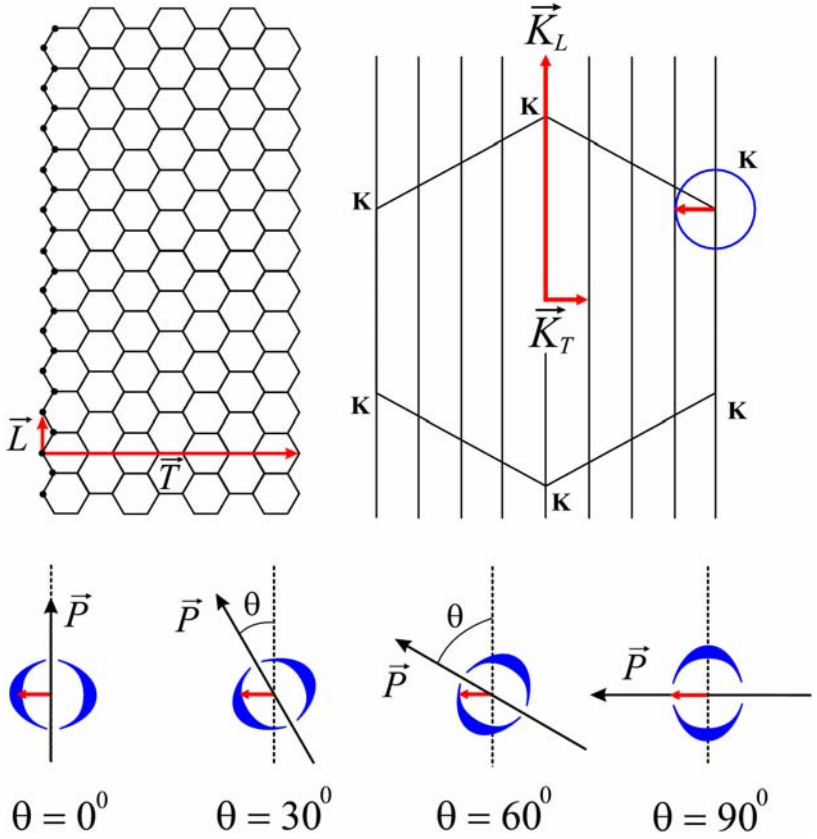
- **Electrophoretic deposition of nano-diamond particles on a HOPG substrate.**
- **At a temperature of 1600^{0}C, the nano-diamond particles are graphitized, forming nanographite sheets and ribbons.**

Affoune et al., Chem. Phys. Lett. **348**, 17 (2001), Langmuir **17**, 547 (2001) .

Raman spectra of graphene ribbons







G_1 - nanographite ribbon
G_2 - HOPG substrate

Cançado *et al.*, Phys. Rev. Lett. **93**, 047403 (2004).

$$W(\vec{k}) \propto \left|\vec{P} \times \vec{k}\right|^2$$

Gruneis *et al.*, Phys. Rev. B **67**, 165402 (2003).

