Tailoring carbon nanostructures: Unraveling the electronic properties of low-dimensional quantum solids

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16.6. 2009, University of Tokyo

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epm

Acknowledgements

Vienna University group:
C. Kramberger: IXS, EELS, Photoemission on aligned SWCNT
A. Grüneis: IXS, Raman/Photoemission of Graphene, GIC
P. Ayala: Raman/Photoemission of separated nanotubes, heteronanotubes
K. de Blauwe, X. Liu, R. Pfeiffer, F. Simon, W. Plank, H. Kuzmany
IFW-Dresden: H. Rauf, M. Rümmeli, M. Knupfer (EELS)
Surrey University: H. Shiozawa
ICN Barcelona: A. Barreiro, A. Bachtold
Synchrotron:
BESSY: D. Batchelor, J. Fink, Grenoble: S. Bossak, M. Kirsch, J. Serrano
Theory:
Donestia San Sebastian: A. Rubio, C. Allicante, Lille Univ.: L. Wirtz,
Univ. Paris 6: F. Mauri, M. Lazzeri, Ecole Polytech.: L. Reining, R. Hambach
Tohoku Univ.: R. Saito
Samples:
AIST: H. Kataura, K. Suenaga (TEM), Tokyo Univ.: S. Maruyama, E. Einarsson
IFW-Dresden: M.H. R. Nagoya Univ: Y. Miyata, R. Kitaura, H. Shinohara

Funding: DFG, FWF, APART, EU

Outline

- Introduction/Motivation/Experimental
- Part 1: Angle resolved dielectric response of SWCNT
  - a) SWCNT bundles vs. individual SWCNT
  - b) Implications on excitation spectrum in 1D,2D
  - c) 1D „Drude“ plasmon in intercalated SWCNT?
- Part 2: Electronic structure of metallicity selected SWCNT
  - a) Textbook example for intrinsic XPS line shapes
  - b) Unravelling the 1D DOS in PES and XAS
  - c) Nature of metallic ground state in metallic SWCNT
- Part 3: Functionalized SWCNT:
  - a) Examples for intercalation, filling and substitution
  - b) Nanochemical reactions inside SWCNT
- Part 4: Electronic and phononic structure of graphene systems
  - a) Electron dispersion, phonon dispersion and EPC
  - b) GIC KC_8 revisited: A key to graphene

- Summary and outlook

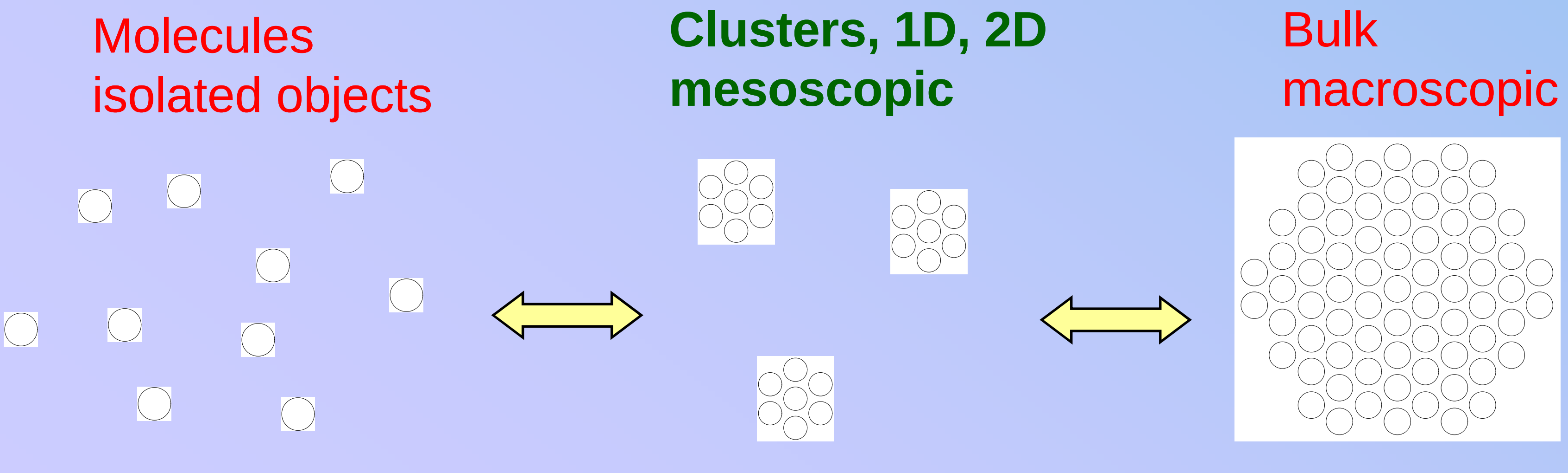
Low dimensional quantum systems?

- All solids are of course quantum systems
- 1D and 2D quantum solids:
  - Mesoscopic systems with size quantization
  - Quantum effects already at room temperature
  - Correlation effects crucial:
    electron-hole, electron-electron, electron-phonon
  - Instabilities in 1D and 2D systems!

⇨ Molecular carbon nanostructures are
archetypical examples of perfect 1D and 2D solids

More general Framework

- Electronic/optical properties: Interaction of light and charges with matter
- Novel behavior in micro- and nano-meshed meta-materials.
- How much do surface and/or bulk properties actually contribute?
- What is the needed separation for isolated objects as low D systems?
- Can we tailor the properties?



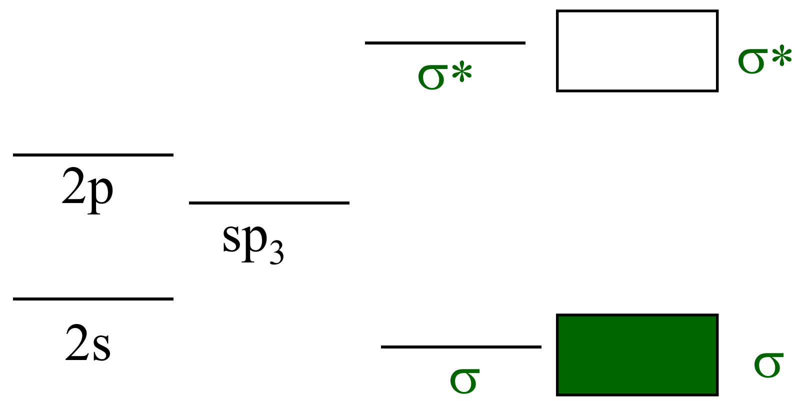
Molecules
isolated objects

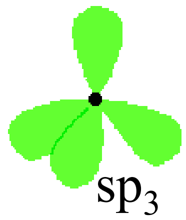
Clusters, 1D, 2D
mesoscopic

Bulk
macroscopic

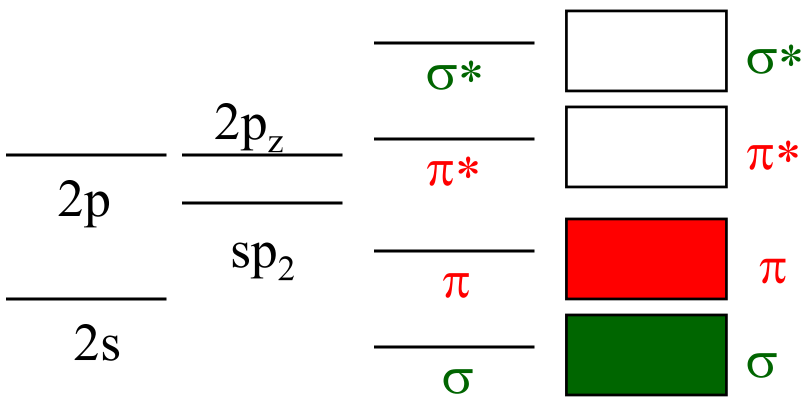
Electronic structure of different carbon allotropes

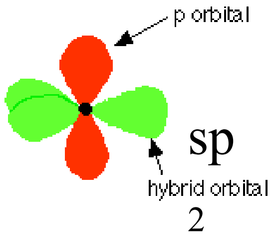
Two 1s core electrons and 4 valence electrons (two 2s and two 2p)



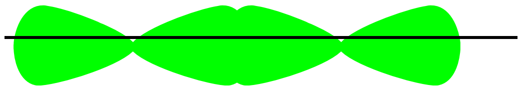


Diamond

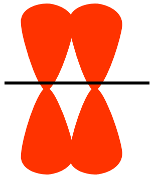




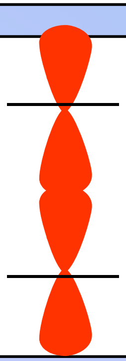
graphite
nanotubes
fullerenes
conj. polymers



σ-bonds: W~50 eV



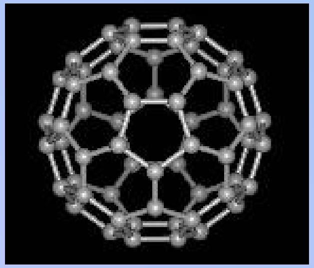
π-bonds
W~ 20 eV



σ–bond
π-orbital:
W~ 0.5 eV

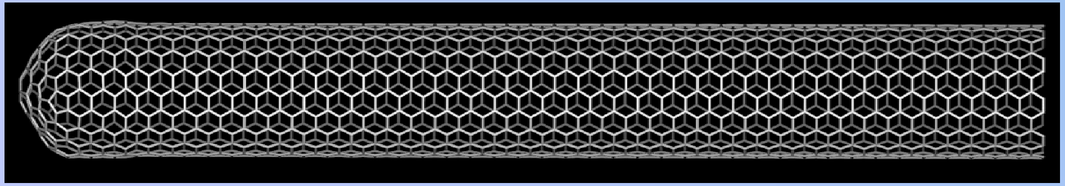
All-carbon Nanostructures

0D



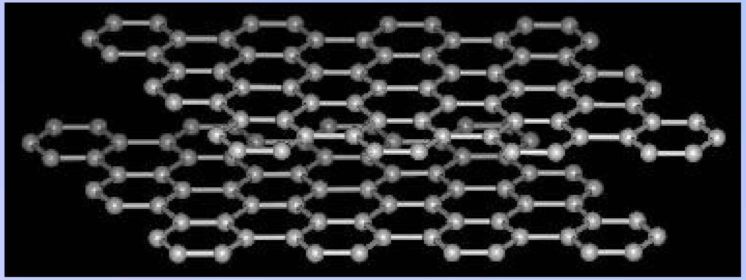
Fullerenes, C_{60}

1D



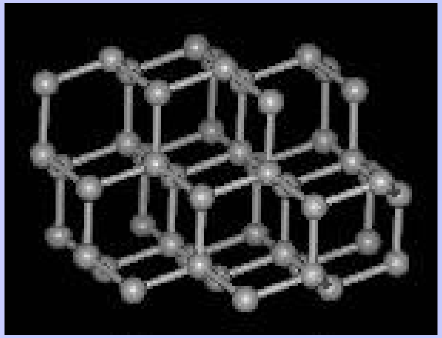
Nanotubes

2D



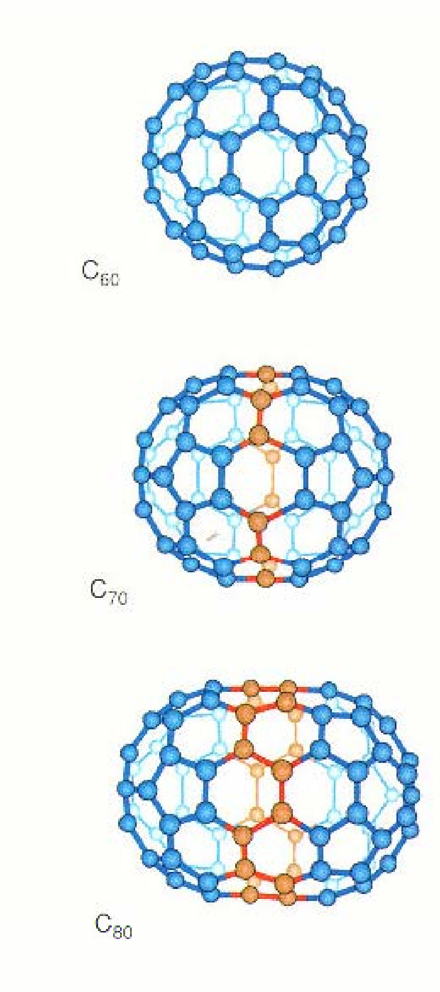
Graphite

3D



Diamond

Carbon nanotubes



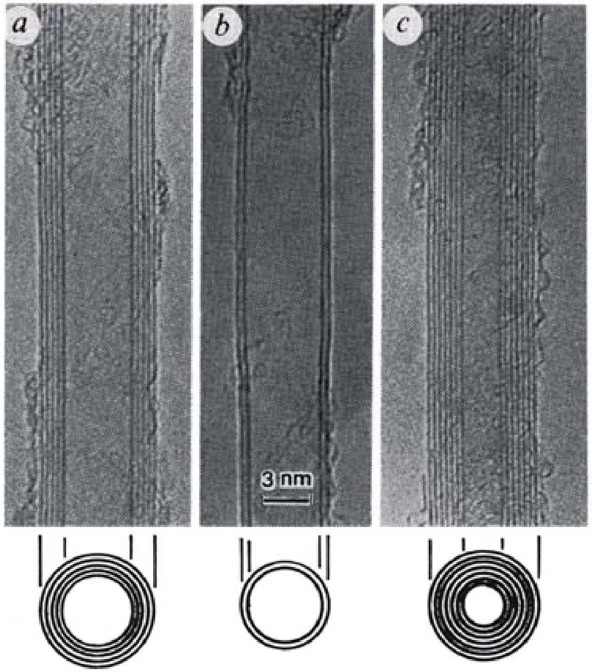
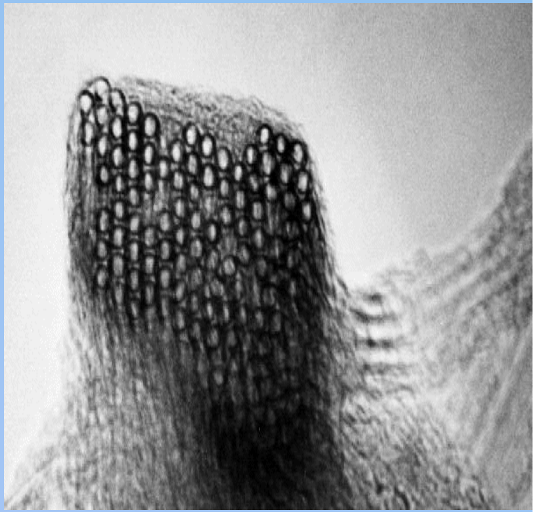
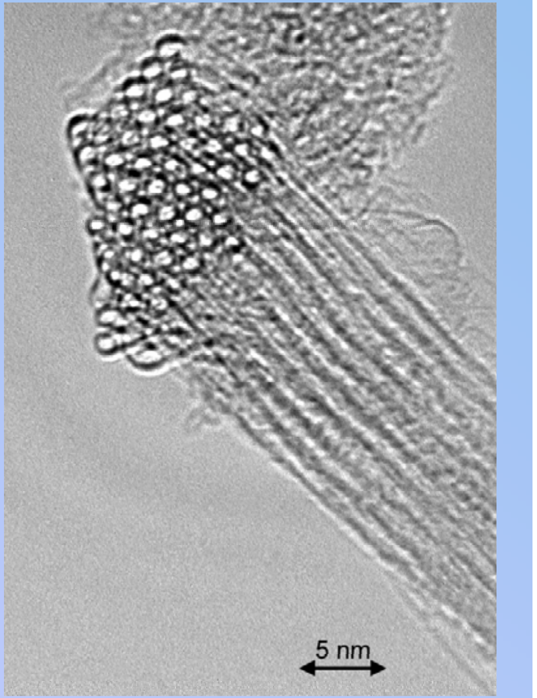


FIG. 1 Electron micrographs of microtubules of graphitic carbon. Parallel dark lines correspond to the (002) lattice images of graphite. A cross-section of each tubule is illustrated. *a*, Tube consisting of five graphitic sheets, diameter 6.7 nm. *b*, Two-sheet tube, diameter 5.5 nm. *c*, Seven-sheet tube, diameter 6.5 nm, which has the smallest hollow diameter (2.2 nm).





1991 Iijima, TEM of carbon nanotubes
d ~ nm, l ~ 100 nm - 1 mm, MWCNT
SWCNT bundles 5-20 nm diameter

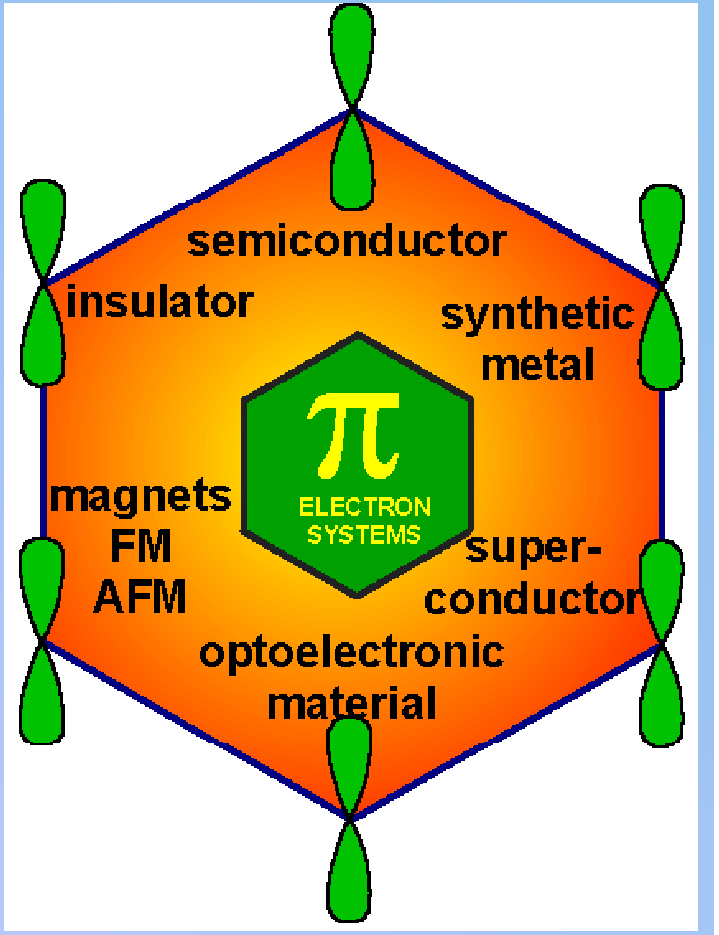
Why carbon nanotubes?

- **Archetypical 1D system:**

New electronic, optical and structural properties:

- Ideal 1D quantumwires
- Hard, ductile Nanowires
- Molecular Magnets, Spintronics
- Protection for reactive elements and molecules
- Gas storage
- FET, VIAS, optoelectronic
- Sources for field emission
- Organic superconductors
- Li-Ion batteries
- Sensors, actuators, NT-yarns, composits, drug delivery…..

⇨ Ideal tools for nanoelectronics/optics/mechanics/(bio)chemistry



Special properties of nanotubes

- Electronic propertieres:

Geometry of SWCNT : 2/3 are semiconducting 1/3 metallic
conductivity tunable by functionalisation

Temendous current carrying capacity: 1 billion A/cm2
no electromigration

Excellent heat conductor: twice as good as diamond

- Mechanical properties:

Strength at least 100 times higher than steel
Youngs modulus 1 Tpa
Flexible → ultimate carbon fibers

- Geometry:

High aspect ratio of 1000 to 10000, 1 nm diameter
High surface area

Why carbon nanotubes?

Ideal one dimensional (1D) objects

Outstanding mechanical and electronic properties

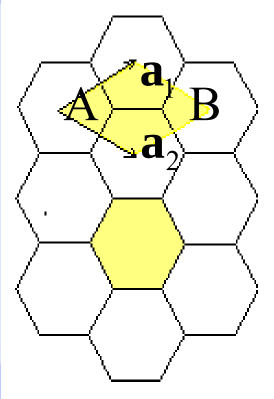
Ideal systems to study basic correlation effects even at room temperature!!!!!!

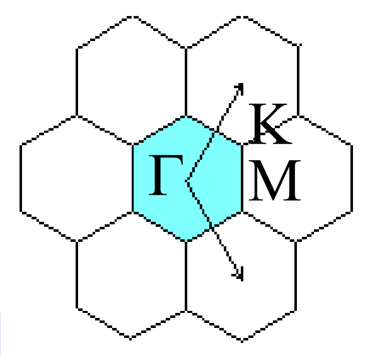
Tuneable electronic properties and interactions!!!