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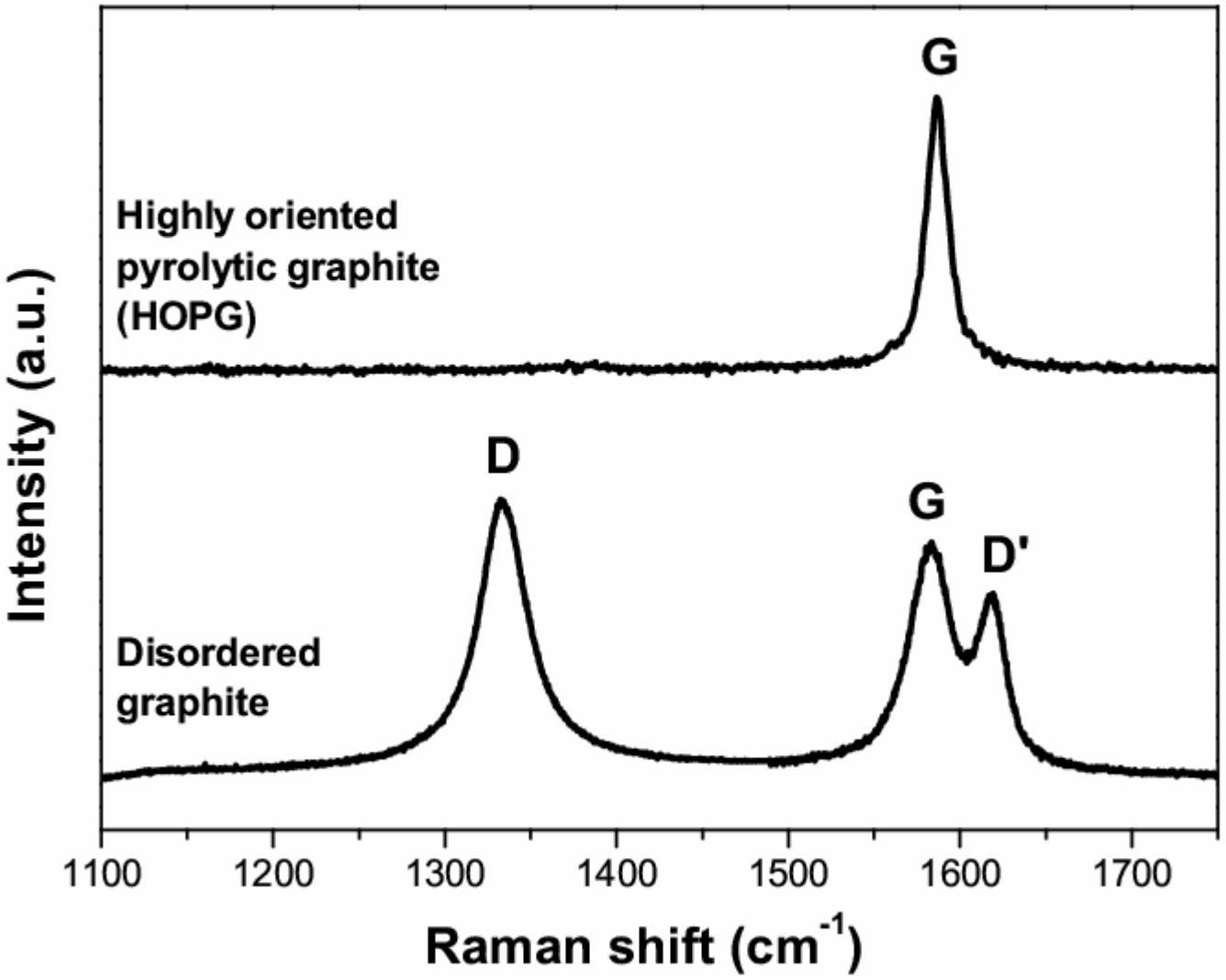
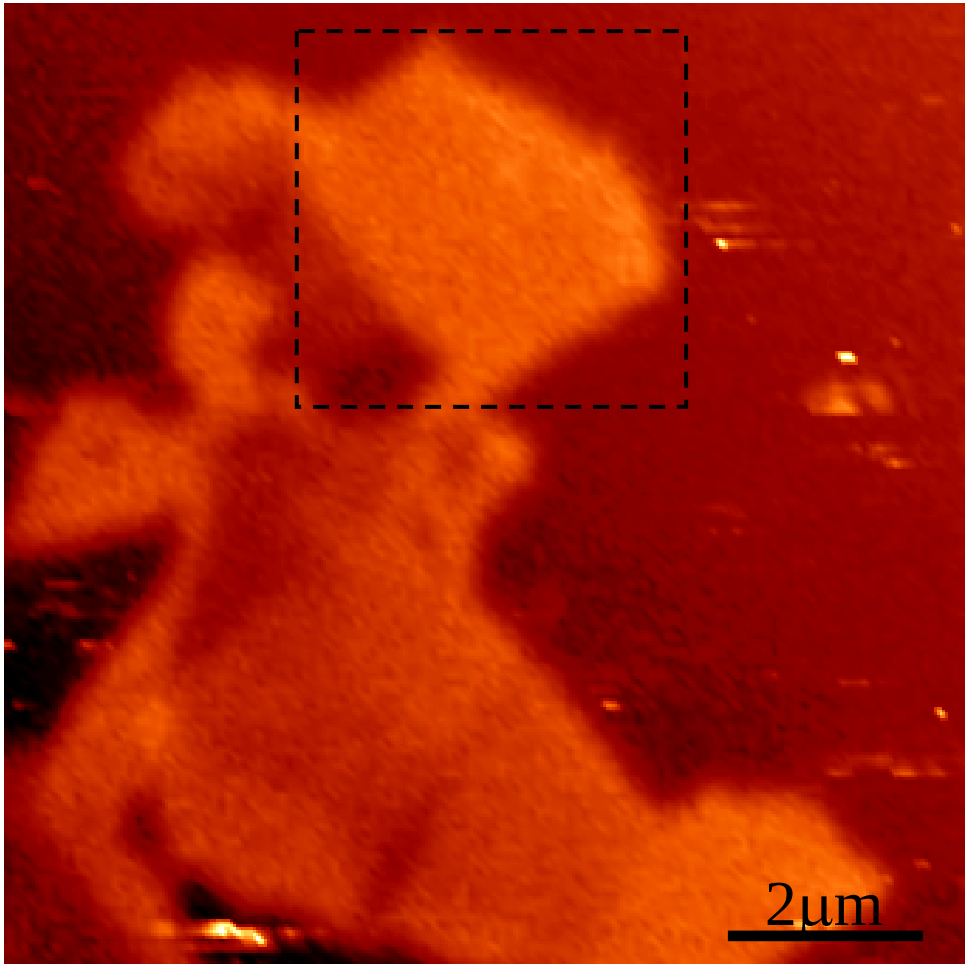
First Order Raman spectra of nanographites



Optical image of HOPG deposited on glass



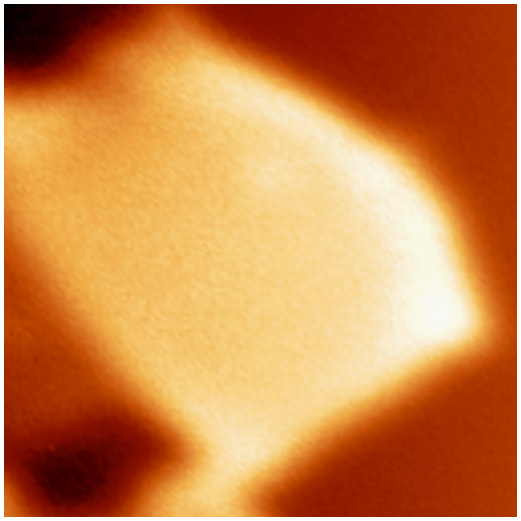
G band intensity

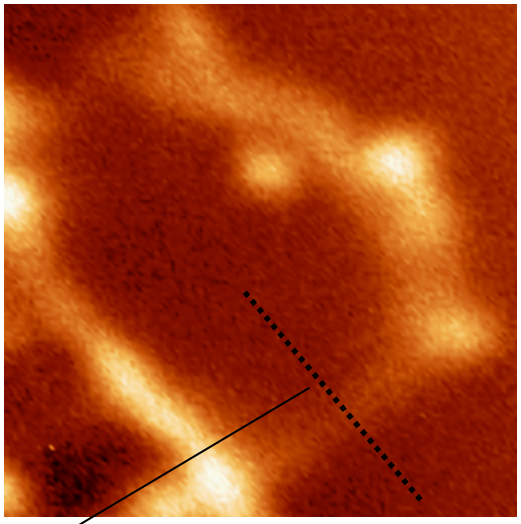
Performed by A..Jorio at Tuebingen Univesity, with A.Hartschuh