⇓

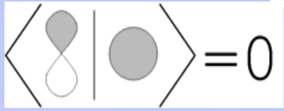
Interesting for both
basic research and applications

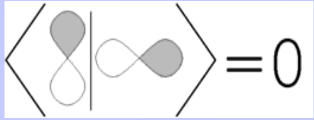
ELECTRONIC STRUCTURE OF GRAPHENE

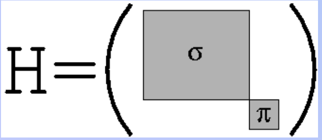




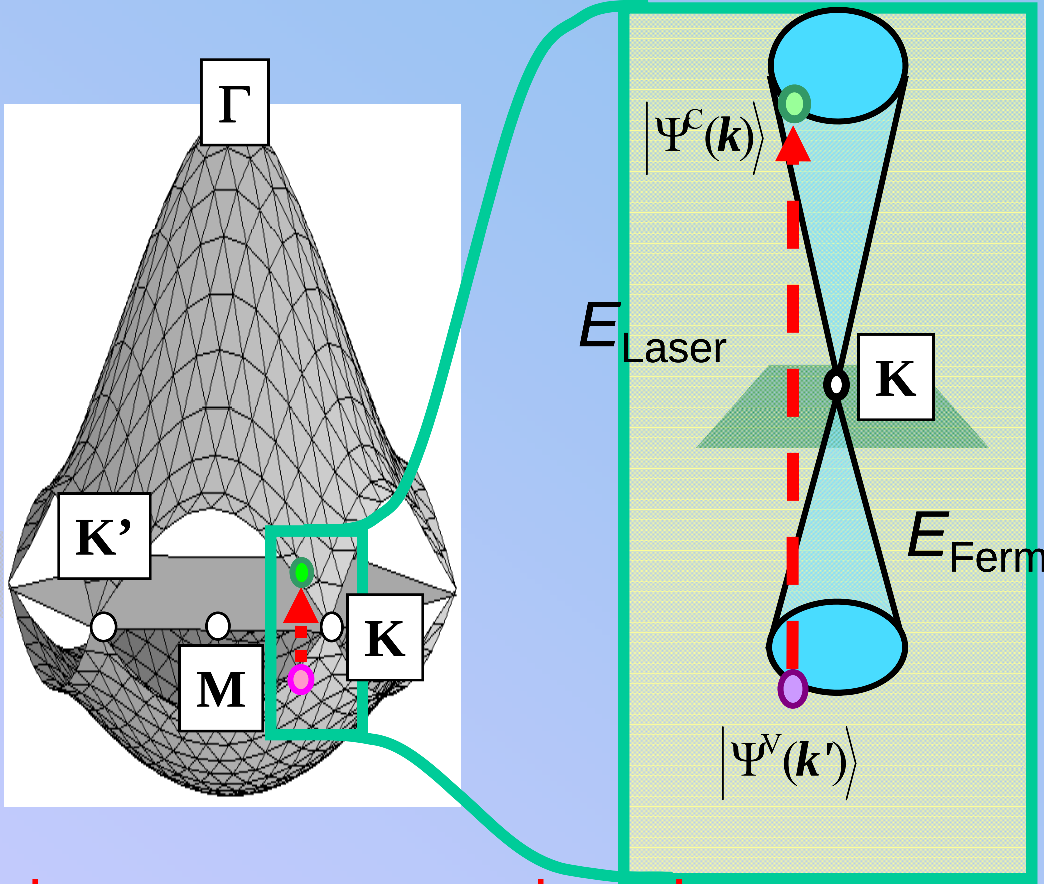
$$H(\mathbf{k})c^j(\mathbf{k}) = E^j(\mathbf{k})S(\mathbf{k})c^j(\mathbf{k})$$

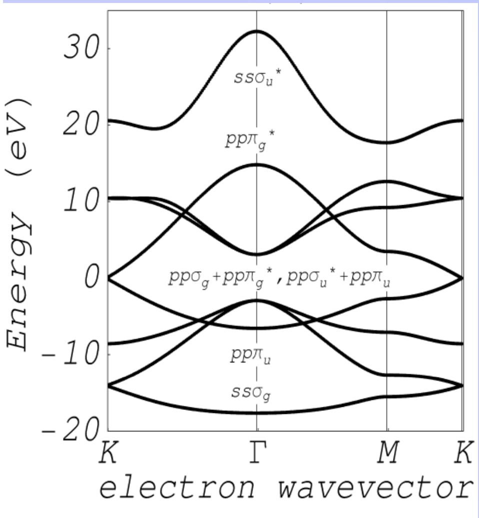






2D BZ



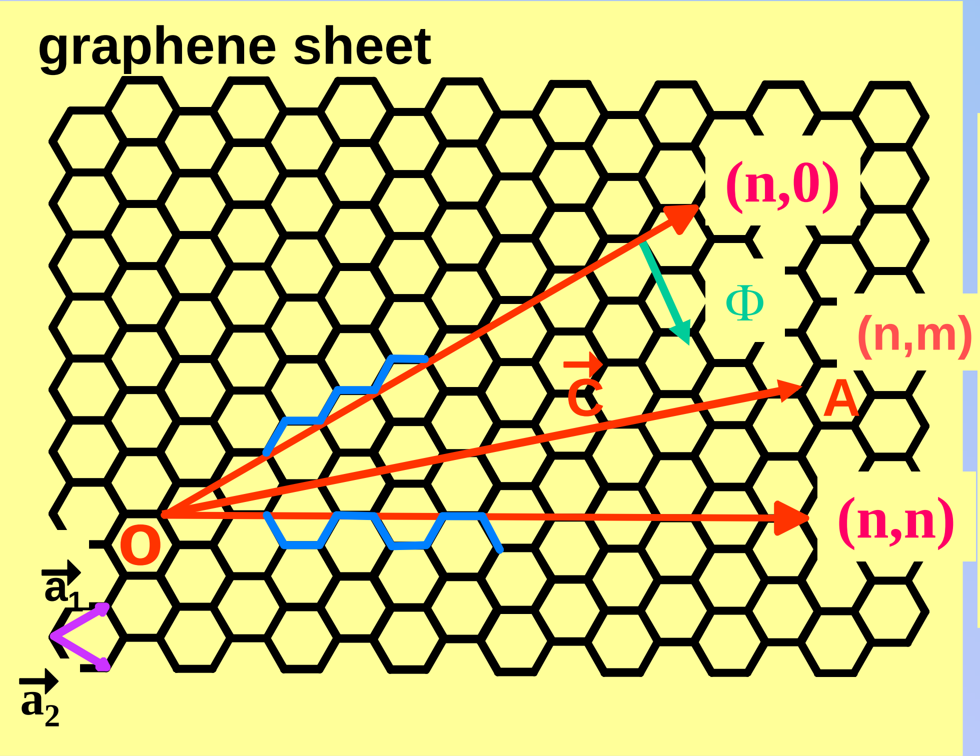


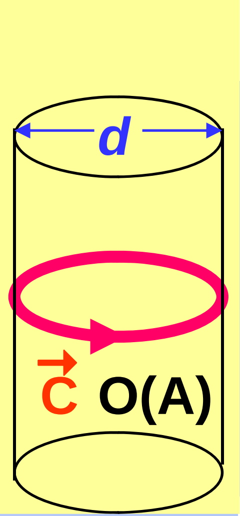
Graphene is a zero gap semiconductor.
Bands at Fermi energy (K point) are linear in k.

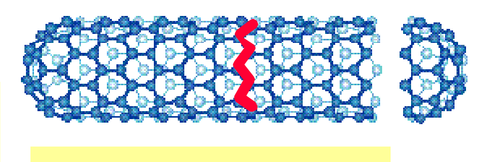
Wallace (1947), Painter and Ellis PRB 1, 4747 (1970)

Introduction: formation of single-wall carbon nanotubes

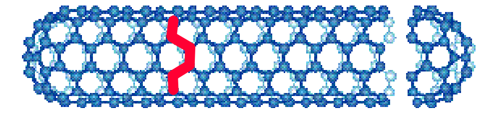
SWCNTs $\vec{C} = n\vec{a}_1 + m\vec{a}_2 = (n,m)$ **Hamada vector**



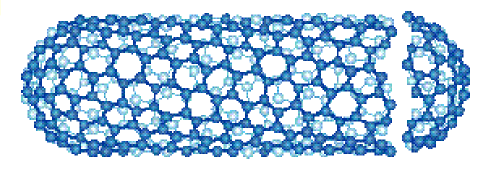




(n,0) zigzag Φ=0



(n,n) armchair Φ=30°



(n,m) chiral 0<Φ<30°

The diameter of SWCNT (n,m):

$$d_{n,m}=|C|/\pi=a(n^2+m^2+mn)^{1/2}/\pi$$

$$a=|a_1|=|a_2|=2.49\ \text{Å}$$

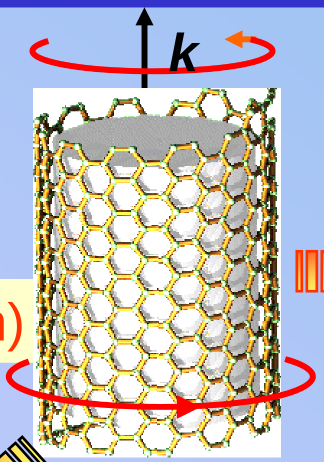
e.g. (10,10) d=1.37nm

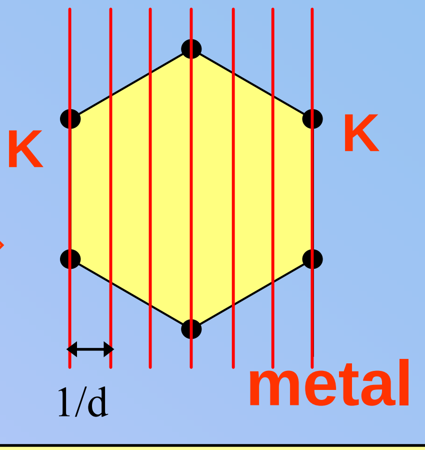
Introduction: electronic properties of SWCNTs

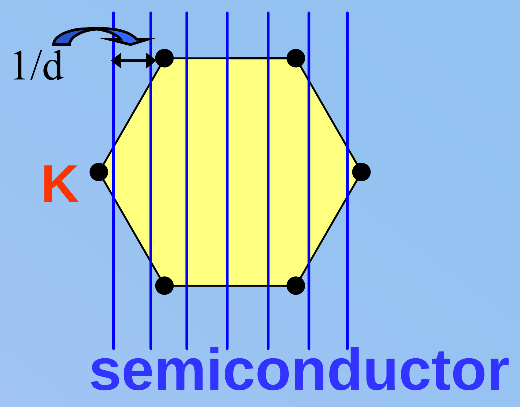
periodic boundaries

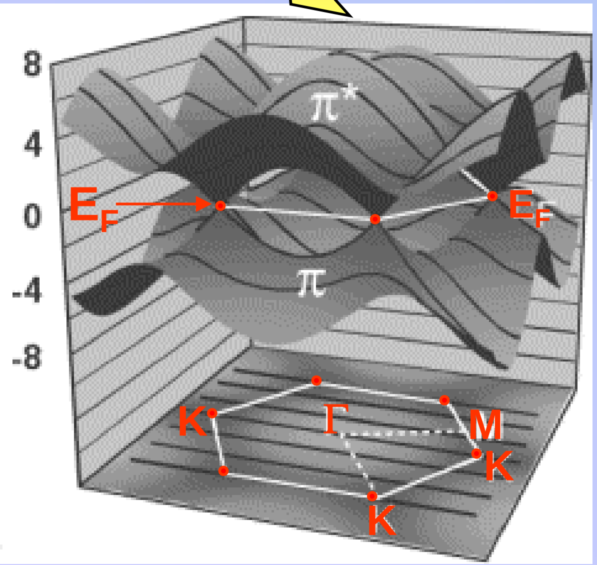
$2\pi d\cdot k_n=2\pi\cdot n$

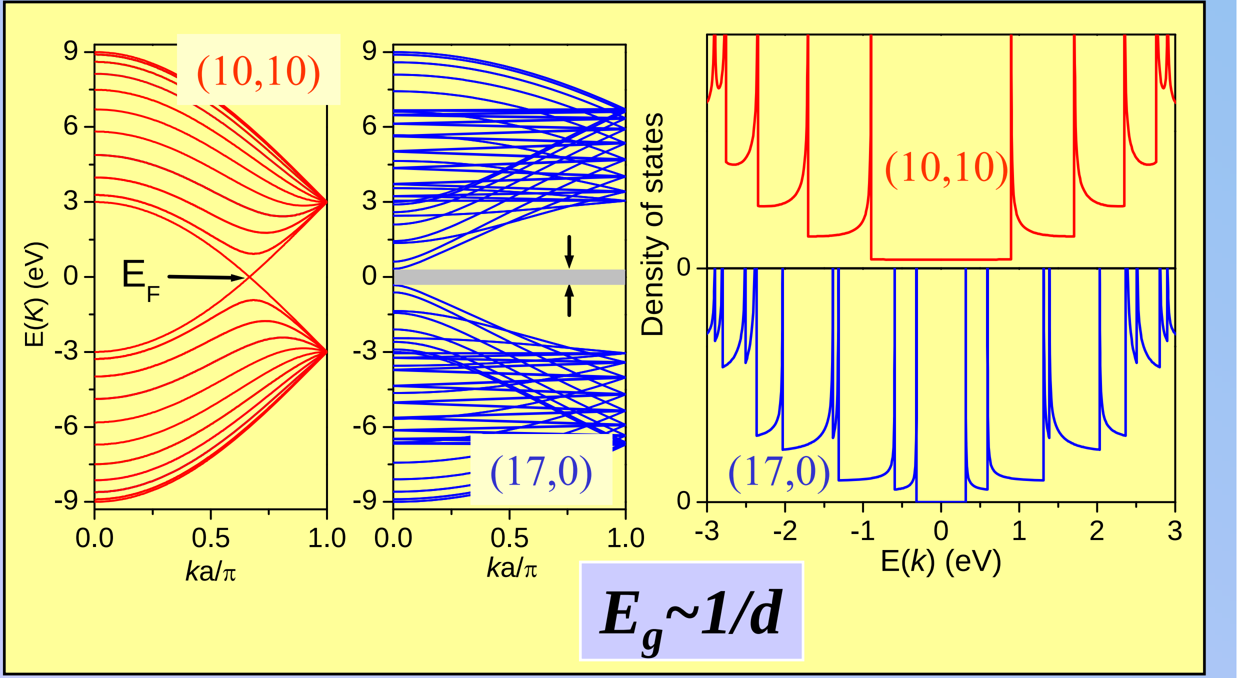
(k_n-quantization)











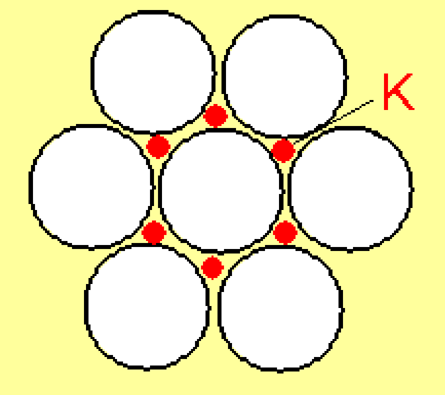
$E_g \sim 1/d$

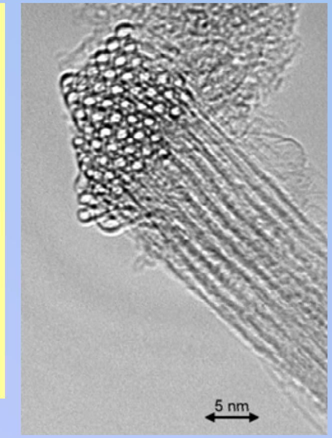
Electronic properties are determined by the structure of SWCNT

using tight binding approximation

Functionalization: doping and filling of SWCNT

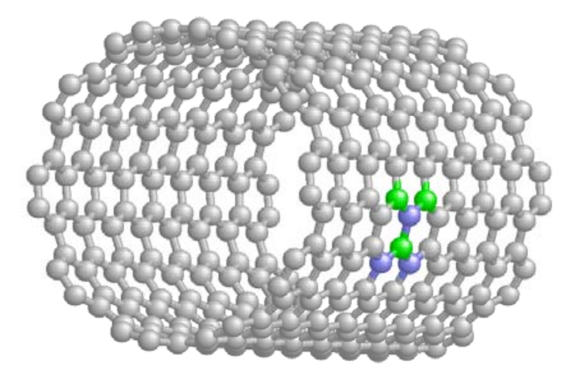
- **Intercalation:**

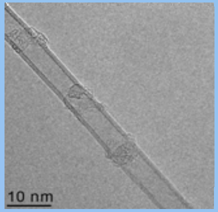


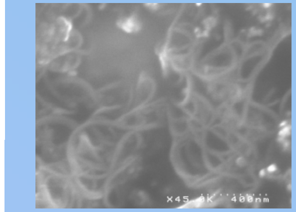


e.g. K_x-SWCNT

Substitution:

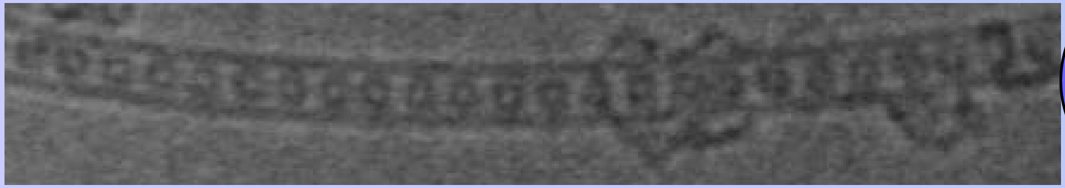


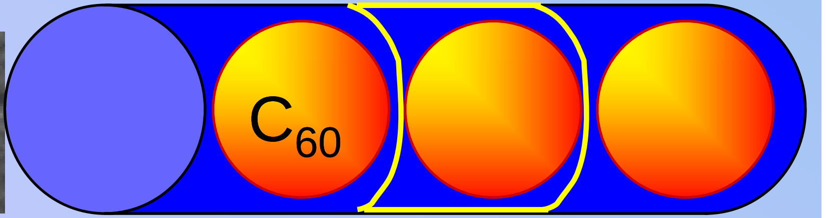




BC_3-SWNT, MWBNT, SiCNT

- **Filling: C_{60} Peapods, DWCNT….**





⇨ Optical and high energy spectroscopy are ideal tools!

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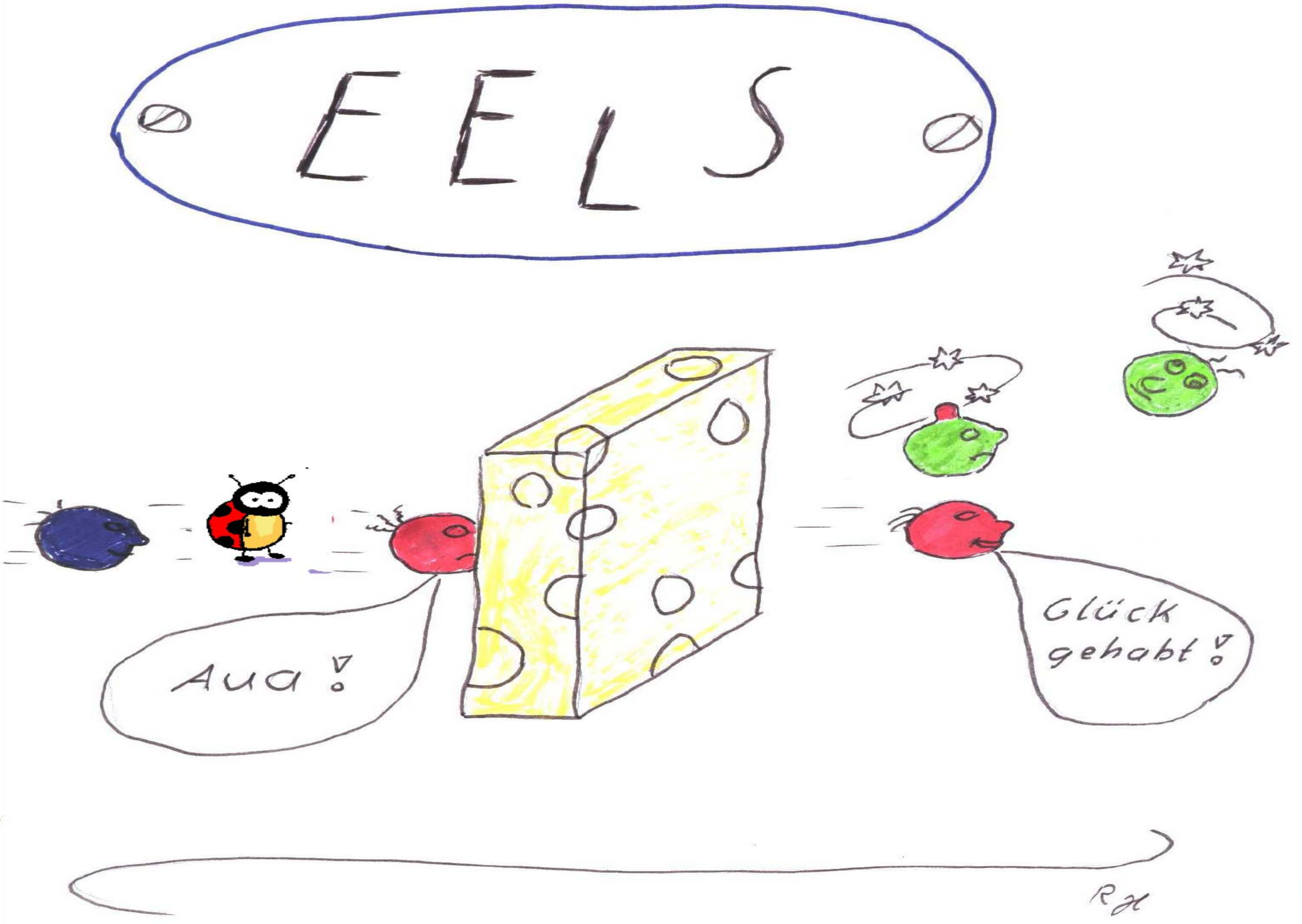
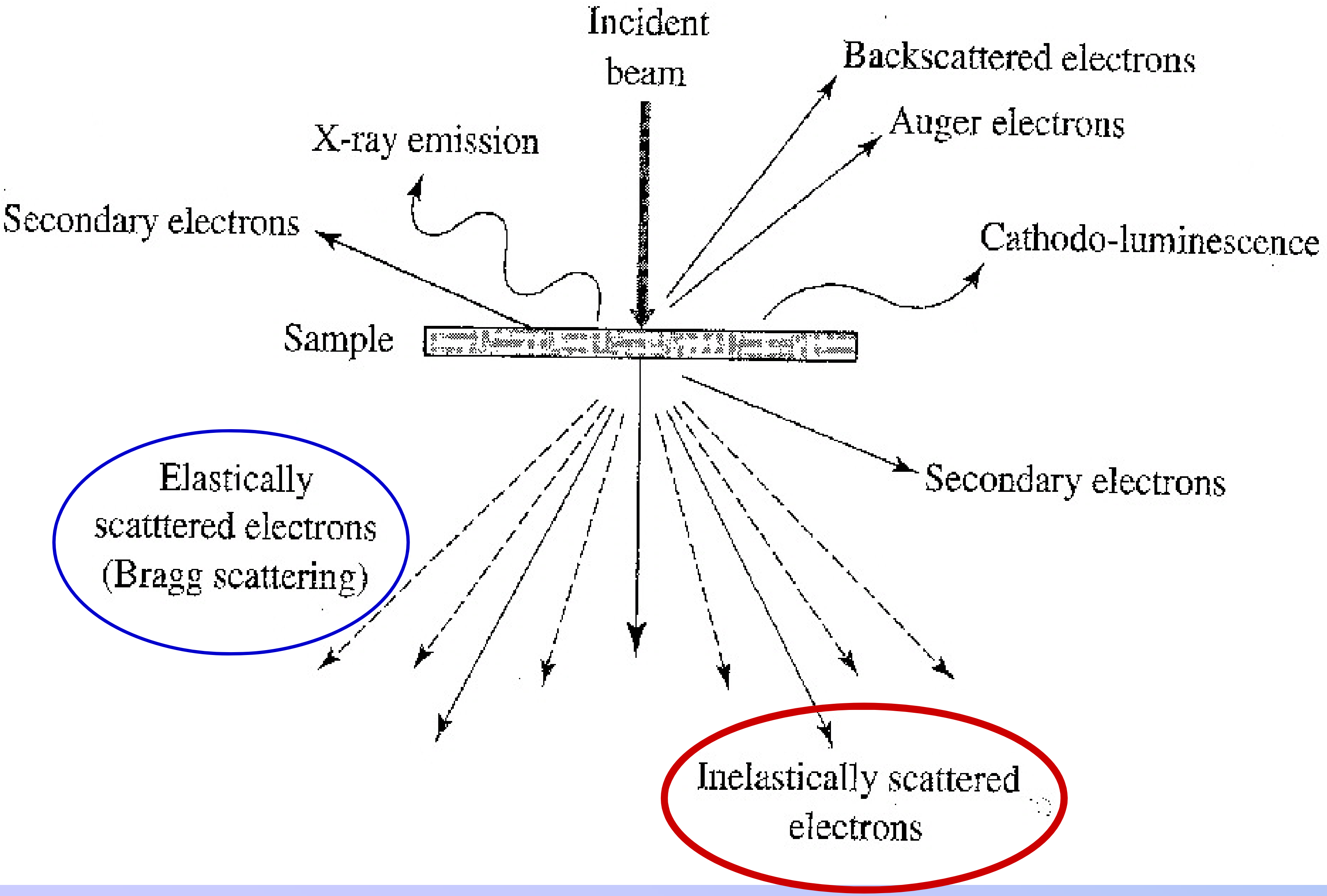
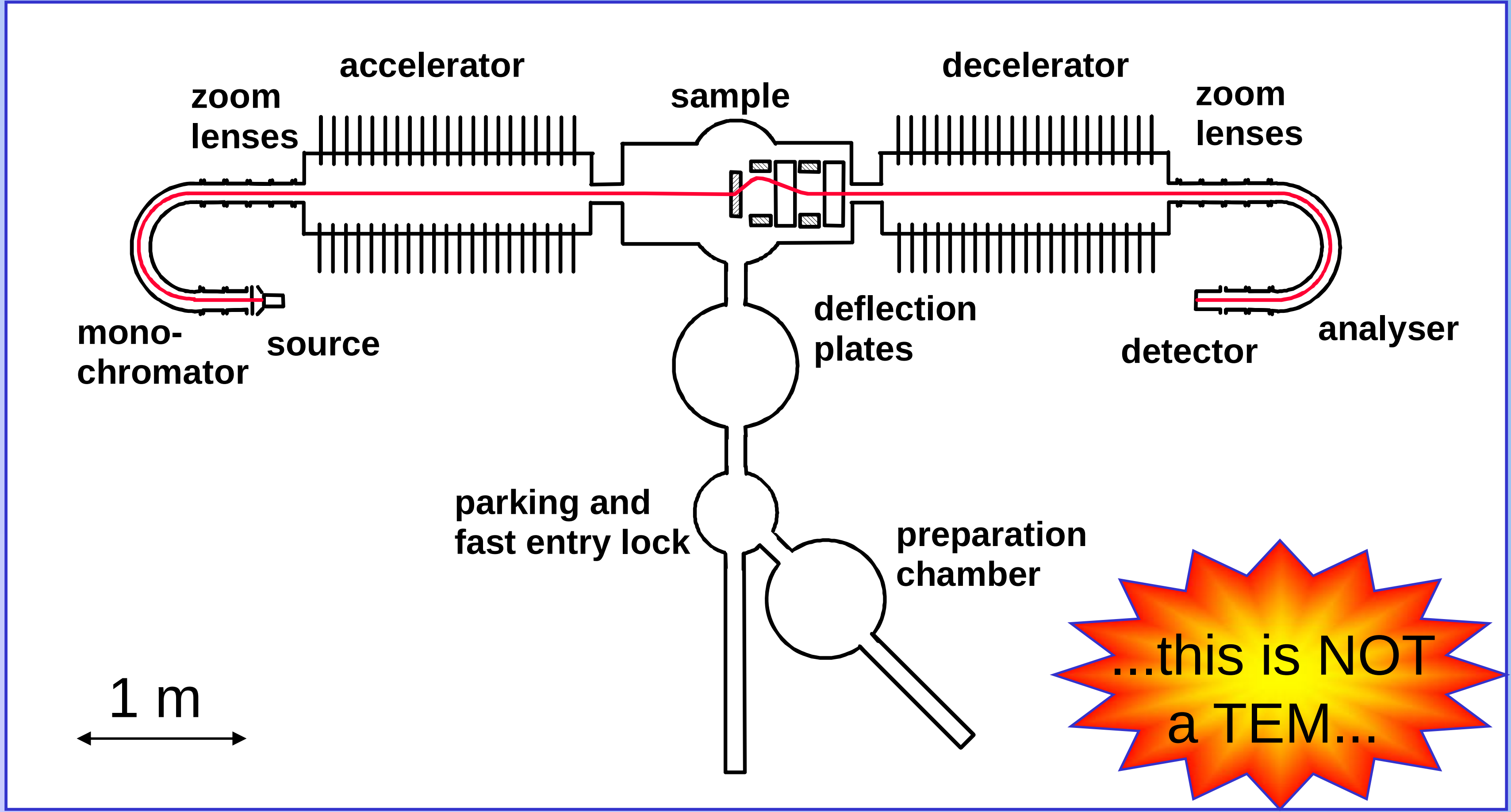