Confocal imaging of HOPG flakes

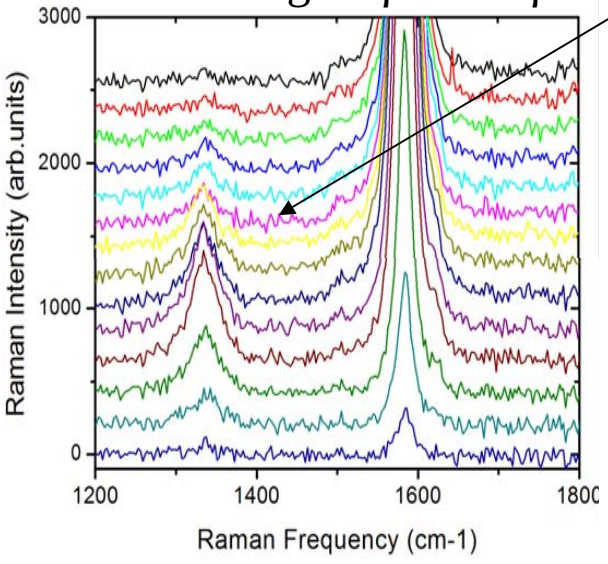
G band imaging

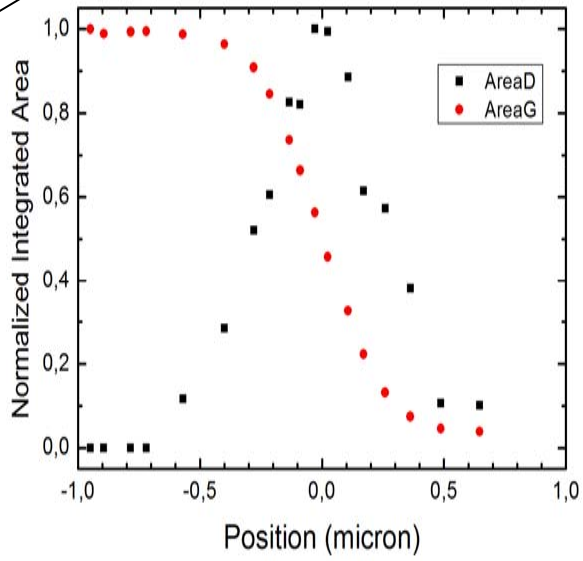
D band imaging





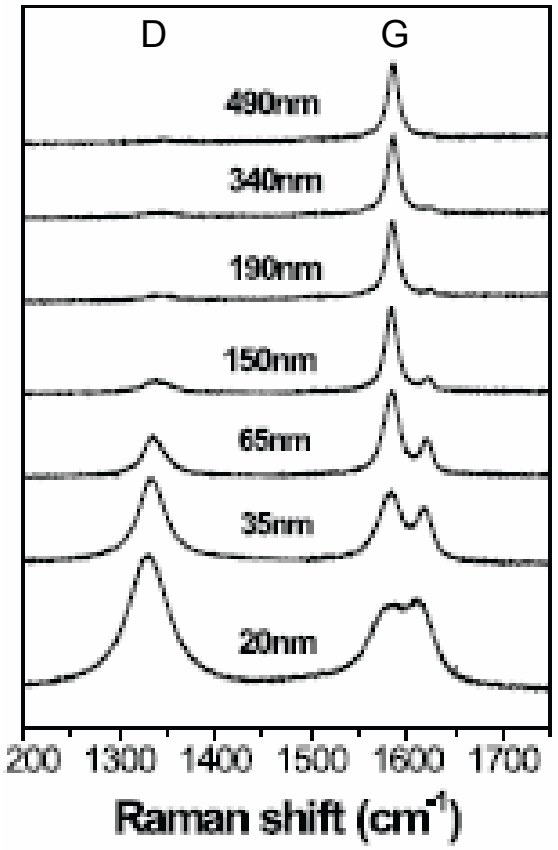
scan range 4 µm x 4 µm



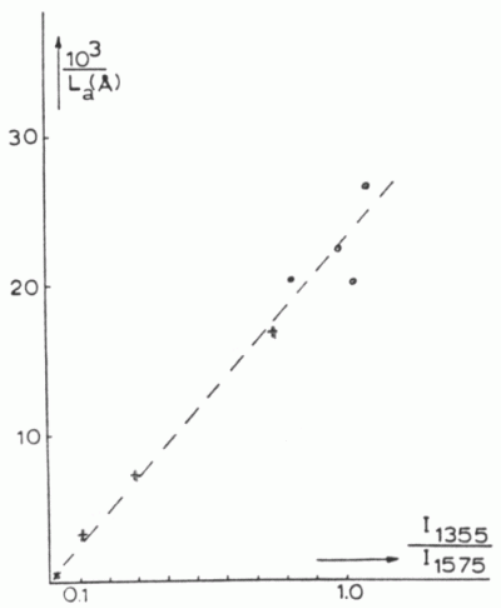


D-band is emphasized at the edge

Dependence of the ratio I_D/I_G on the crystallite size (L_a) in the Raman spectra of disordered graphite



$$L_a = \kappa \left[\frac{I_D}{I_G}\right]^{-1}$$

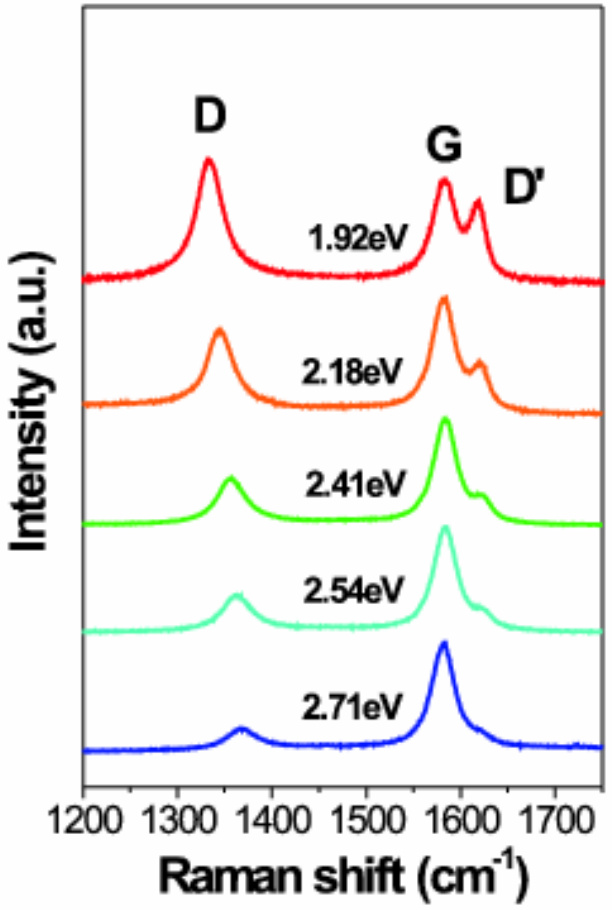


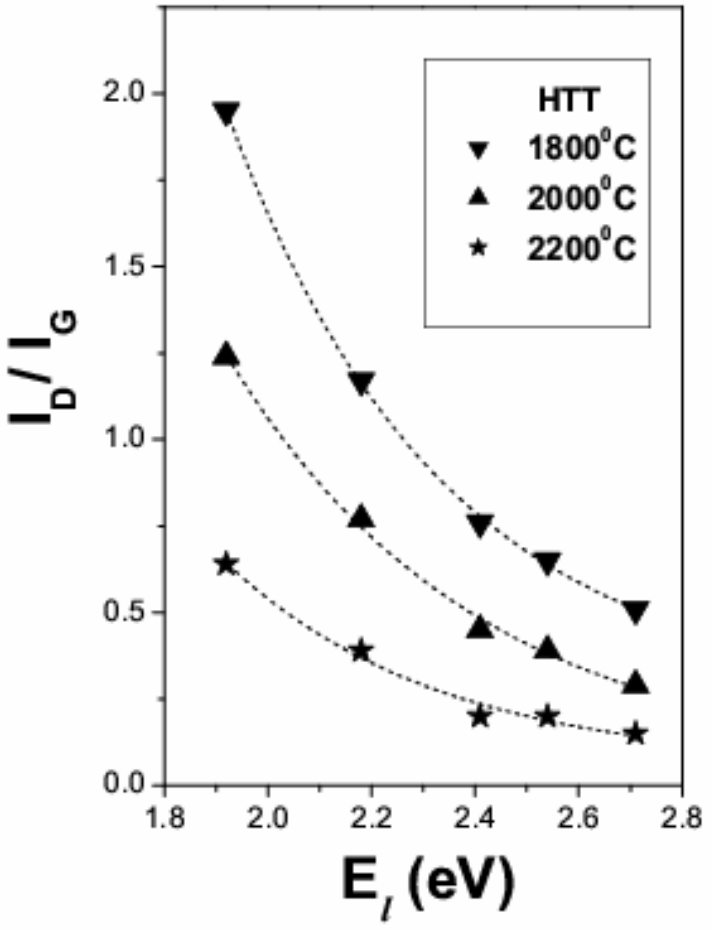
Tuinstra *and* Koenig, *J. Chem. Phys.* **53**, 1126 (1970).
Tuinstra *and* Koenig, *J. Compos. Mater* **4**, 492 (1970).

κ = 4.4 nm for λ = 514nm (2.41eV)

Knight and White, J. Mater. Res. **4**, 385 (1989).

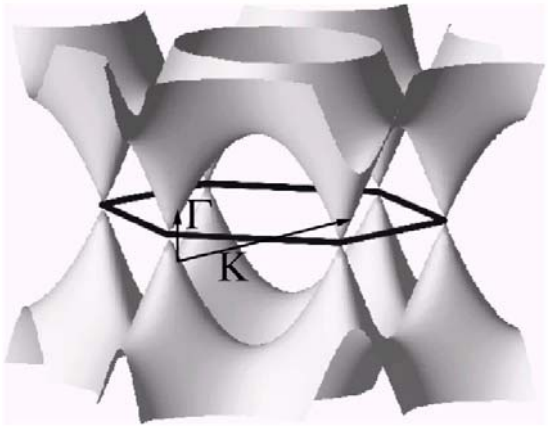
Dependence of the ratio I_D/I_G on the laser excitation energy E_l in the Raman spectra of disordered graphite