EELS
Aua!
Glück gehabt!
RH

Transmission of fast electrons through a solid: *what can happen ?*



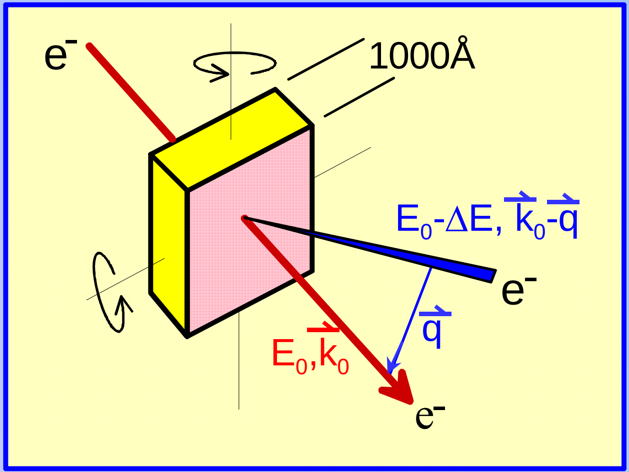
EELS in transmission system: purpose built



E_0=170 keV ΔE=100meV Δq=0.03Å^{-1},
k_0=228.4Å^{-1} λ=0.0275Å, θ=0.25°

J. Fink, Adv. Electron. Electron Phys., 75, 121 (1989)

What is measured: EELS in transmission



- **Transmission:**

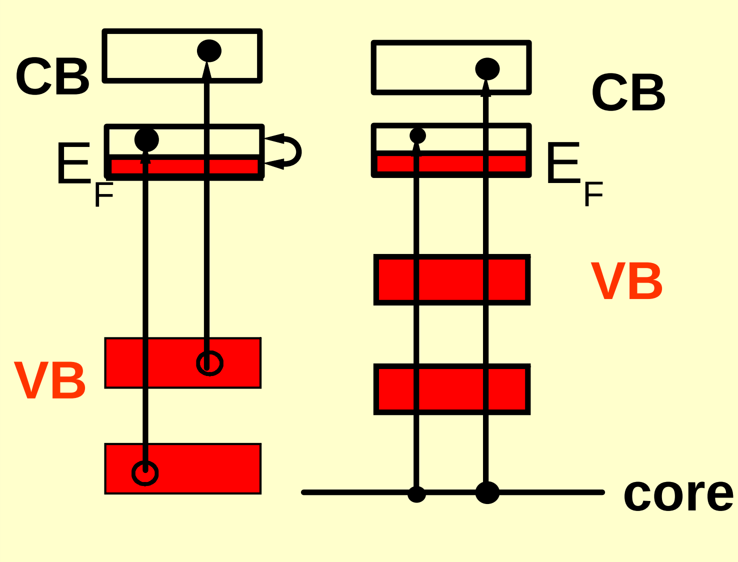
  d ~ 100nm

⇒ **bulk sensitive probe**

- **Structural analysis**

ΔE=0: ⇒ Electron diffraction

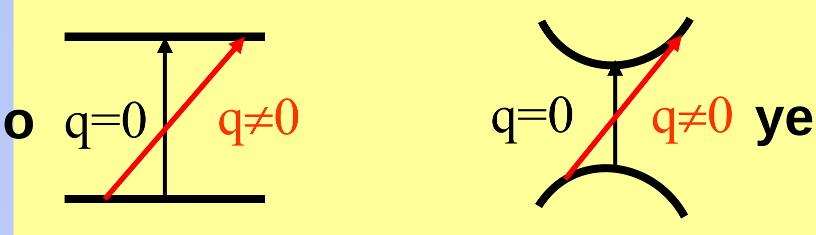
Excitations



● Electronic properties

loss function=Im[-1/ε(ω,q)]

● **Optical properties vs. *q* dependence**



⇒ **dispersion: curvature of bands**

E_0=170 keV ΔE=180meV Δq=0.03Å^{-1}

Some theoretical aspects

The cross section

$$\frac{d^2\sigma}{d\Omega dE} = \left(\frac{d\sigma}{d\Omega}\right)_{Ruth} S(q,\omega)$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{Ruth} = \frac{4}{a_0^2 q^4}$$

Rutherford scattering

$$S(q,\omega) = \frac{1}{2\pi\hbar N}\int e^{-i\omega t}\left\langle n_q(t) n_{-q}(0)\right\rangle dt$$

dynamic structure factor
(system response)

$n_q(t)$ = density operator

compare to elastic scattering (form factor):

$$S(q,\omega=0) = S(q) = (Z - F(q))^2$$

Some theoretical aspects

Connection to the dielectric properties

$$\frac{d^2\sigma}{d\Omega dE} = \left(\frac{d\sigma}{d\Omega}\right)_{Ruth} S(q,\omega)$$

$$= \frac{\hbar}{(\pi e a_0)^2}\frac{1}{q^2}\,\mathrm{Im}\left[-\frac{1}{\varepsilon(q,\omega)}\right]$$

loss function

$$\varepsilon(q,\omega) = \text{dielectric function} = \varepsilon_1 + i\varepsilon_2$$

$$\mathrm{Im}[-1/\varepsilon] = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2}$$

Some theoretical aspects

EELS probes longitudinal excitations

- **the quantity measured in EELS is** $\frac{1}{q^2} \operatorname{Im}\left[-\frac{1}{\varepsilon(q,\omega)}\right]$
- $\operatorname{Im}\left[-\frac{1}{\varepsilon(q,\omega)}\right]$ **has a maximum when ε small (zero)**

⇛ **fast electrons excite longitudinal waves !**

in addition: $\mathbf{k} \times \mathbf{E} = \omega \mathbf{H} = 0$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{H}}{\partial t} = 0$$ ⇛ **no magnetic contributions**

Some theoretical aspects

Kramers Kronig relations and sum rule

- **Kramers-Kronig relation:**

$$\mathrm{Re}\left[\frac{1}{\varepsilon(q,\omega)}\right]-1=\frac{1}{\pi}\,\mathrm{P}\int_{-\infty}^{\infty}\frac{d\omega'}{\omega'-\omega}\,\mathrm{Im}\left[\frac{1}{\varepsilon(q,\omega)}\right]$$

- **sum rule:**

$$\int_{0}^{\infty}\omega\,\mathrm{Im}\left[\frac{1}{\varepsilon(q,\omega)}\right]d\omega=\frac{\pi}{2}\omega_p^2\,,\qquad \omega_p^2=\frac{ne^2}{\varepsilon_0 m}$$

Plasma freuqency

BUT!!! Macroscopic not always = Microscopic ε

Macroscopic ε

Regular case:
macroscopic isotropic bulk electron density, crystal symmetry cancels off-diagonal elements

$$\varepsilon = \varepsilon_M\left(\left|\vec{r}_i - \vec{r}_j\right|\right)$$

$$E(\vec{q},\omega) = \varepsilon_M^{-1}(\vec{q},\omega)D(\vec{q},\omega)$$

Random Phase Approximation
Quasi free particles in a mean field. Works well if electrons are reasonably screened

$$\varepsilon_M(\vec{q},\omega) \approx \varepsilon_{RPA}(\vec{q},\omega) = 1 - V_q\chi_0(\vec{q},\omega)$$

Lindhart susceptibility

Coulomb potential

The Drude-Lorentz dielectric function

Solution for damped and driven harmonic oscilator

$$x = \frac{eE_0 e^{i\omega t}}{m(\omega_T^2 - \omega^2 - i\omega/\tau)}$$

and

$$P = nex = \chi_e \varepsilon_0 E$$

and

$$\varepsilon = (1 + \chi_e)$$

$$\boxed{\varepsilon(\omega) = 1 + \frac{ne^2}{\varepsilon_0 m} \frac{1}{\omega_T^2 - \omega^2 - i\omega/\tau}}$$

Dielectric function with **real** and **imaginary** part

$$\omega_p^2 = \frac{ne^2}{\varepsilon_0 m}$$

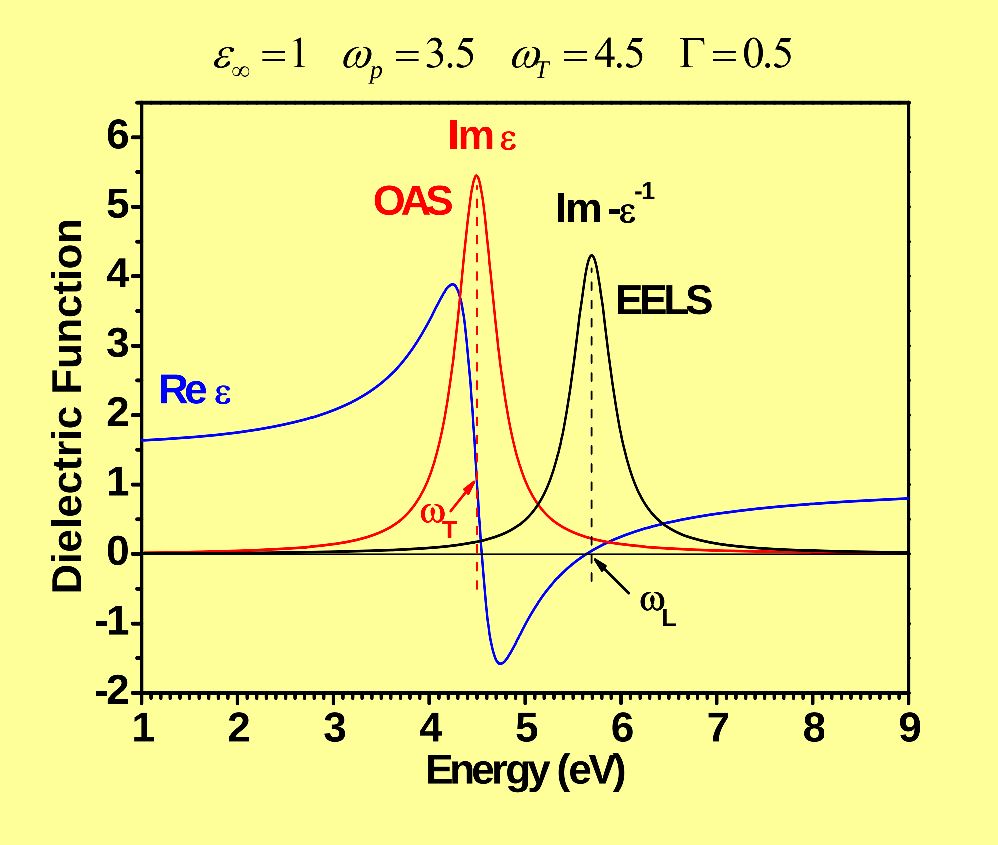
plasma frequency scales with charge density

$$\omega_T = 0$$

no spring constant, free electrons, **Drude** model

Drude-Lorentz dielectric function and spectroscopy

High plasma frequency ω_p



ω_T transversal plasma frequency
resonant absorption of light

Optical **A**bsorption **S**pectroscopy
For thin samples OAS ~Im(ε)

ω_L longitudinal plasma frequency
resonant energy loss of e$^-$

Electron **E**nergy **L**oss **S**pectroscopy
EELS Im(-ε^{-1})

$$\varepsilon = \varepsilon_\infty + \sum_i \frac{\omega_{p,i}^2}{(\omega_{T,i}^2 - \omega^2) + i\omega\Gamma_i}$$

$$\omega_L^2 = \omega_T^2 + \omega_p^2$$

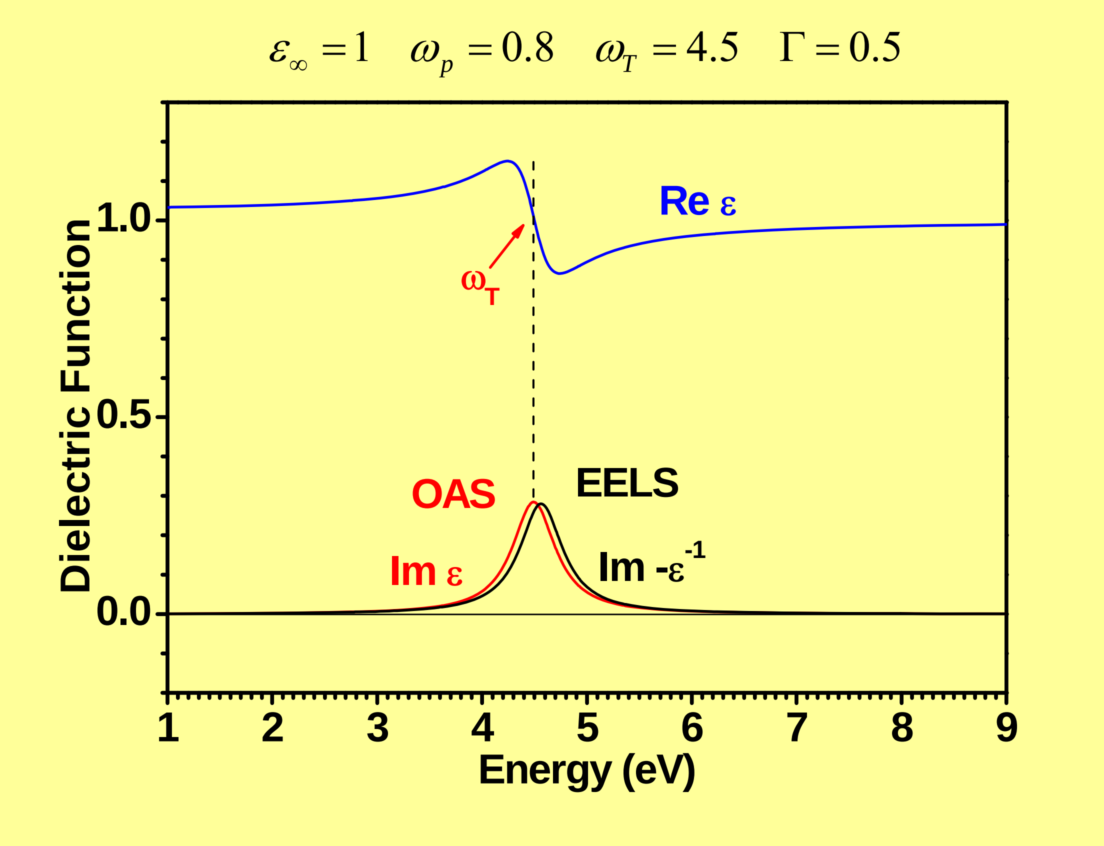
$\omega_L > \omega_T$

EELS>OAS

$$\Gamma = 1/\tau$$

Isolated systems and free objects

Low plasma frequency ω_p
(everything else the same)



Weak ω_p (low e$^-$ density) causes only weak modulation in Re(ε)

⇓

ω_L and ω_T are very close

$$\omega_L^2 = \omega_T^2 + \omega_p^2$$

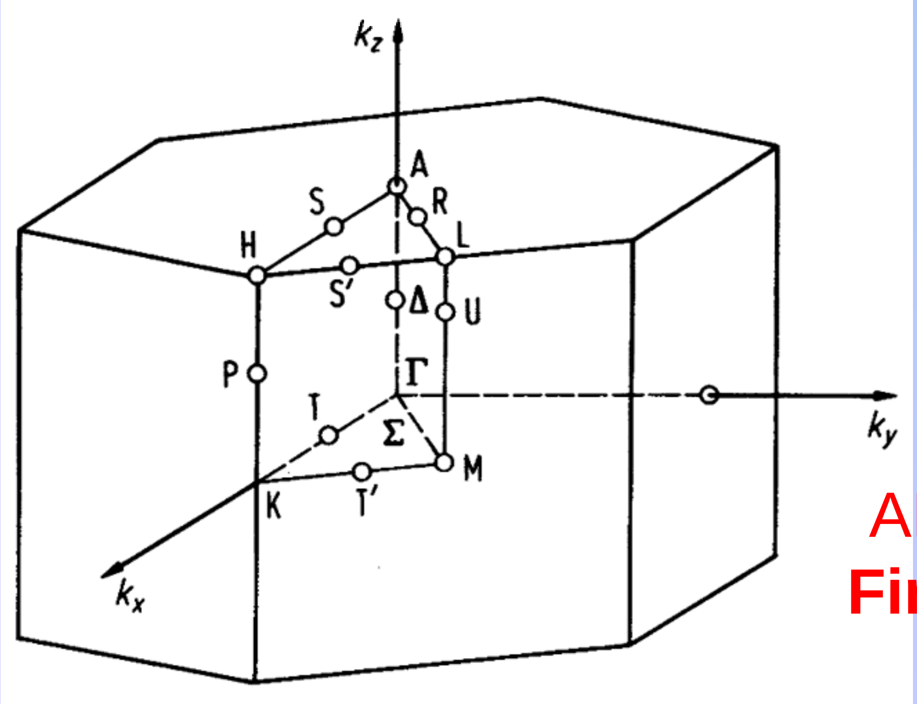
$\omega_L \sim \omega_T$

EELS~OAS

OAS (ω_L) and EELS (ω_T) are degenerate in diluted systems

EELS Beyond the optical range (q>0)

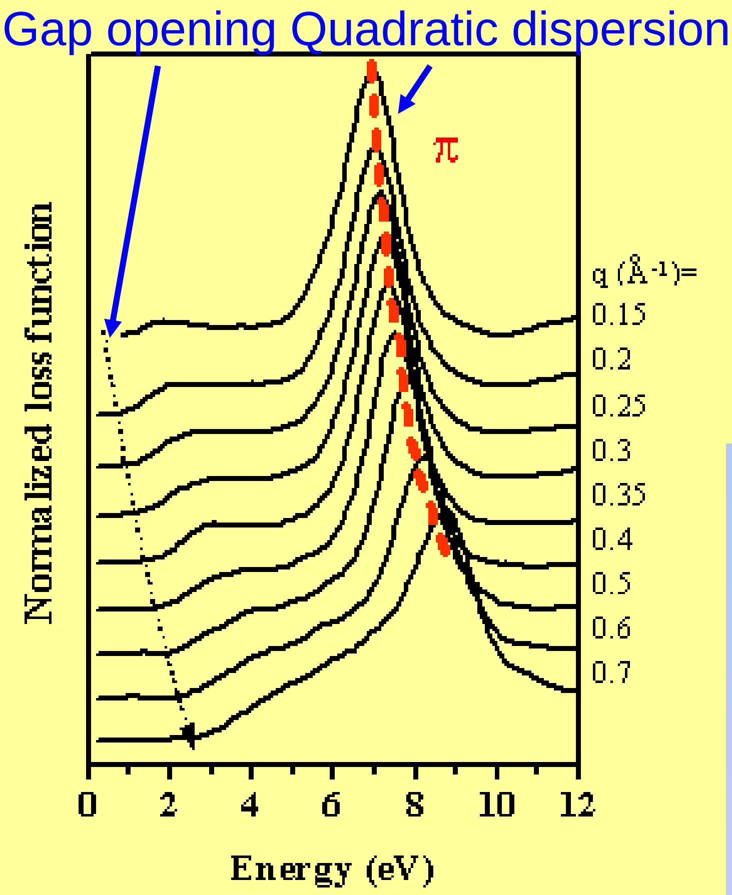
visible light	0.0001 A^{-1}	direct transitions
Brillouin zone	3 A^{-1}	(100) Bragg
172 keV e^-	228 A^{-1}	**whole zone**