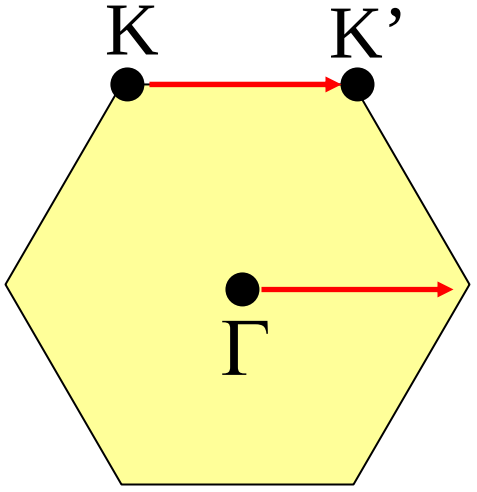


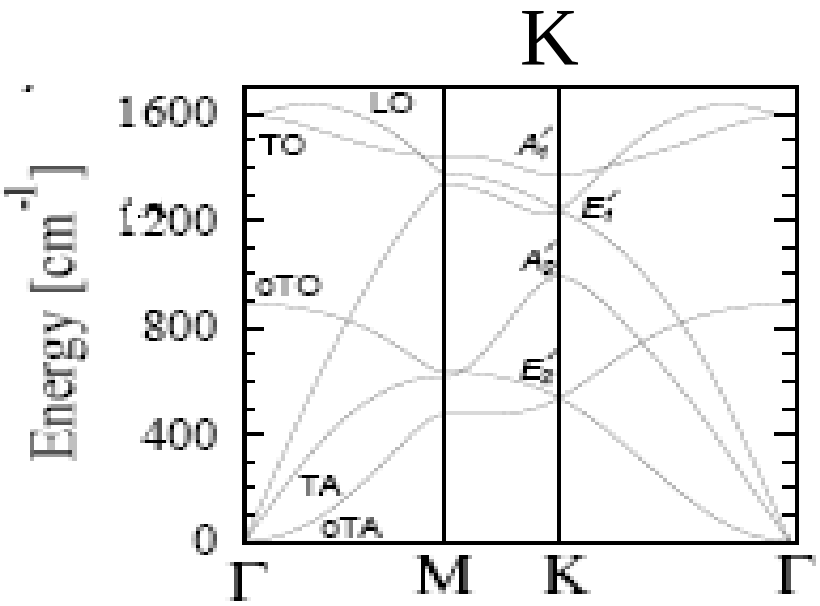


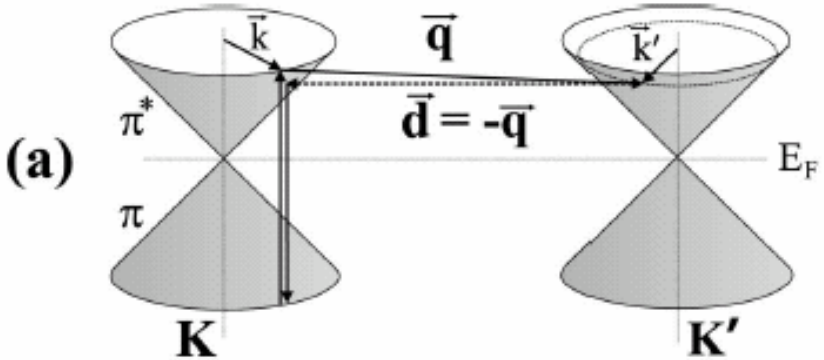
Mernagh *et al.*, Carbon **22**, 39 (1984).

Double resonance Raman scattering







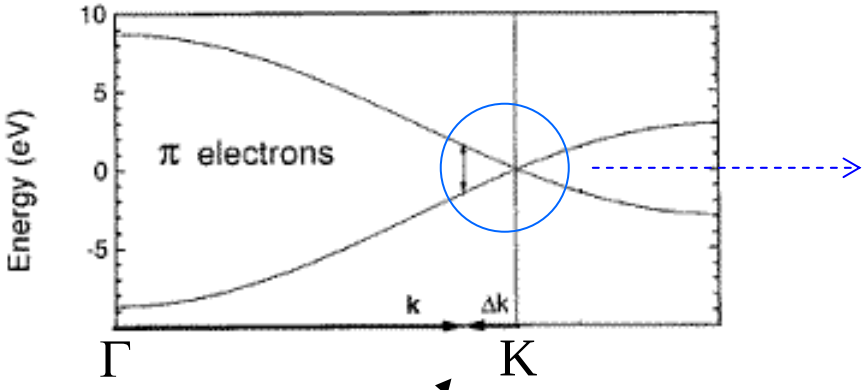


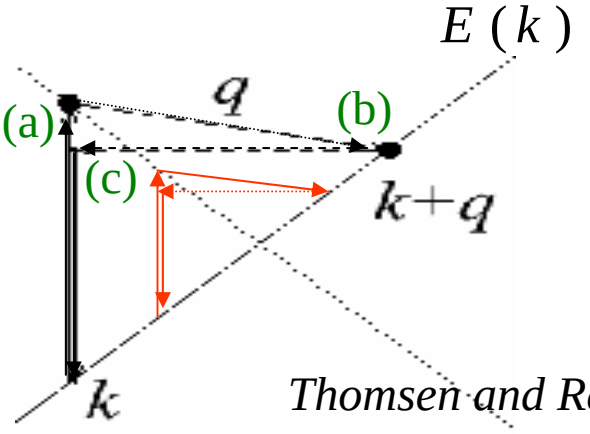
Thomsen and Reich, Phys Rev Letters, 85, 5214 (2000)

Saito et al, Phys Rev. Letters, 88, 027401 (2002)

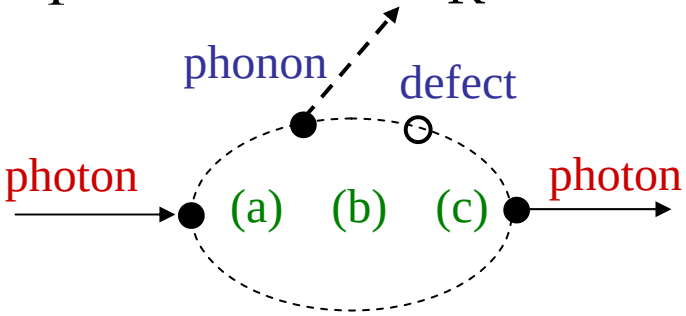
$$I = C \sum_{A,B,C} \frac{M}{(\hbar\omega_i - E_a - i\gamma)(\hbar\omega_i - \hbar\omega_q - E_b - i\gamma)(\hbar\omega_i - \hbar\omega_q - E_c - i\gamma)}$$