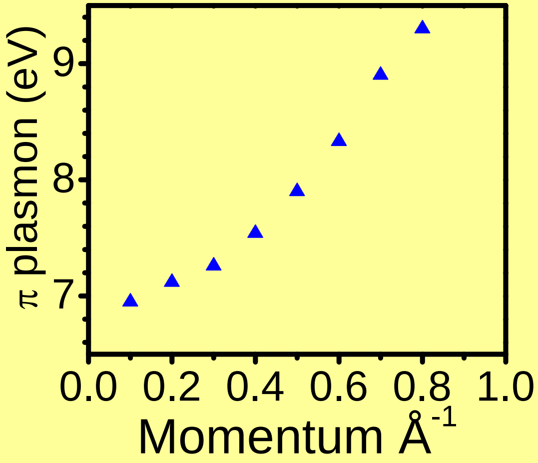


AR-EELS probes the dispersion

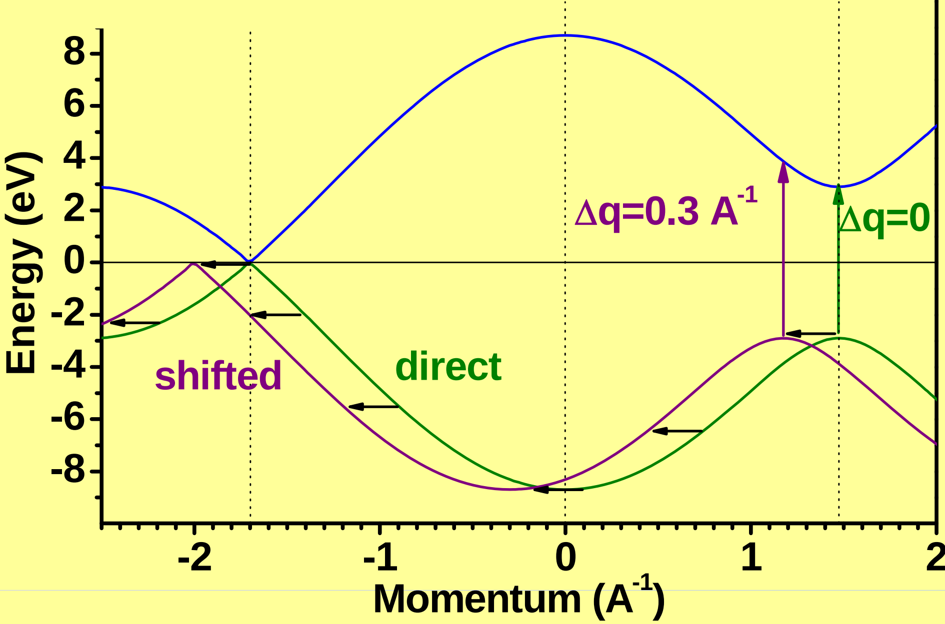
Fingerprint of solids/molecules

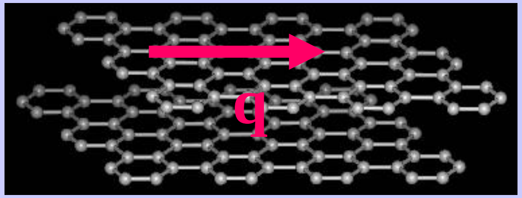
Example 1: Graphite





π plasmon
(M point)
3D system

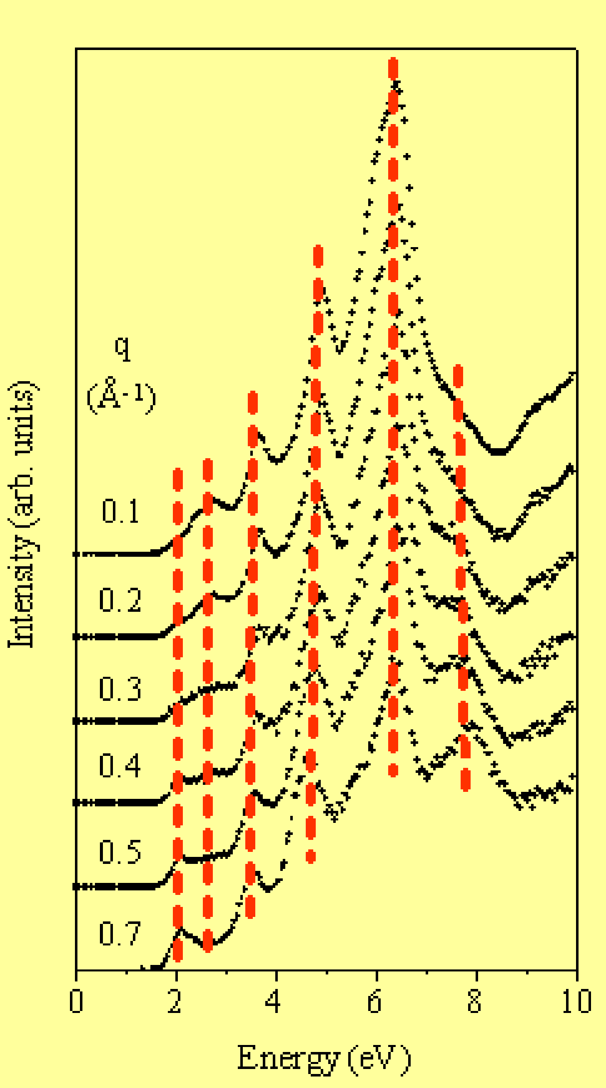


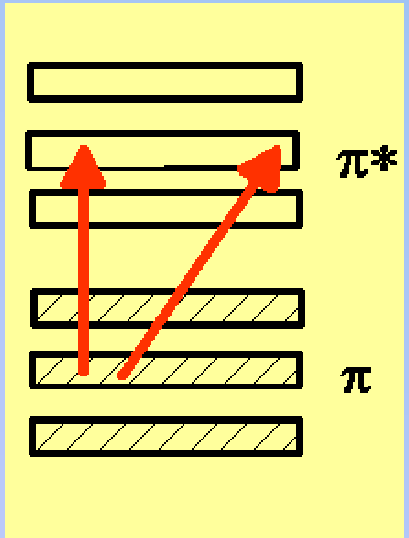


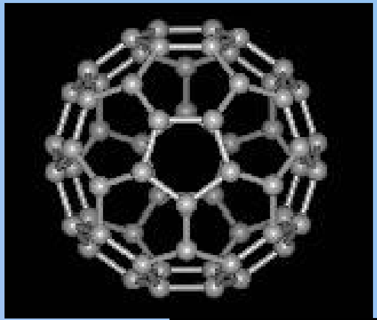
A. G. Marinopoulos *et al*, PRL, **89**, 076402, (2002)

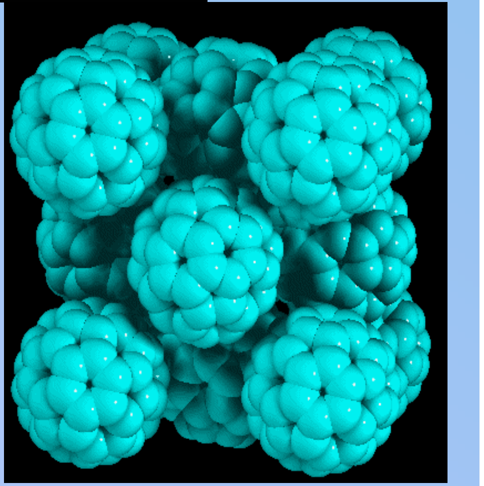
Example 2: Fullerenes

EELS of C_{60}: „0-D“ system







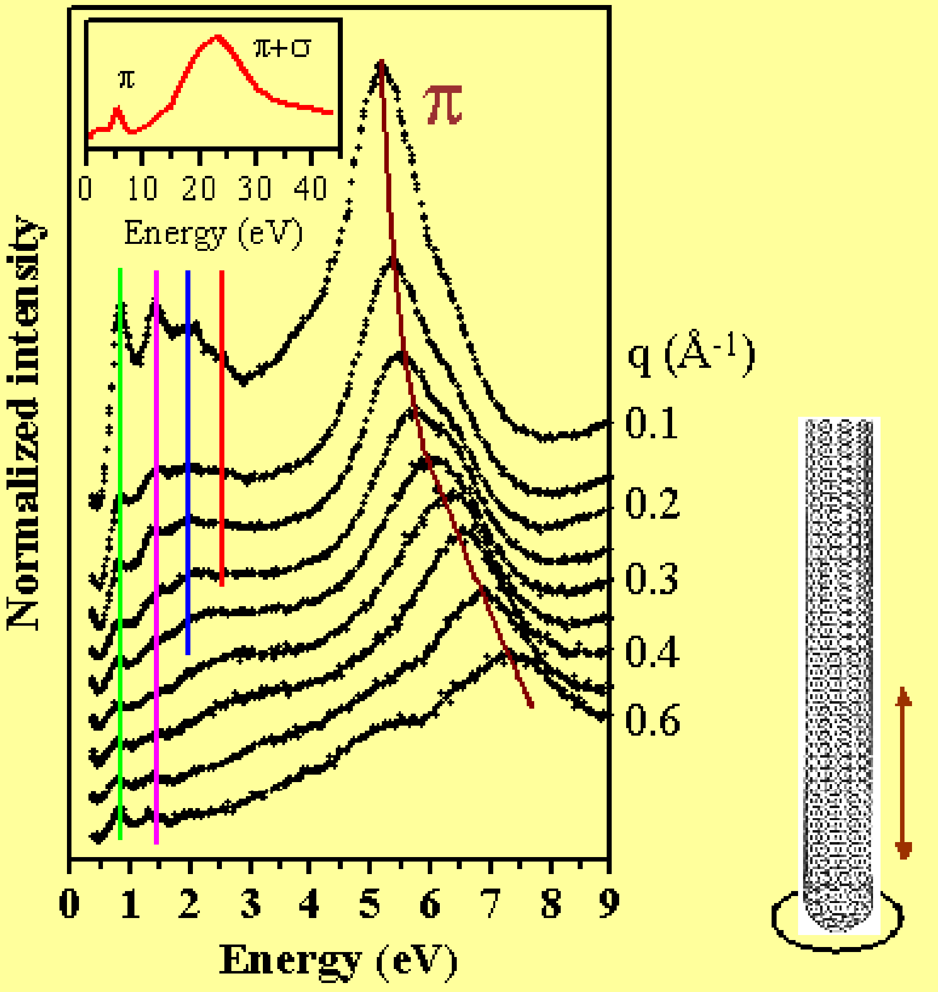


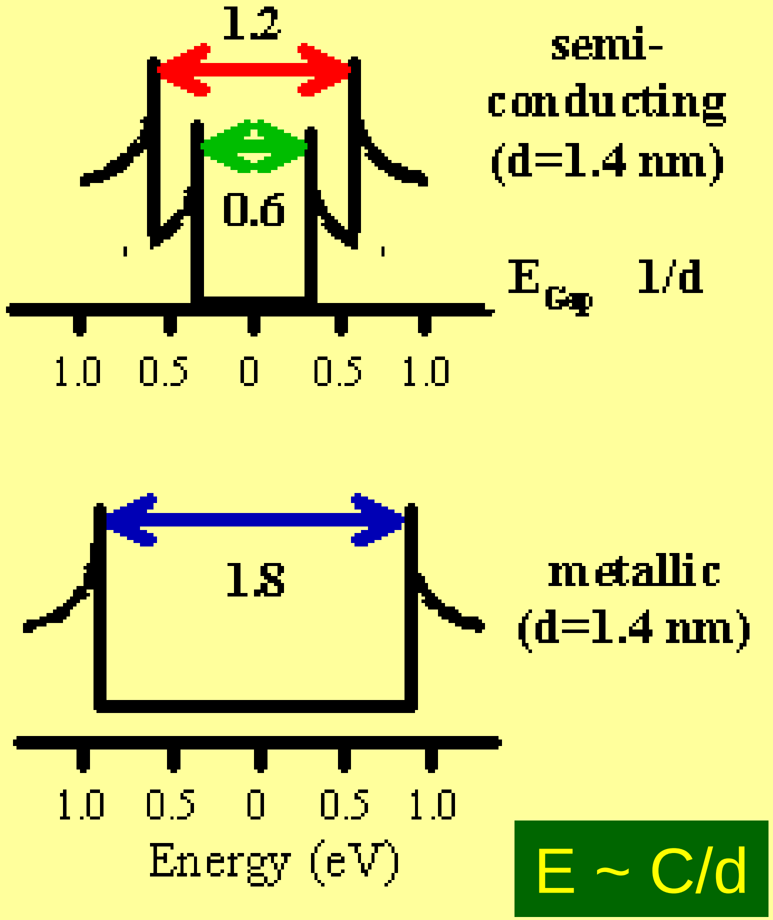
Transitions between flat π-Bands - no dispersion.

fcc C_{60} ist a moleculares (0D) system.

Example 3: bundled SWCNT

EELS of SWCNT bundles : quasi 1D system





E ~ C/d

T. Pichler et al. PRL 80, 4729 (1998)

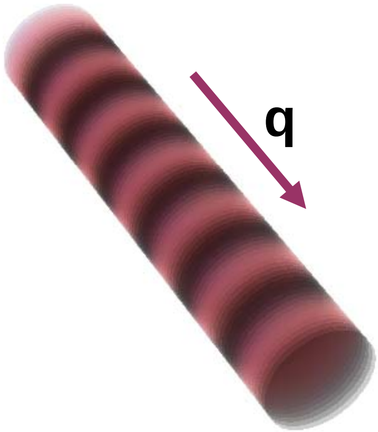
Plasmons in 1D

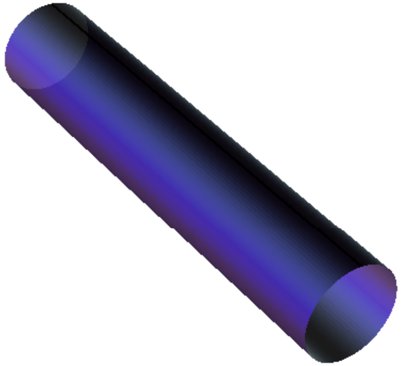
On-axis

1D solid, dispersion

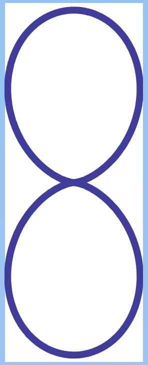
Circumferencial

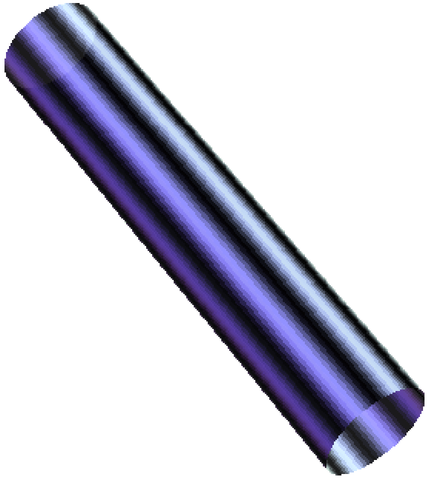
multipoles, no dispersion



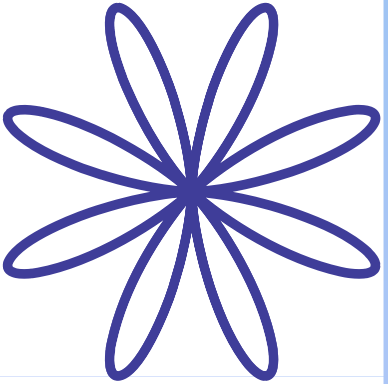


$m = 2$





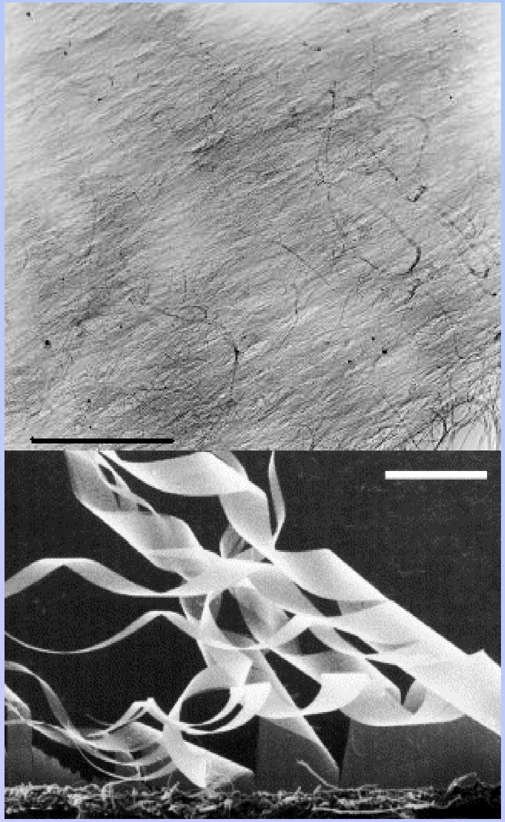
$m = 8$



MA-SWCNT

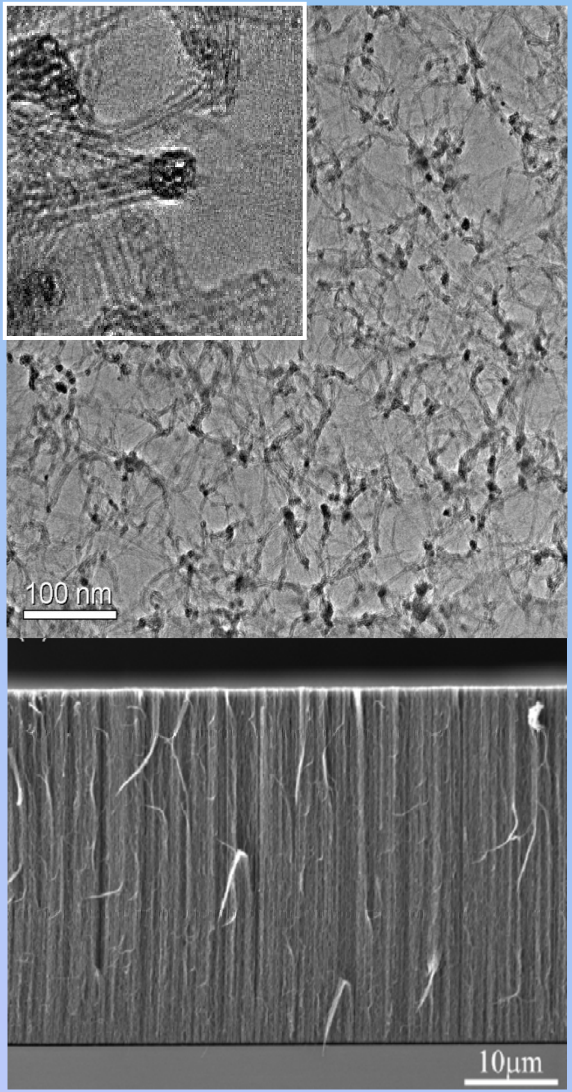
Aligned-SWCNT

VA-SWCNT



Laser ablation
In plane
~1.3 g/cm³
←

CVD
Out of plane
~0.05 g/cm³
→



Batch	Orientation	Method	Domain	σ	β	ξ
MA-SWNT	in-plane	ED	bulk	20°	19.2°	0.84
VA-SWNT	perpendicular	XAS	surface	37°	32.7°	0.56
VA-SWNT	perpendicular	OAS	bulk	26°	24°	0.75

E. Einarsson, C. Kramberger, *et al*. J.Phys. Chem. C, **111**, 17861, (2007)
X. Liu, et al. Synth. Met.**121**, 1183, 2001

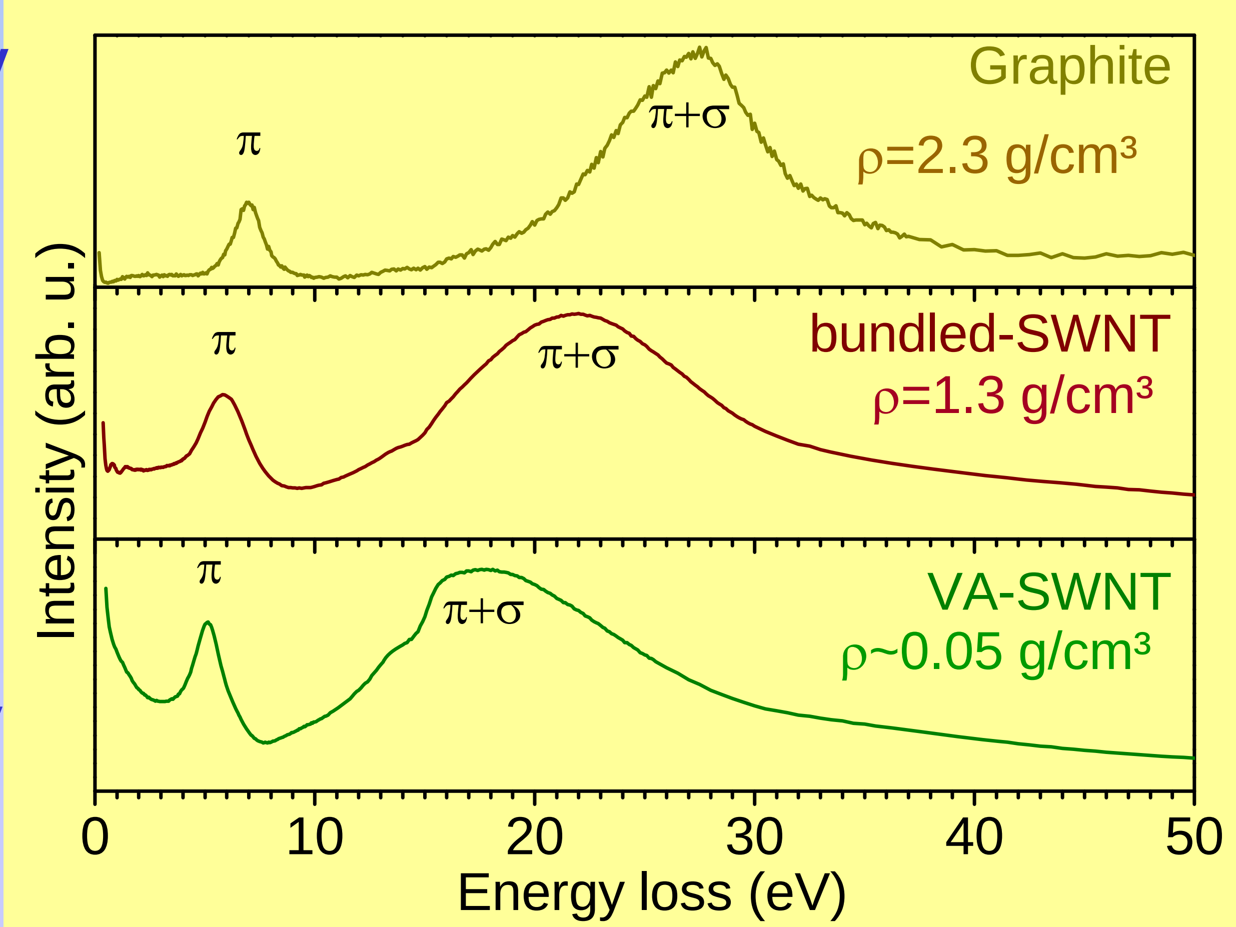
sp² carbon at different densities

High Density

ω_p

Low Density

ω_p



Bulk Graphite

Bundled SWCNT

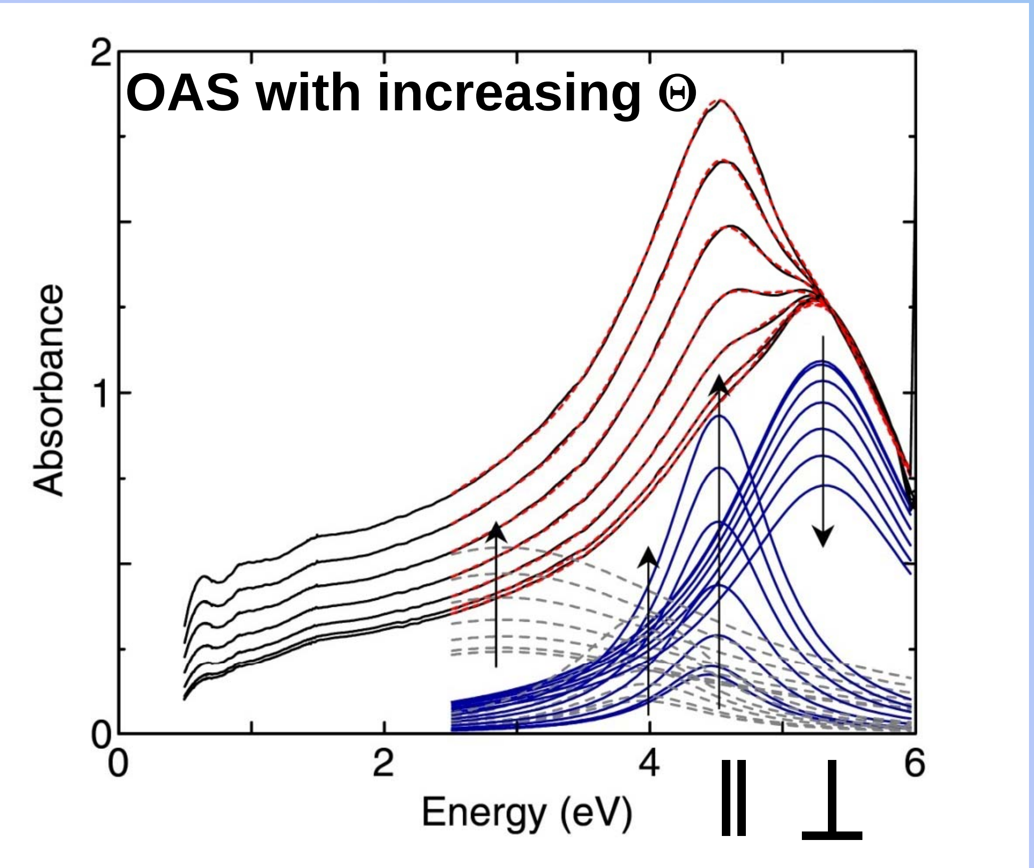
Isolated SWCNT

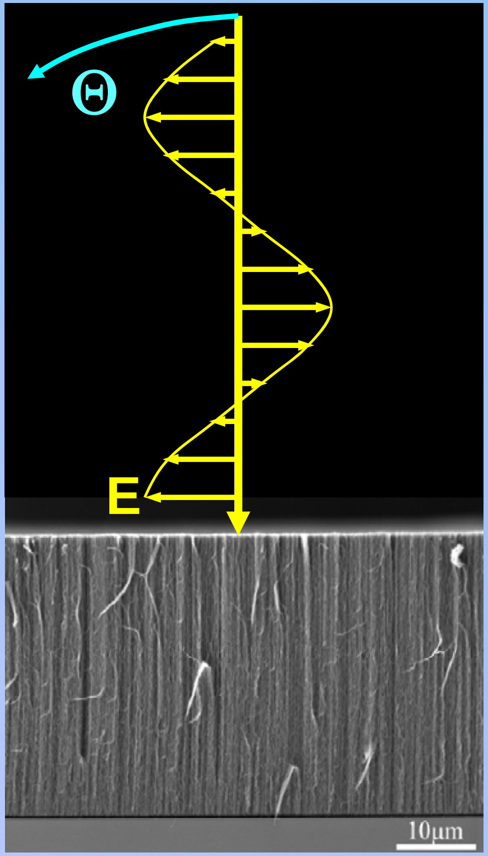
$$\omega_L^2 = \omega_T^2 + \omega_p^2$$

$$\omega_p^2 = \frac{ne^2}{m^* \varepsilon_0}$$

But only one π plasmon!

Optical absorption on VA-SWCNT

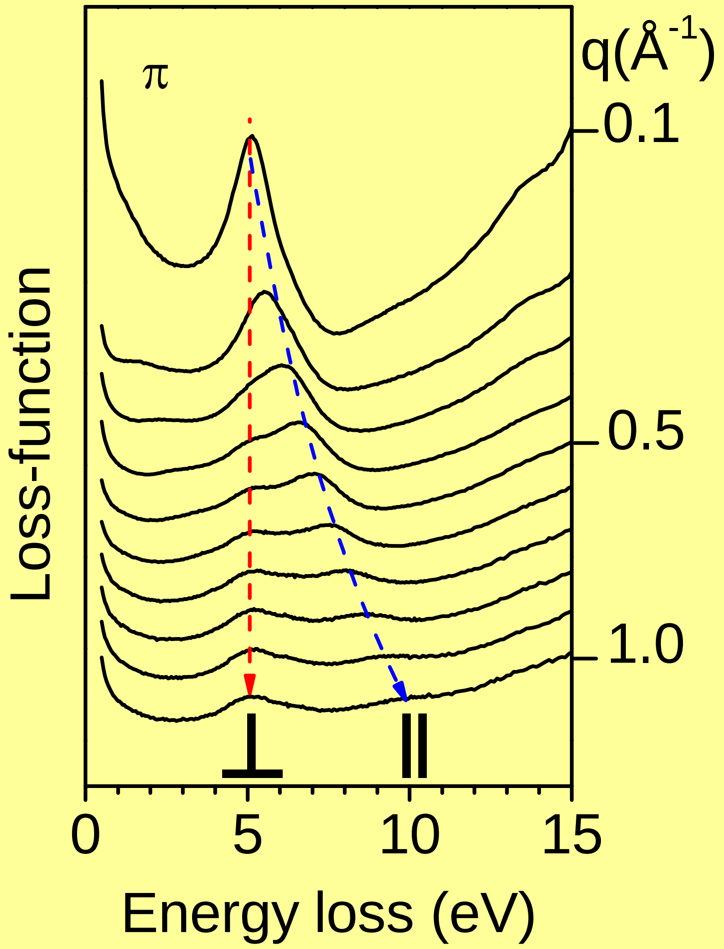




on-axis at 4.5 eV, crossed at 5.25 eV

Y. Murakami *et al*, PRL, **94**, 087402, (2005)

π plasmon dispersion in isolated VA tubes



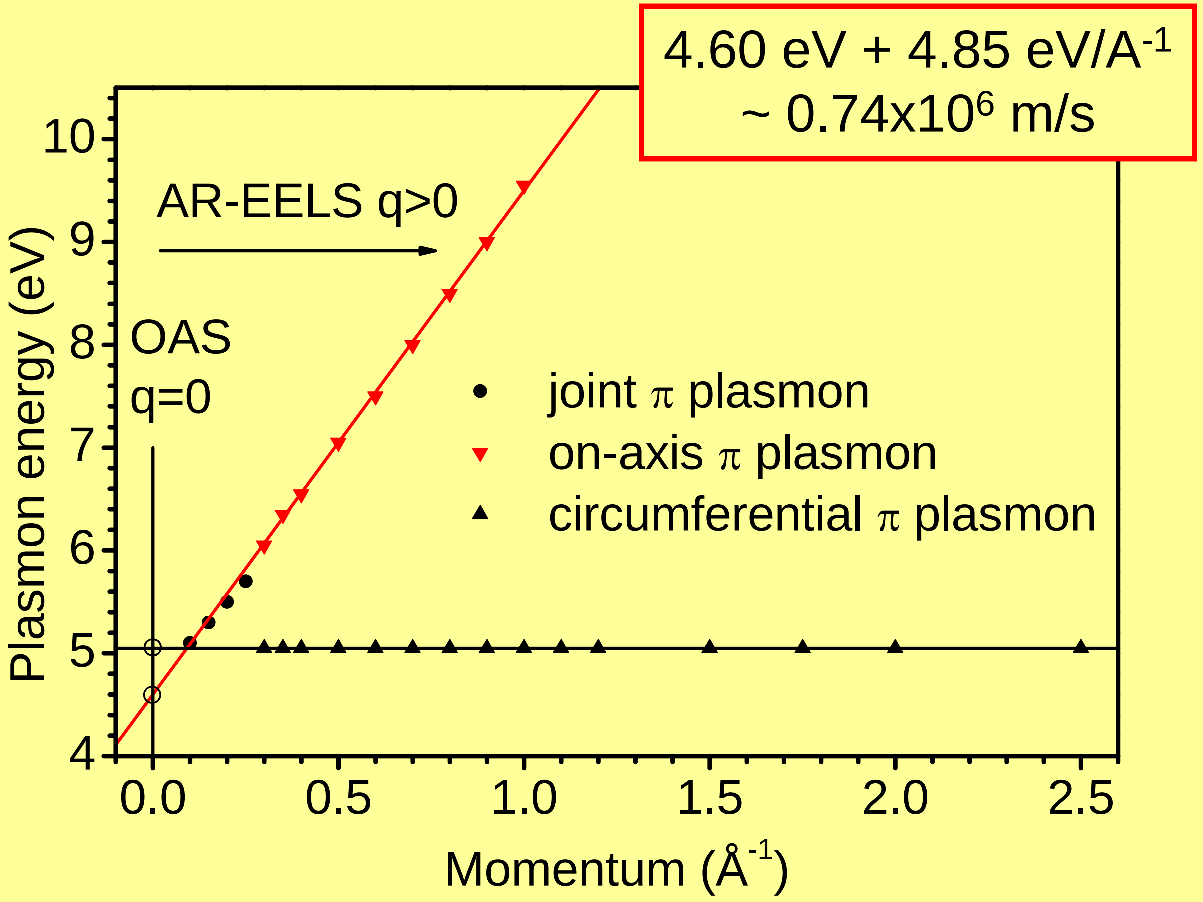
twofold π plasmon dispersion!

Perpendicular plasmon
No dispersion

On-axis plasmon
Dispersion

C. Kramberger *et al*, PRL, **100**, 196893 (2008)

Twofold π plasmon dispersion paradox!



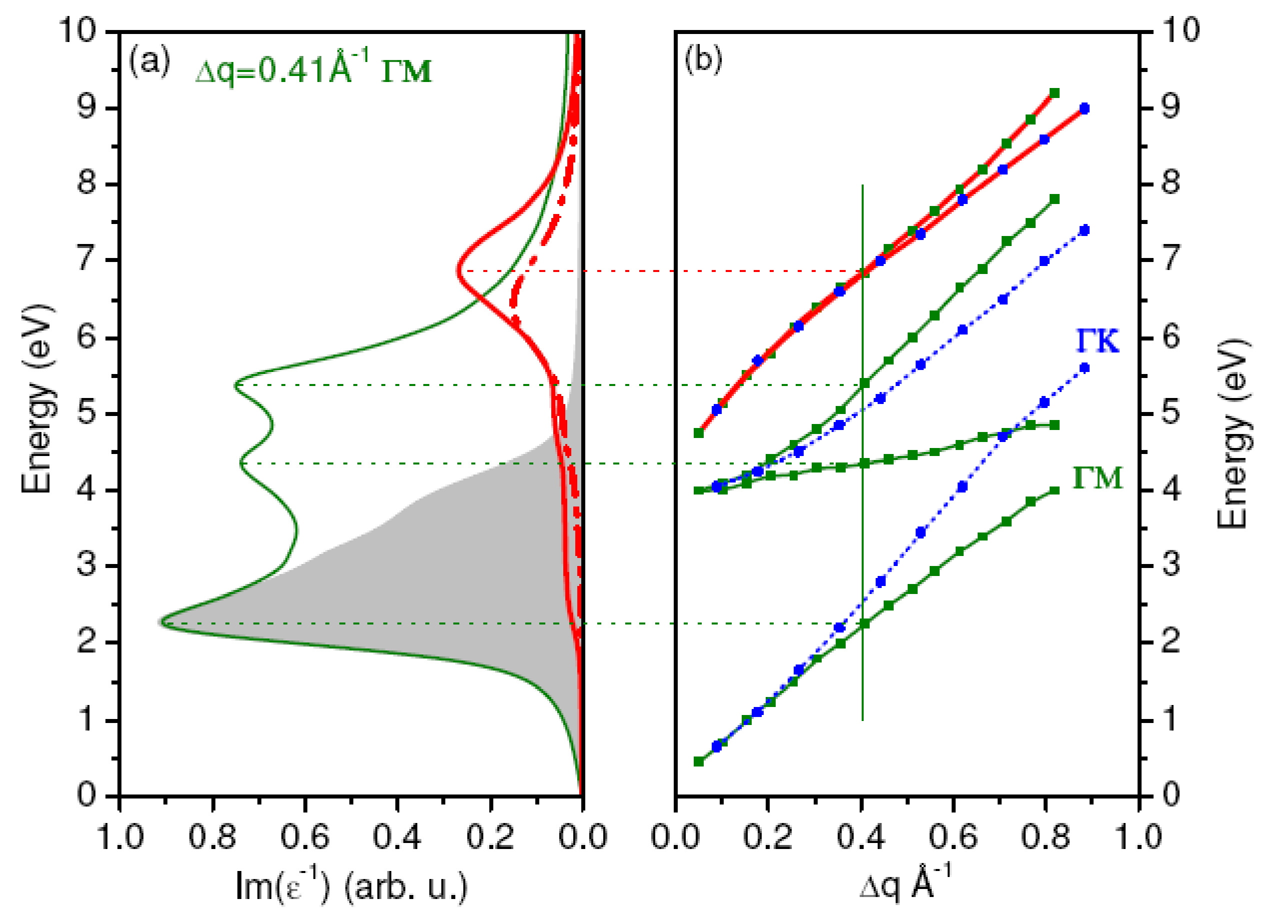
Linear dispersion!

Is this π plasmon dispersion **REALLY** related to the K point in graphene?

optical limit ~ 4.6 eV parallel
~ 5.1 eV perpendicular

→ **Excellent match to OAS**

DFT calculations of loss function of graphenes including LFE

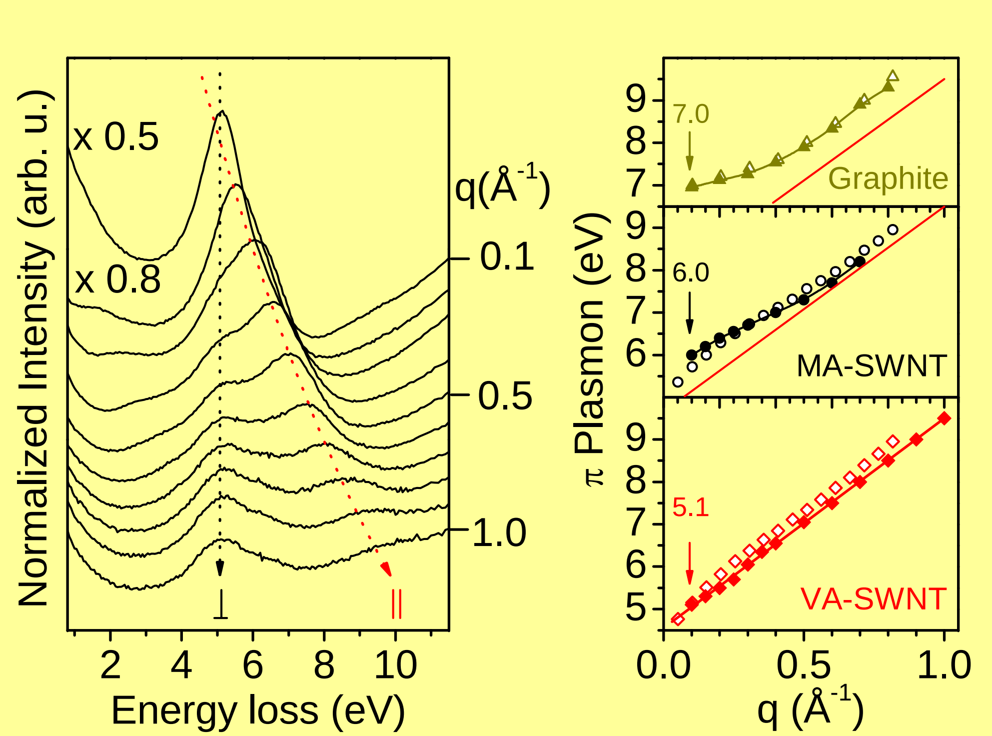


bare RPA (green line) and including depolarization effects (red line).

strong intermixing of exitations close to the Dirac point yields linear dispersion

C. Kramberger *et al*, PRL, **100**, 196893 (2008)

Quantitative microscopic description

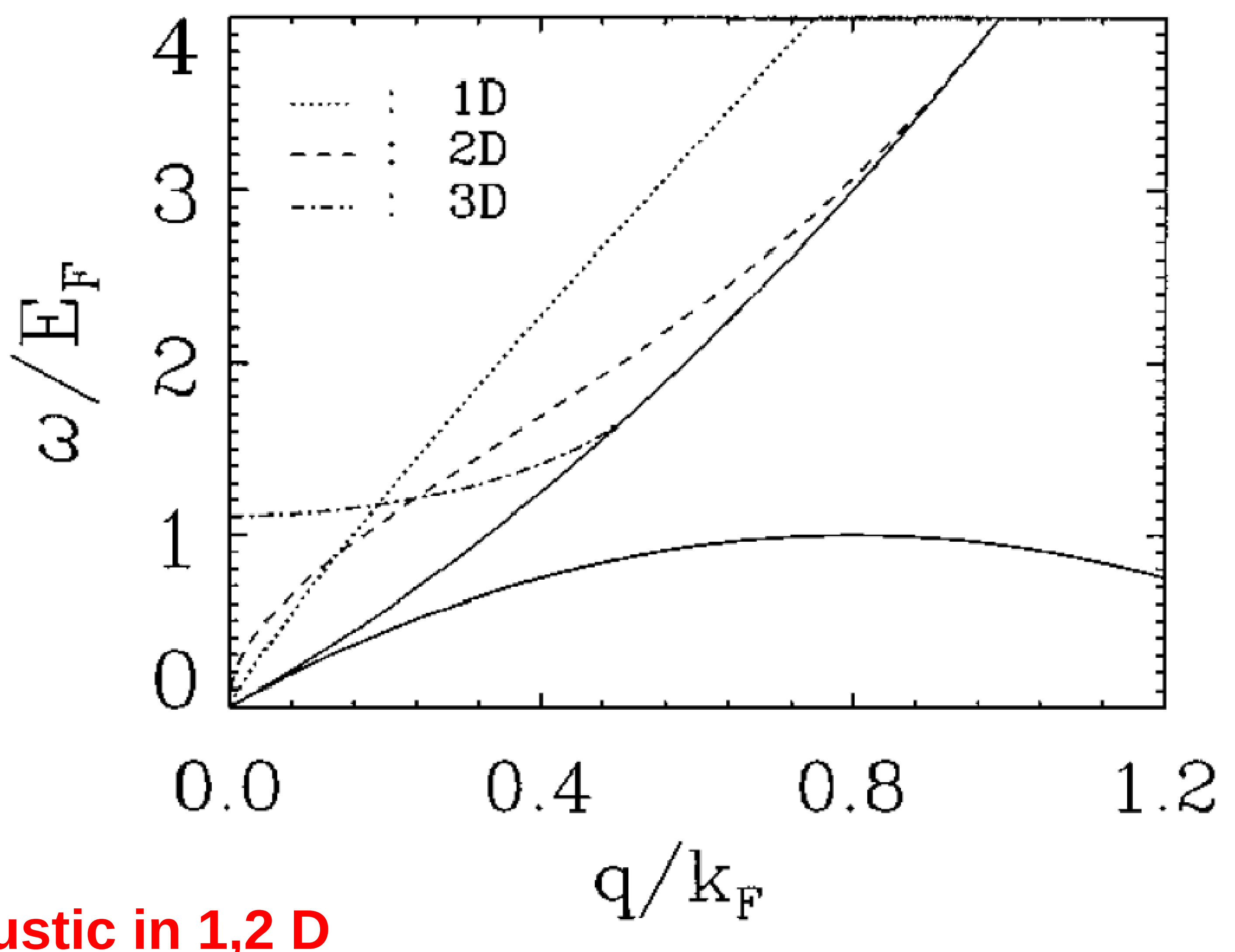


Sample	**Model**
bulk graphite	bulk graphite
bundled SWCNT	bi-layer
isolated SWCNT	graphene

On-axis interband excitations are equivalent to in-plane excitations of isolated graphene!