Double resonance Raman scattering

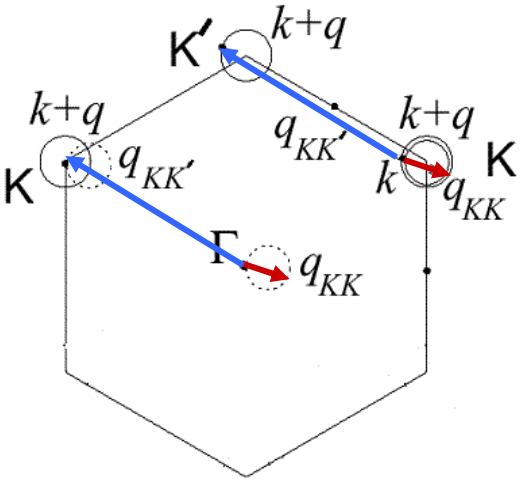




Thomsen and Reich, Phys. Rev. Letters 85, 5214 (2000)



Intra-valley and inter-valley Double resonance



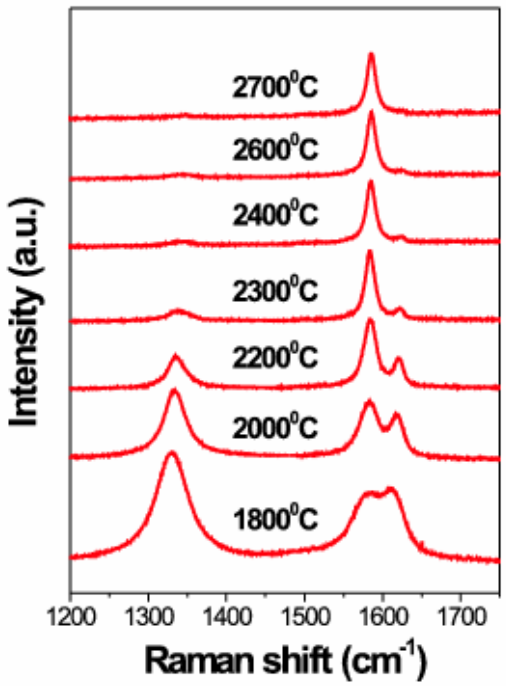
R. Saito, A. Jorio, A. G. Souza Filho, G. Dresselhaus, M.S. Dresselhaus, M.A. Pimenta,

Phys. Rev. Letters, 588, 027401 (2002)

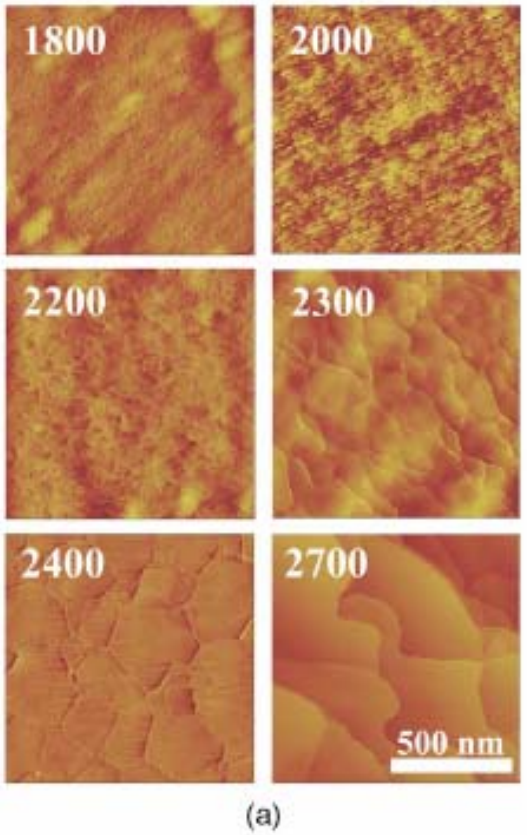
Intra-valley process: probing phonons near the Γ point

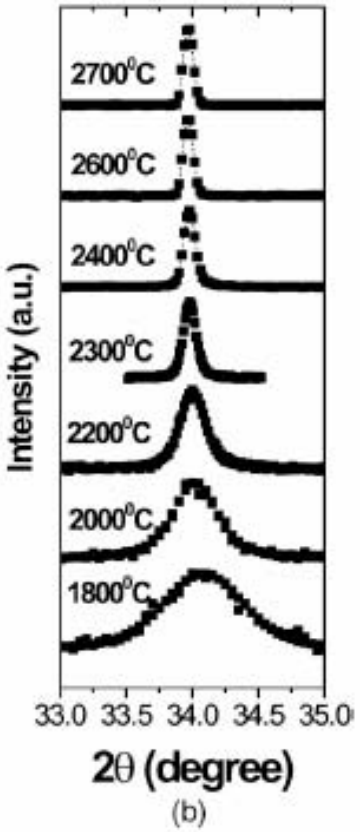
Inter-valley process: probing phonons near the K point

General equation for the determination of the crystallite size L_a of nanographite by Raman spectroscopy