C. Kramberger *et al*, PRL, **100**, 196893 (2008)

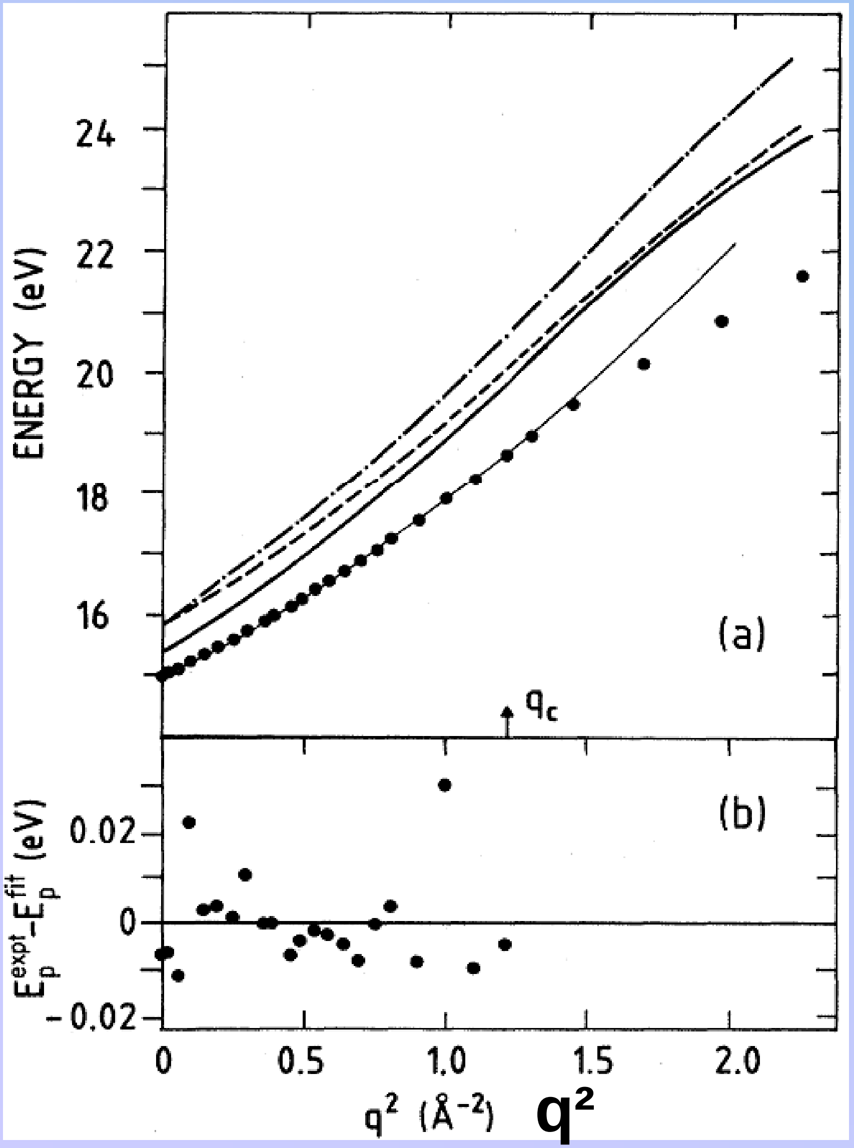
Charge carrier plasmon dispersion in different dimensions



Acoustic in 1,2 D

S. Das Sarma and E. H. Hwang PRB 54, 1936 (1996)

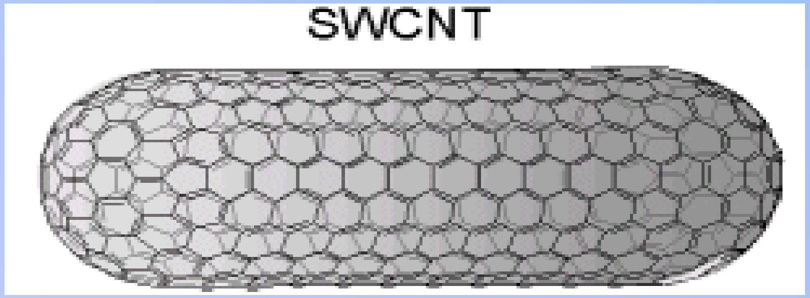
Charge carrier plasmon in 3D: Example Al



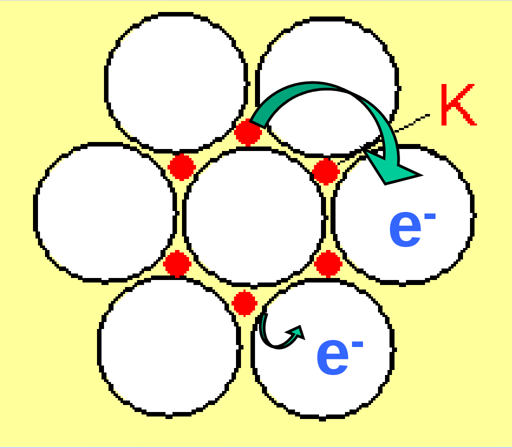
Quadratic dispersion in 3D metal!

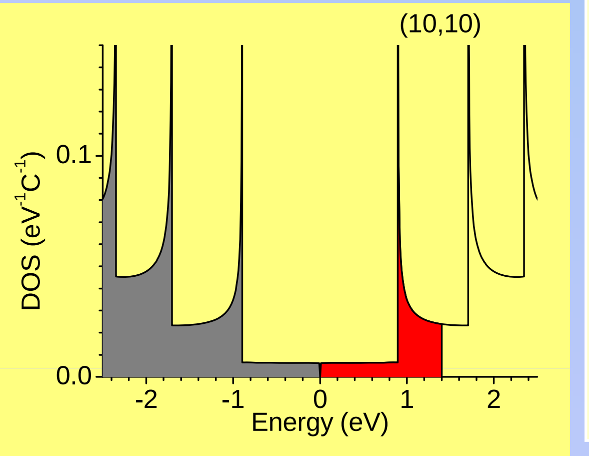
J. Sprösser-Prou, *et al.* PRB **40**, 5799 (1989)

Intercalation

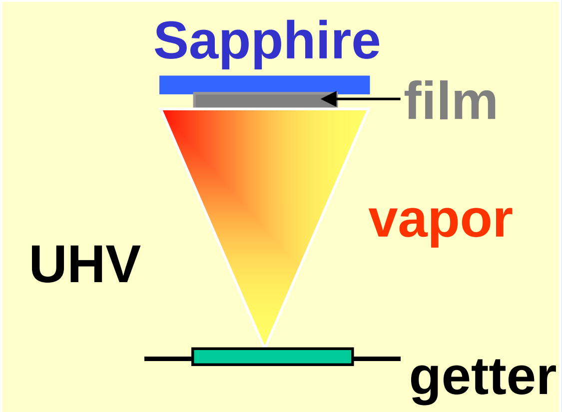


doping





Alkali-metal intercalation

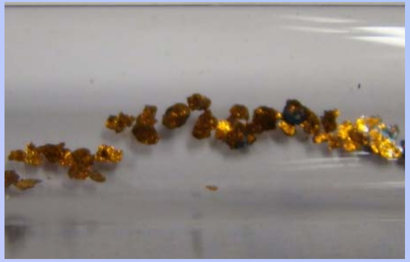


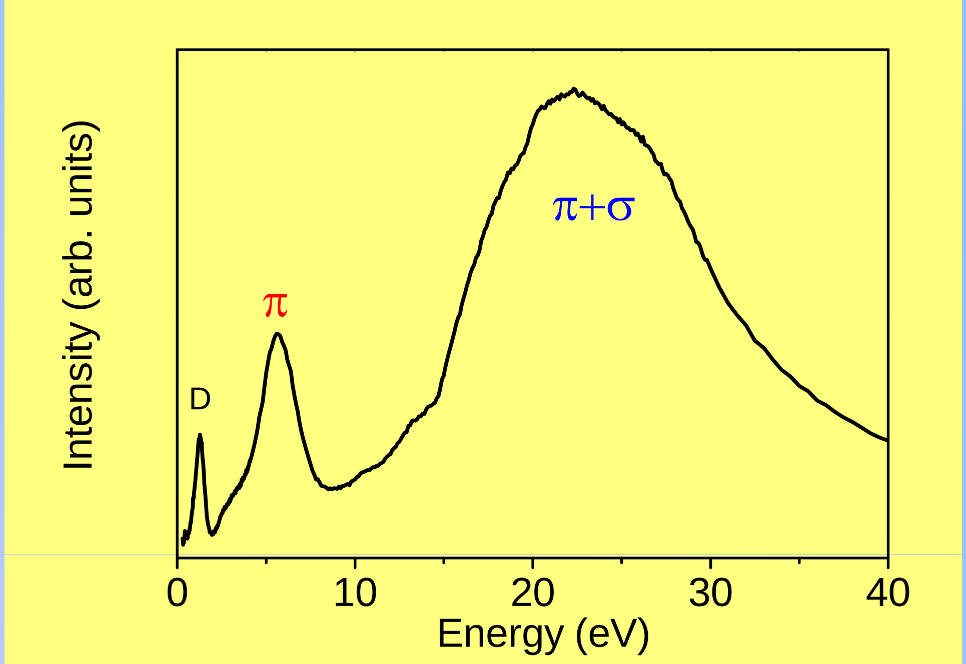
in-situ **doping:**
UHV evaporation
(5×10^{-10} mbar)
Na, K, Rb, Cs and
Ba SAES getters

Analysis of the loss function in sp^2 carbon systems

Drude-Lorentz model

Example KC$_8$:



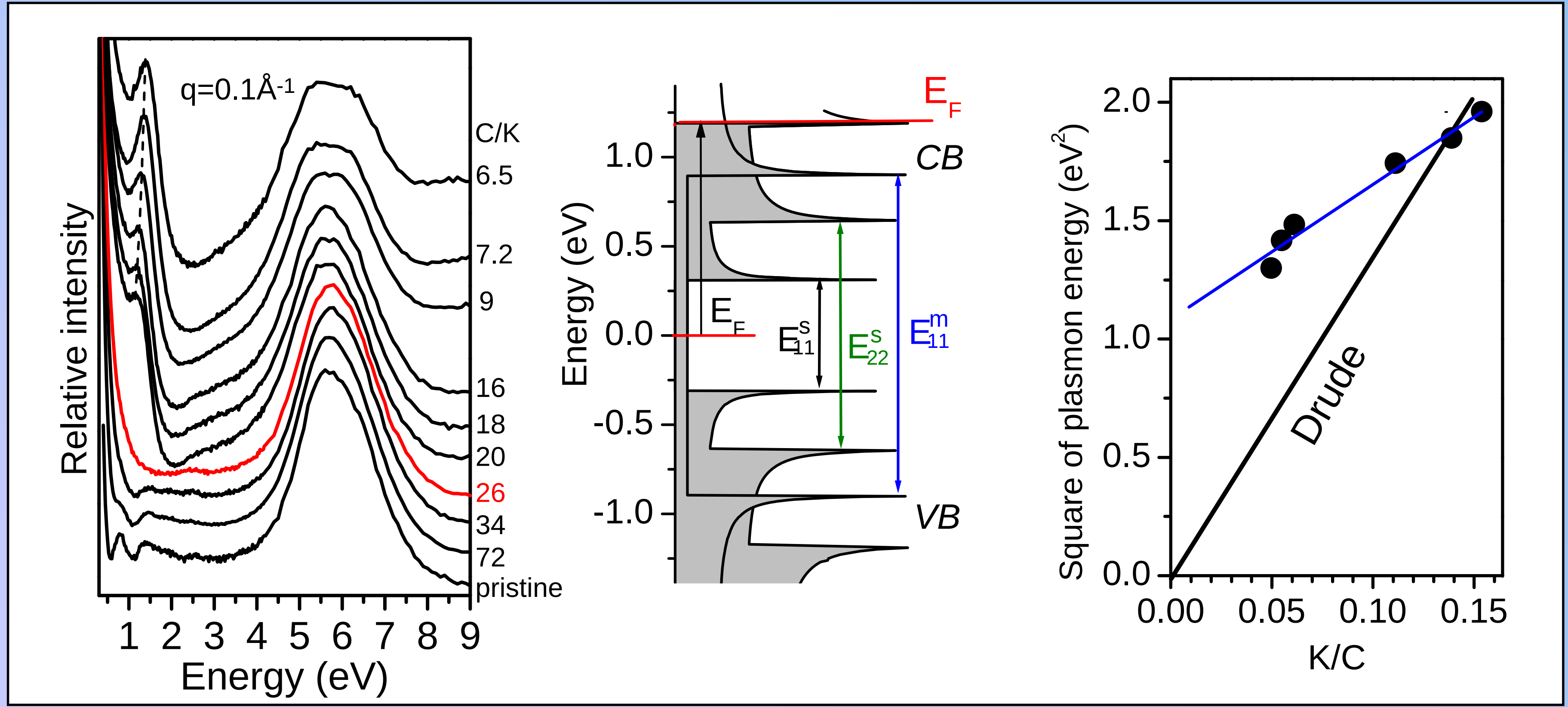


Drude π plasmon π+σ plasmon

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(i\gamma + \omega)} + \frac{\omega_{p,\pi}^2}{(\omega_{T,\pi}^2 - \omega^2) - i\gamma_\pi \omega} + \frac{\omega_{p,\pi+\sigma}^2}{(\omega_{T,\pi+\sigma}^2 - \omega^2) - i\gamma_{\pi+\sigma} \omega}$$

- Screening effect: → downshift of Drude plasmon
- π, π+σ plasmons = effective dielectric background (ε_∞)
- $\varepsilon_\infty = \varepsilon_\infty^{\pi} + \varepsilon_\infty^{\pi+\sigma}$

EELS response upon doping (K-doping)



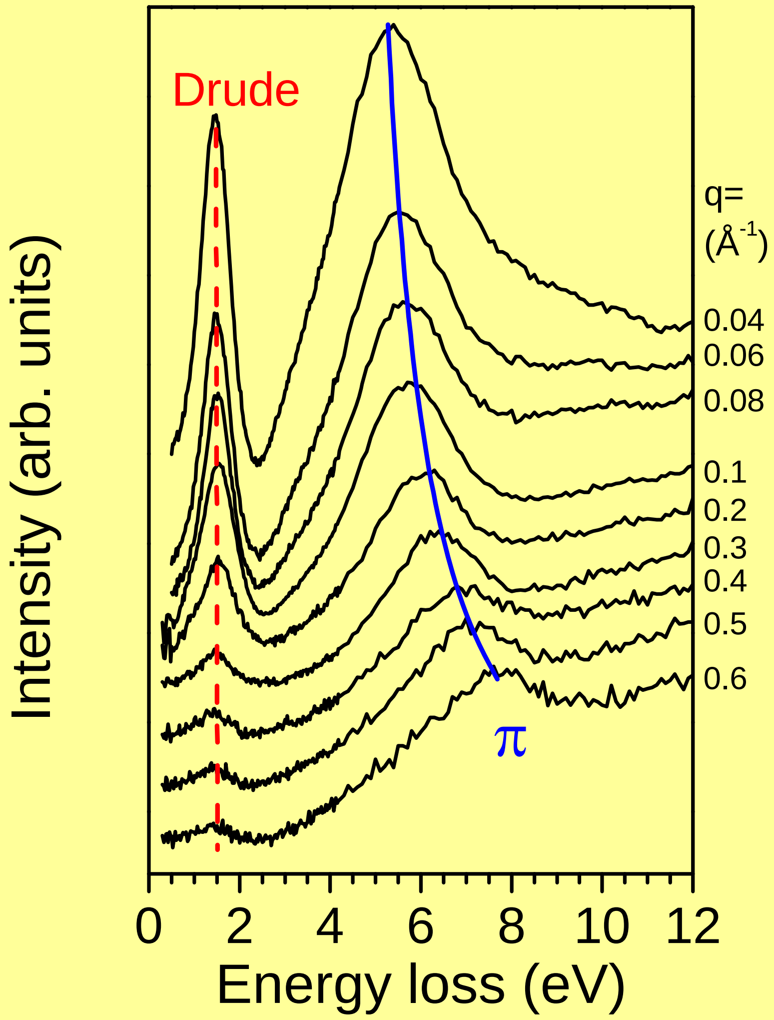
- Interband transitions disappear (up to C/K=26)
  Free charge carrier (Drude) plasmon above C/K=26 , Fermi liquid behaviour.
- Plasmon energy (E_p^2) ~ charge density (*n*):

$$E_p^2 = \hbar n e^2 /(m^* \varepsilon_\infty \varepsilon_0)$$

$m^*\varepsilon_\infty$ ~ doping dependent (not constant)

X. Liu et al., PRB 67, 125403 (2003)

Plasmon dispersion in a doped SWCNT bundle



Unchanged π dispersion

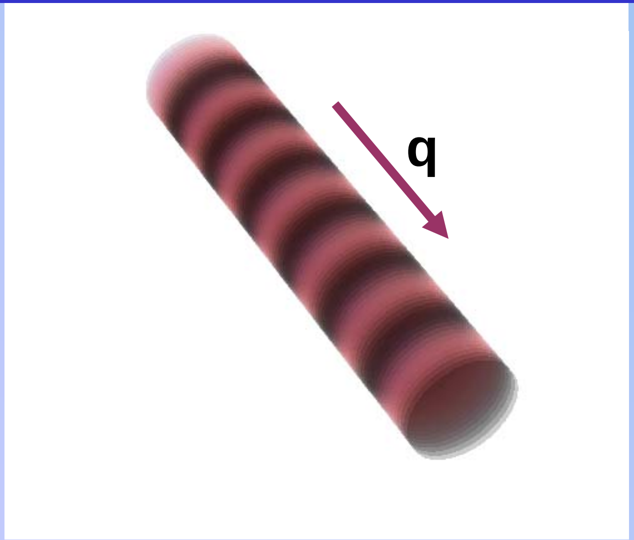
Localized Drude plasmon

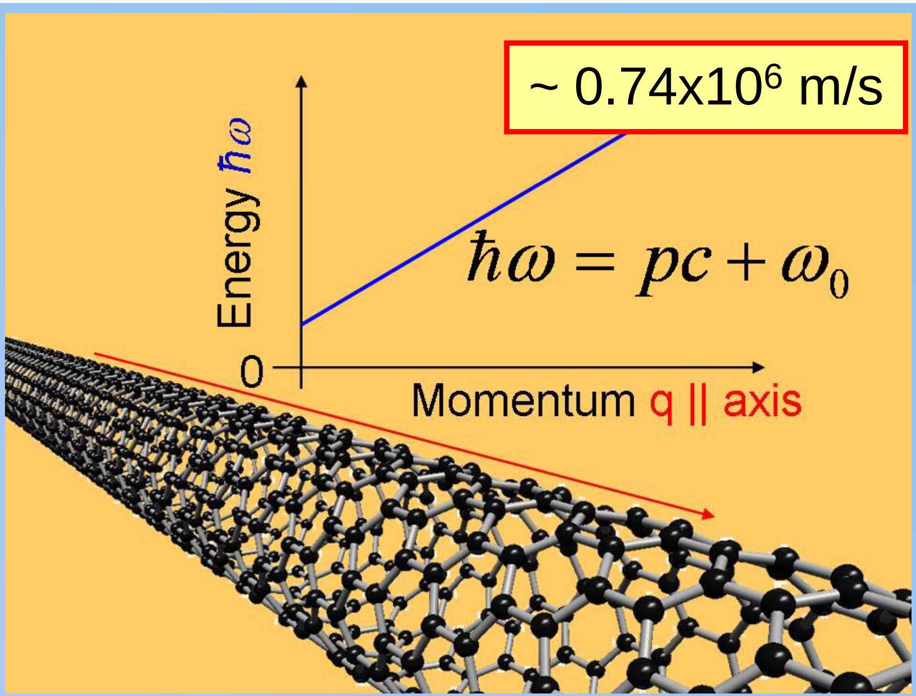
No 3D dispersion

So far **bulk**
What about isolated?

X. Liu *et al.* PRB **67** 125403 (2003)

Summary: Part 1





Isolated VA-SWCNT are truley 1D!

Ist all surface properties, no dielectric screening

a) **Dispersive π plasmon is linear!**

→ mimic K-point excitation in graphene.

b) Charge carrier plasmons in isolated SWCNT are tunable between 0.85 eV and 1.1 eV.

→ similar limits are expected for doped graphene.

Open issue: Why is there no plasmon dispersion?

Where is the acustic plasmon in 1D,2D? Connection to localized VHS?

Outline

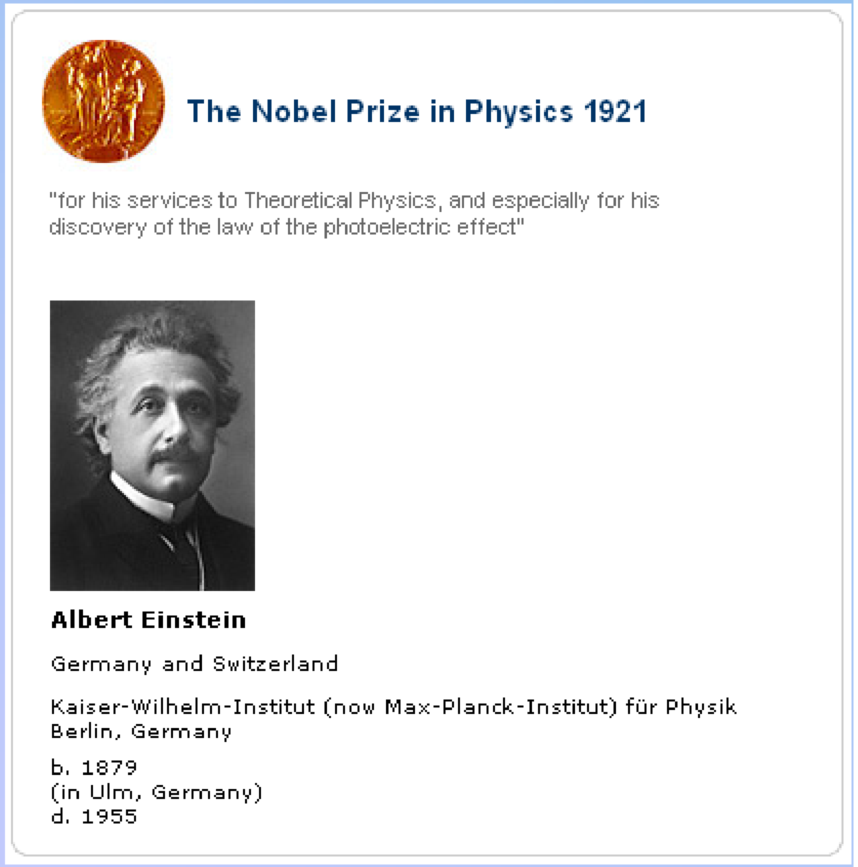
- Introduction/Motivation/Experimental
- Part 1: Angle resolved dielectric response of SWCNT
  - a) SWCNT bundles vs. individual SWCNT
  - b) Implications on excitation spectrum in 1D,2D
  - c) 1D „Drude“ plasmon in intercalated SWCNT?
- Part 2: Electronic structure of metallicity selected SWCNT
  - a) Textbook example for intrinsic XPS line shapes
  - b) Unravelling the 1D DOS in PES and XAS
  - c) Nature of metallic ground state in metallic SWCNT
- Part 3: Functionalized SWCNT:
  - a) Examples for intercalation, filling and substitution
  - b) Nanochemical reactions inside SWCNT
- Part 4: Electronic and phononic structure of graphene systems
  - a) Electron dispersion, phonon dispersion and EPC
  - b) GIC KC_8 revisited: A key to graphene
- Summary and outlook

Photoemission principles

Albert Einstein

$$E_{kin} = h\nu - \phi$$

1905



The Nobel Prize in Physics 1921

"for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect"

Albert Einstein

Germany and Switzerland

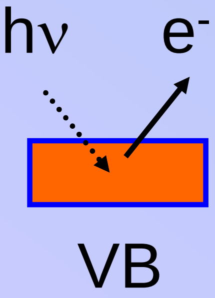
Kaiser-Wilhelm-Institut (now Max-Planck-Institut) für Physik
Berlin, Germany

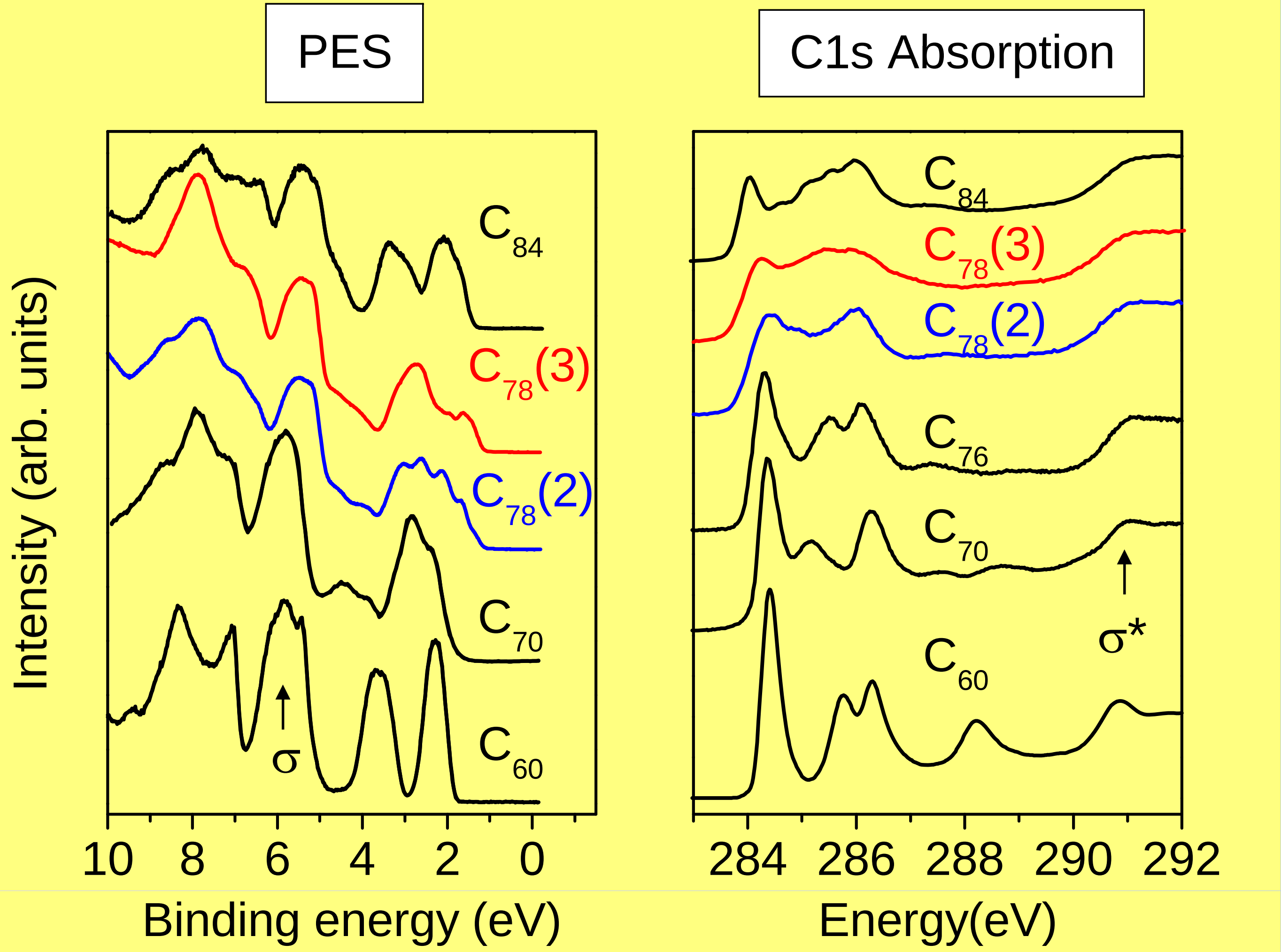
b. 1879
(in Ulm, Germany)
d. 1955

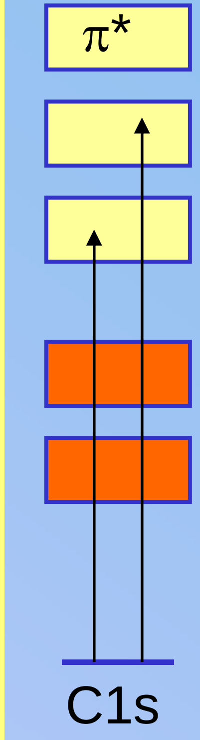
….. 1 Meuro question in Austria in march (2008) ….

Example: PES, XAS on fullerenes

DOS of molecular orbitals revealed:

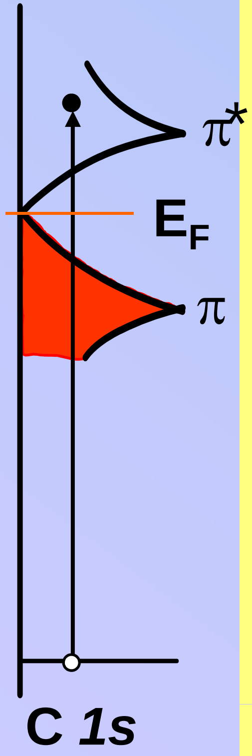


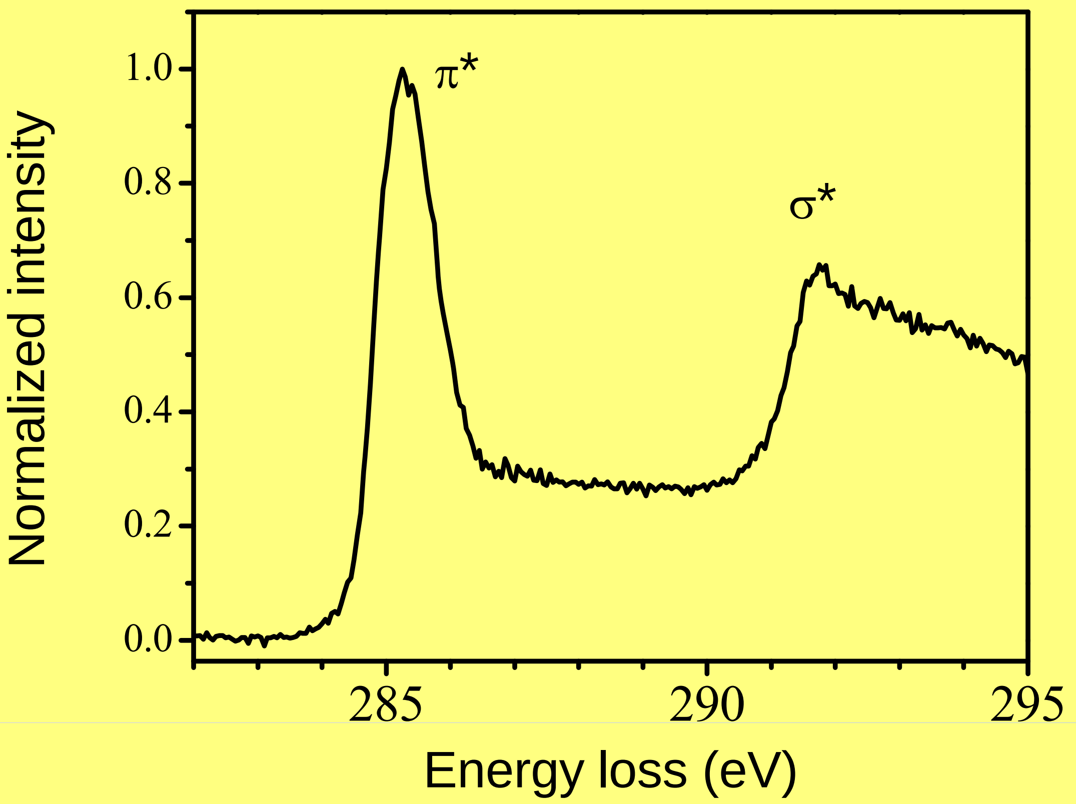




Additional gain from EELS, XAS with high energy resolution

Example: C1s XAS/EELS of graphite:

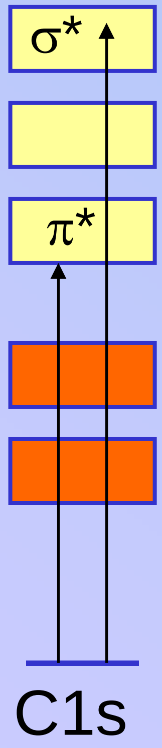


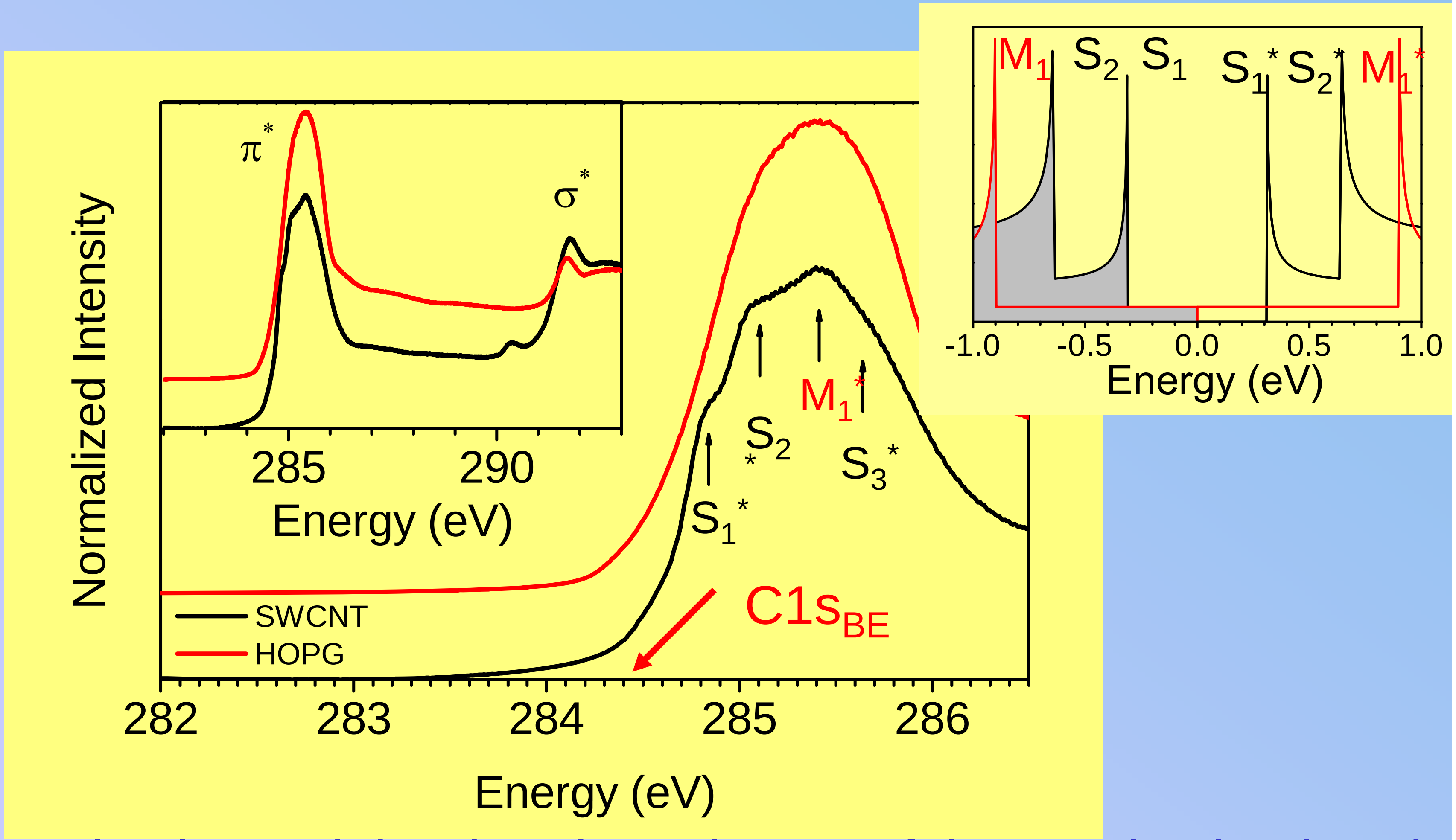


Site selective projected DOS of the conduction band strongly excitonic by core hole effects:

e.g. Bruhwiler PRL 76, 1761 (1996)

XAS: Conduction band of metallicity mixed SWCNT bundles





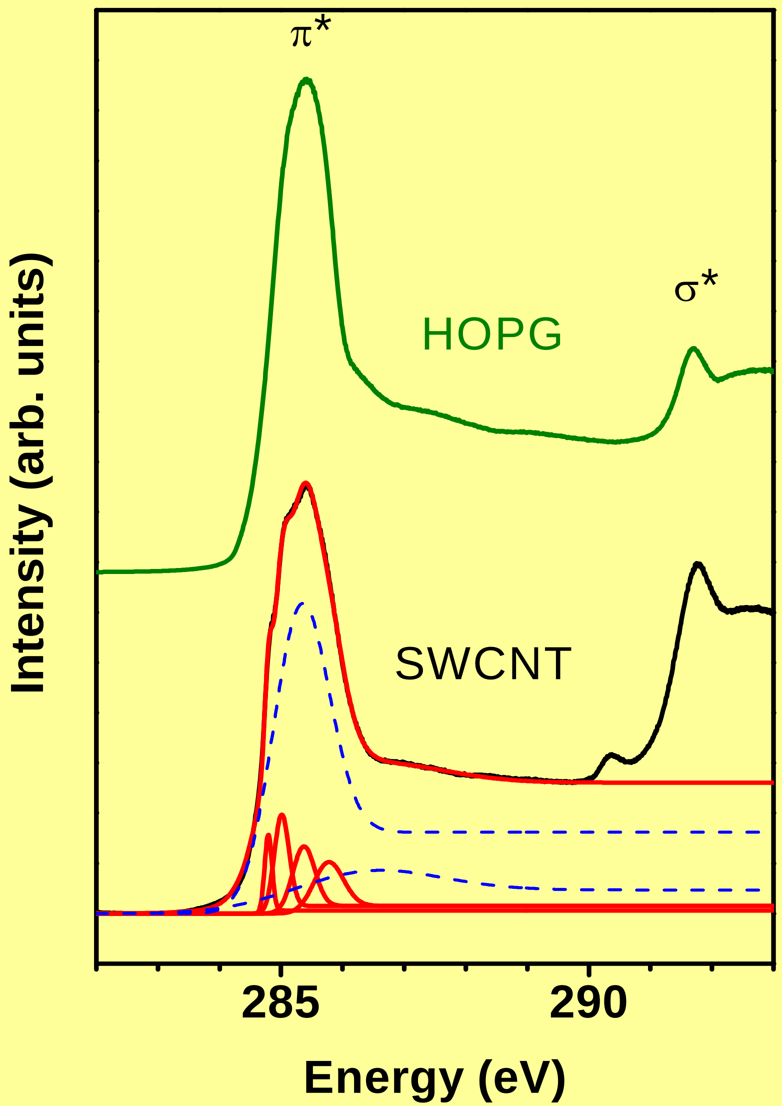
Site selective weighted projected DOS of the conduction band

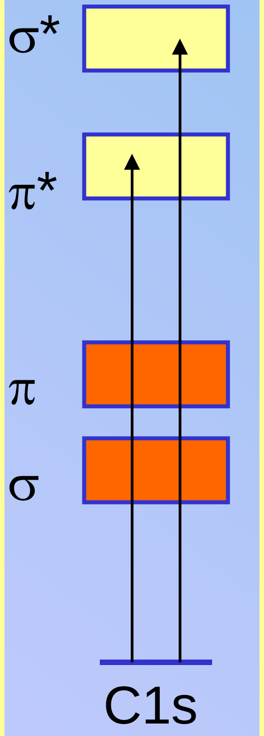
Fine structure in π* resonance: S_1*,S_2*, S_3*, and M_1*.

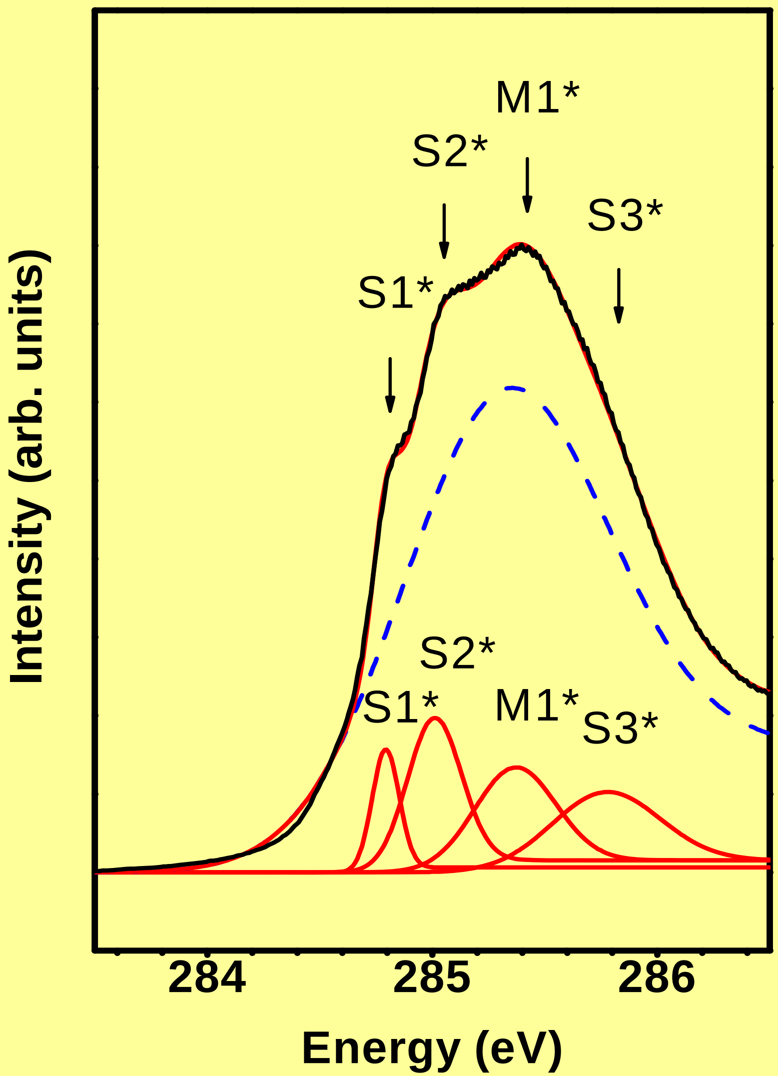
But: exitonic effects: $\Delta S=0.25$ eV

C. Kramberger et al. PRB, 75, 235437 (2007)

High Resolution XAS of metallicity mixed SWCNT



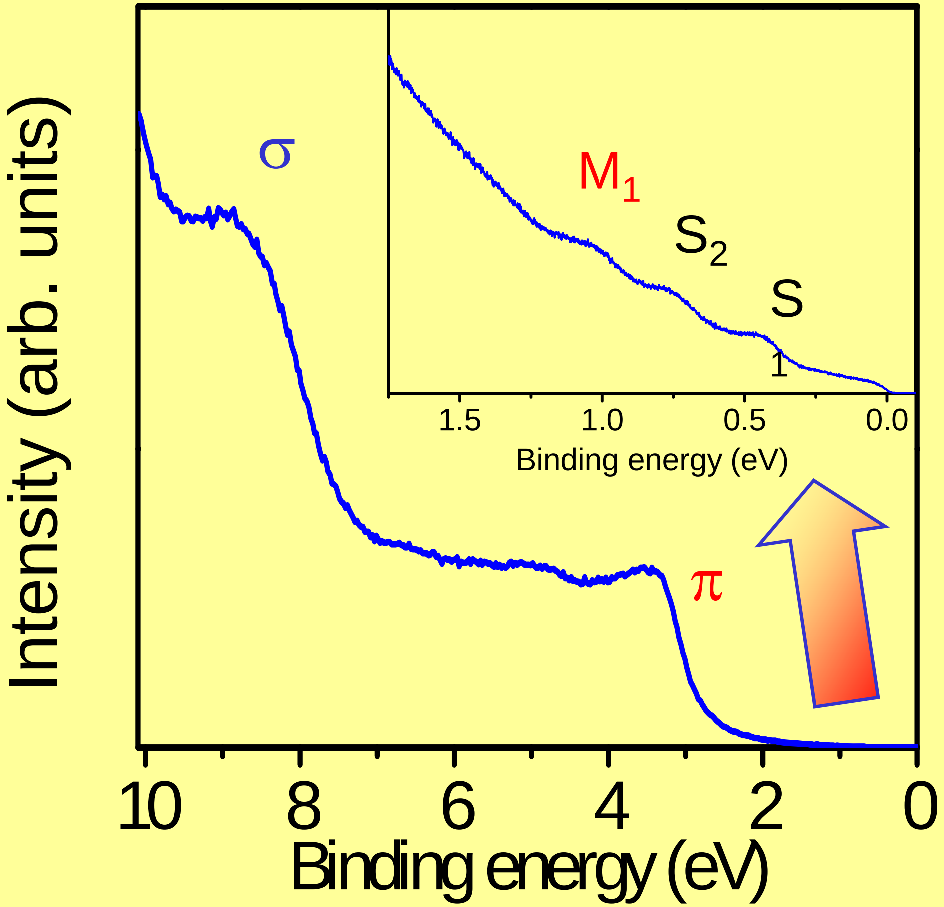


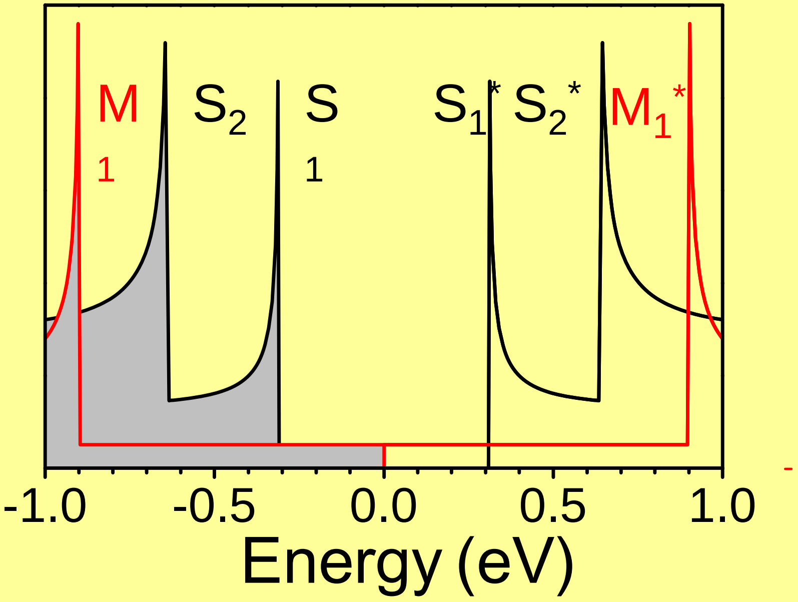


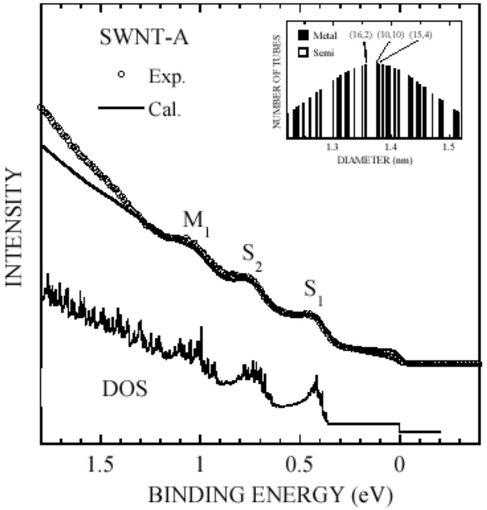
C. Kramberger et al. PRB, 75, 235437 (2007)

Valence band of a metallicity mixed SWCNT bucky paper

High resolution angle integrated photoemission at T=35 K:







vHS of tubes: S_1, S_2, M_1

good agreement with TB calculations

e.g. H. Ishii et al, Nature, 426, 540 (2003), H. Rauf et al.