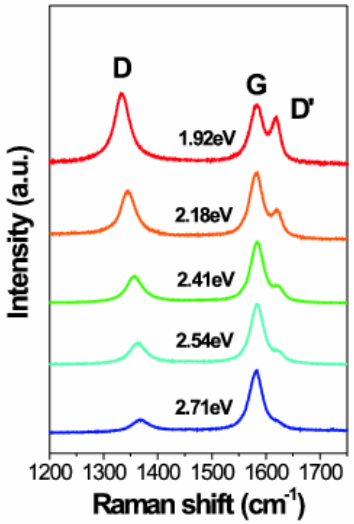
HTT (°C)	L_a (nm) (X ray)	L_a (nm) (STM)
2700	490	550
2600	340	300
2400	190	220
2300	150	120
2200	65	60
2000	35	40
1800	20	20





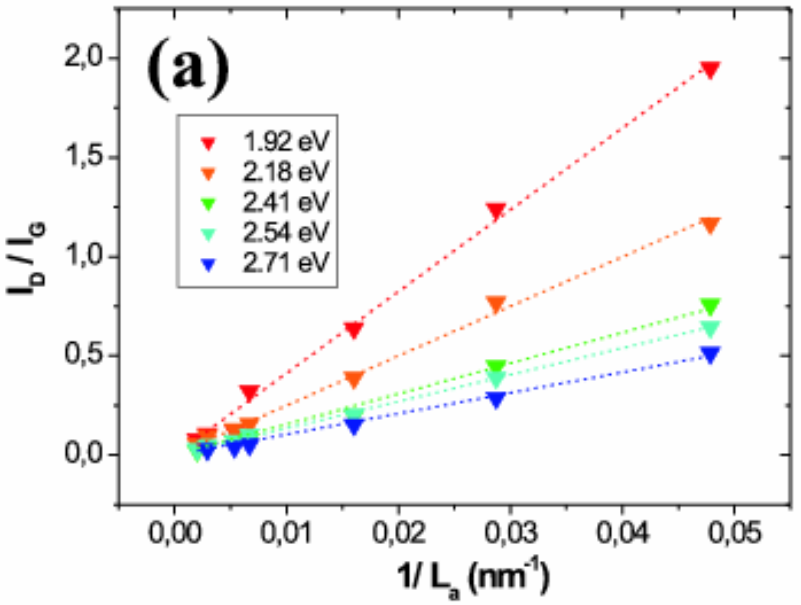
Cançado *et al.*, Applied Physics Letters **88**, 163106 (2006).

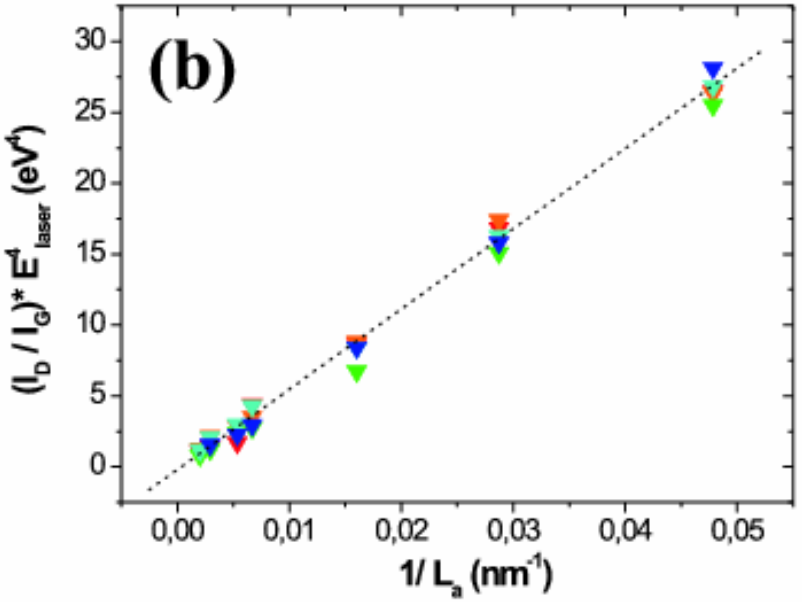
General equation for the determination of the crystallite size L_a of nanographite by Raman spectroscopy



$$L_a(\text{nm}) = \frac{560}{E_l^4}\left(\frac{I_D}{I_G}\right)^{-1}$$

$$L_a(\text{nm}) = (2.4 \times 10^{-10})\lambda_l^4\left(\frac{I_D}{I_G}\right)^{-1}$$





Cançado *et al.*, Applied Physics Letters **88**, 163106 (2006).

Physics of Nanotubes, Graphite and Graphene

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Outlook

- Nanostructured carbon systems (fullerenes, nanotubes, graphite) grow out of graphene.
- Graphene research is now expanding rapidly because of intrinsic interest with many new areas also opening up through suggestions from nanotubes, graphite, etc.
- Carbon nanostructure fields are in various stages of development. This situation promotes cross stimulations between these fields to advance both science and applications