Scaling in 1D and 3D metals: gain from photoemission

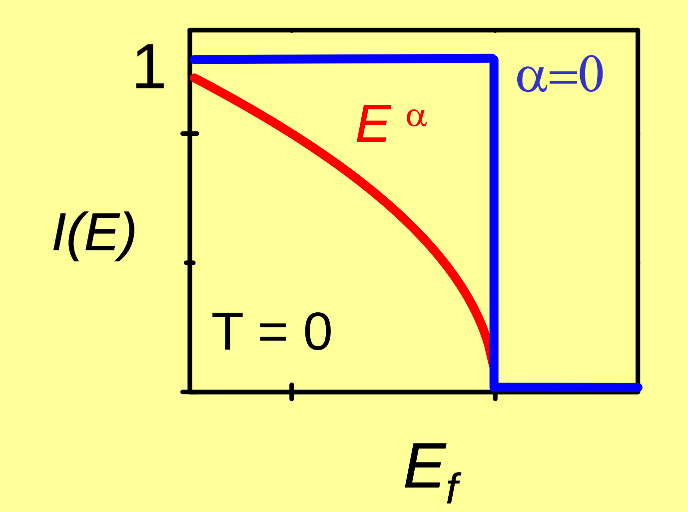
Photoemission intensity: $I(E) \sim n(E)\, f(E)$

3D metal: Fermi-liquid

•PES shows Fermi edge

$$f(E) = \frac{1}{\exp[(E-E_f)/kT] + 1}$$

$n(E) \sim const,\ \alpha=0,\ g=1$



1D metal: Tomonaga-Luttinger liquid

- 1D paramagnetic metal
- correlated electron state
  interaction parameter g

g<< 1 repulsive Coulomb interaction

g>1 attractive interaction

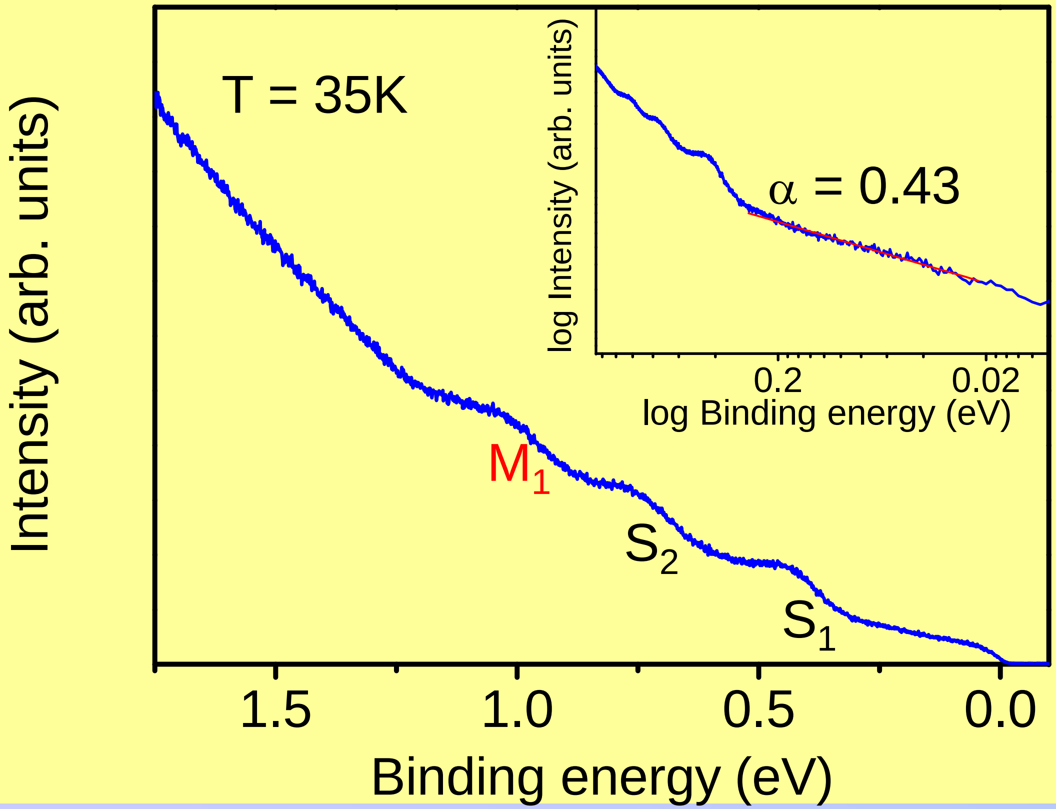
power law dependence of n(E):

$n(E) \sim E^{\alpha}$

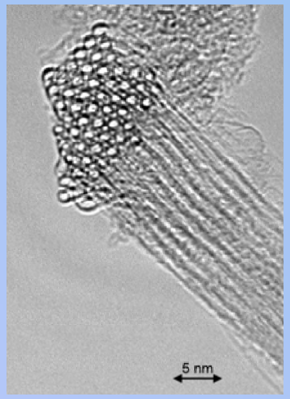
For SWCNT:

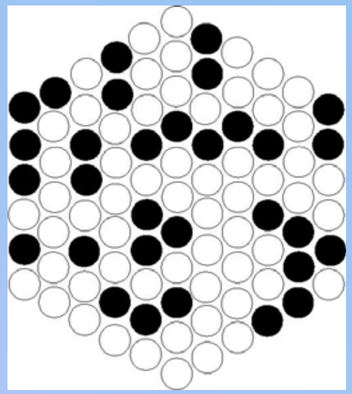
$\alpha=(g+1/g-2)/8 = 0.3-0.5$

Effect of dimensionality: Photoemission



Metallic SWCNT in a bundle of SWCNT have the renormalization of a Tomonaga-Luttinger liquid





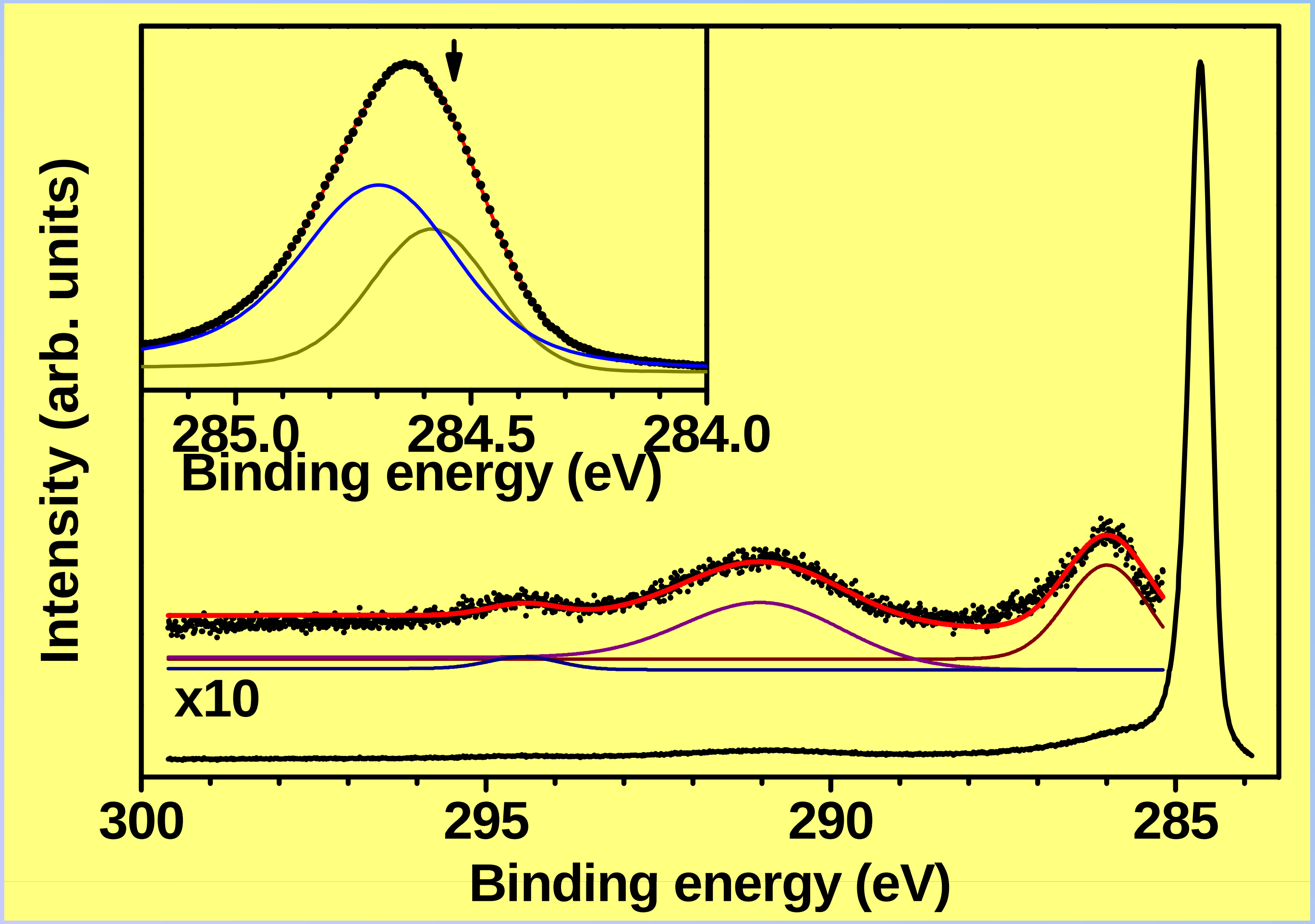
○ semiconducting
● metallic

$\alpha = 0.43$, $g=0.18$

good agreement with theoretical predictions and results from transport measurements

H. Ishii et al, Nature, 426, 540 (2003); H. Rauf et al, PRL 93, 096805 (2004)

High resolution XPS of metallicity mixed SWCNT



- C1s for SWCNT has two components at different binding energy
- One Doniac-Sunjic lineshape (metallic SWCNT)
  One Voigthian (semicond. SWCNT)

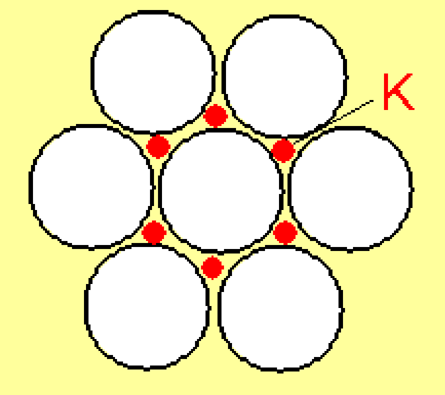
C. Kramberger et al. PRB, 75, 235437 (2007)

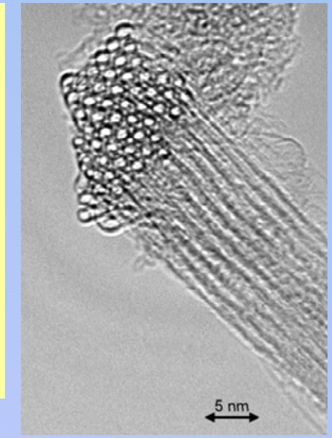
Outline

- Introduction/Motivation/Experimental
- Part 1: Angle resolved dielectric response of SWCNT
  - a) SWCNT bundles vs. individual SWCNT
  - b) Implications on excitation spectrum in 1D,2D
  - c) 1D „Drude“ plasmon in intercalated SWCNT?
- Part 2: Electronic structure of metallicity selected SWCNT
  - a) Textbook example for intrinsic XPS line shapes
  - b) Unravelling the 1D DOS in PES and XAS
  - c) Nature of metallic ground state in metallic SWCNT
- Part 3: Functionalized SWCNT:
  - a) Examples for intercalation, filling and substitution
  - b) Nanochemical reactions inside SWCNT
- Part 4: Electronic and phononic structure of graphene systems
  - a) Electron dispersion, phonon dispersion and EPC
  - b) GIC KC_8 revisited: A key to graphene
- Summary and outlook

Functionalization: doping and filling of SWCNT

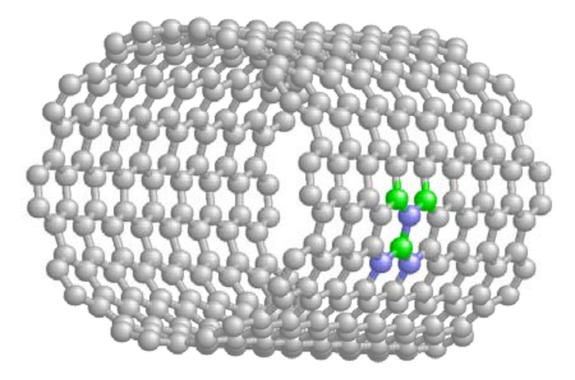
- **Intercalation:**

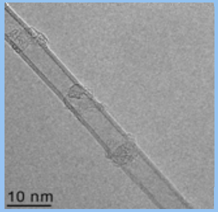


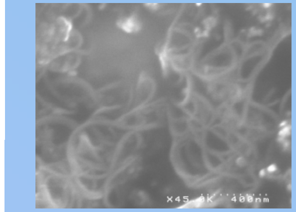


e.g. K_x-SWCNT

Substitution:

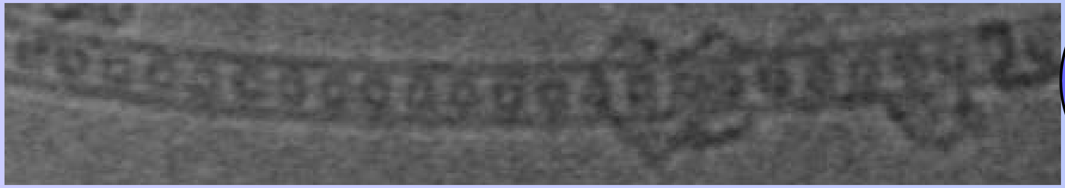


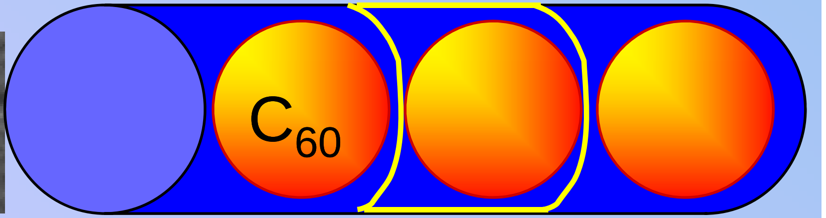




BC_3-SWNT, MWBNT, SiCNT

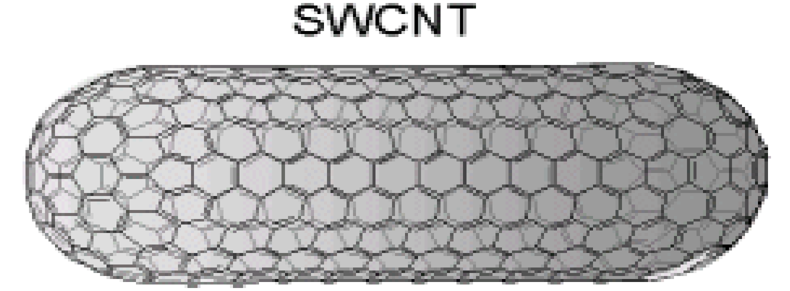
- **Filling: C_{60} Peapods, DWCNT….**



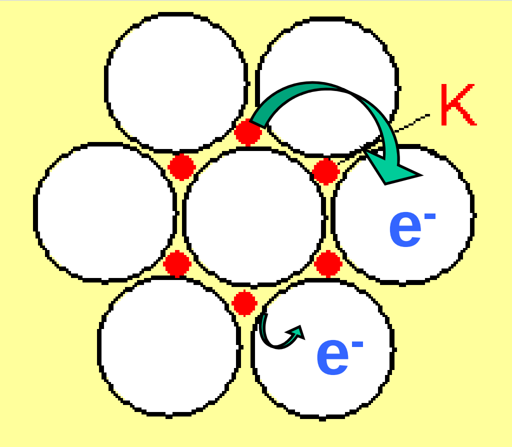


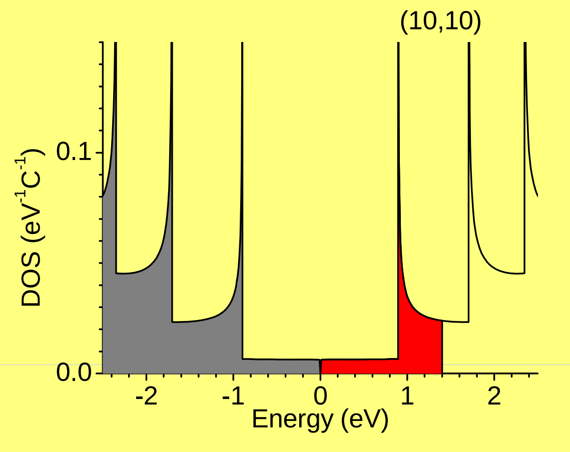
⇨ Optical and high energy spectroscopy are ideal tools!

Intercalation

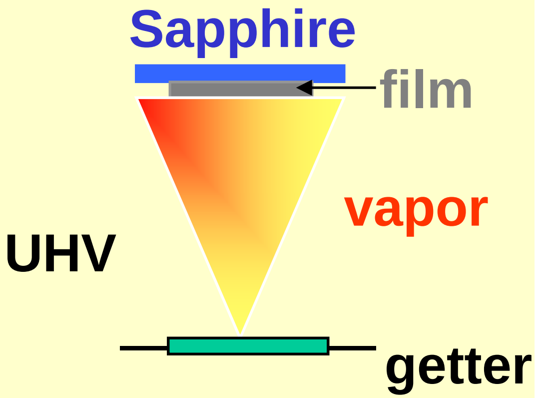


doping



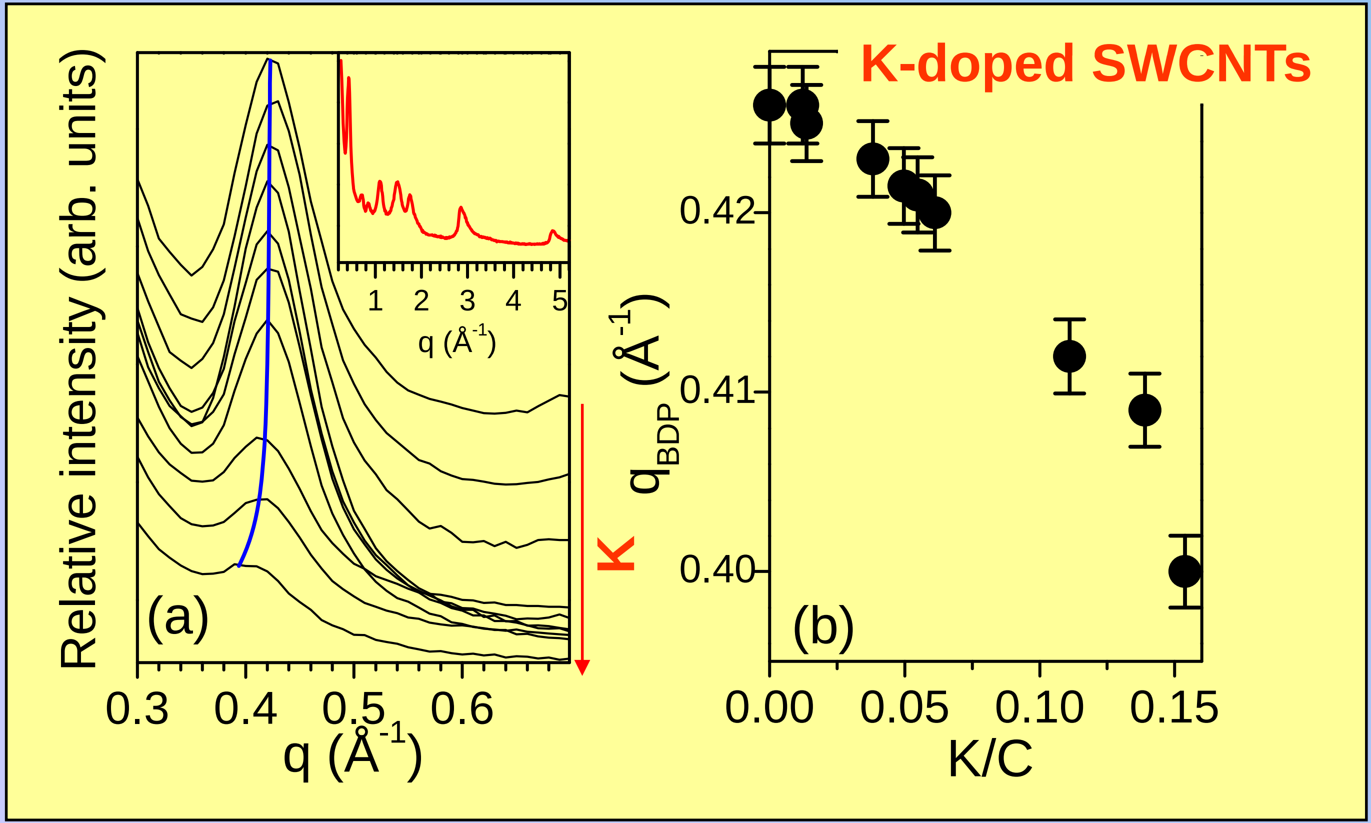


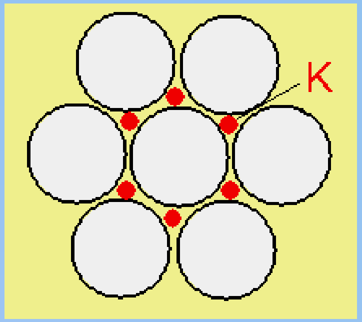
Alkali-metal intercalation



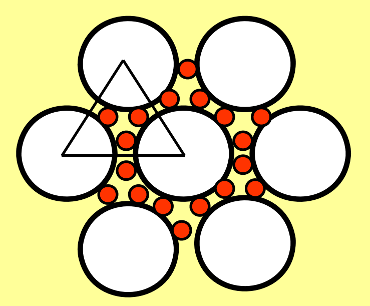
***in-situ* doping:**
UHV evaporation
($5x10^{-10}$ mbar)
Na, K, Rb, Cs and
Ba SAES getters

Structural analysis of alkali-metal doped SWCNTs





no expansion



expansion

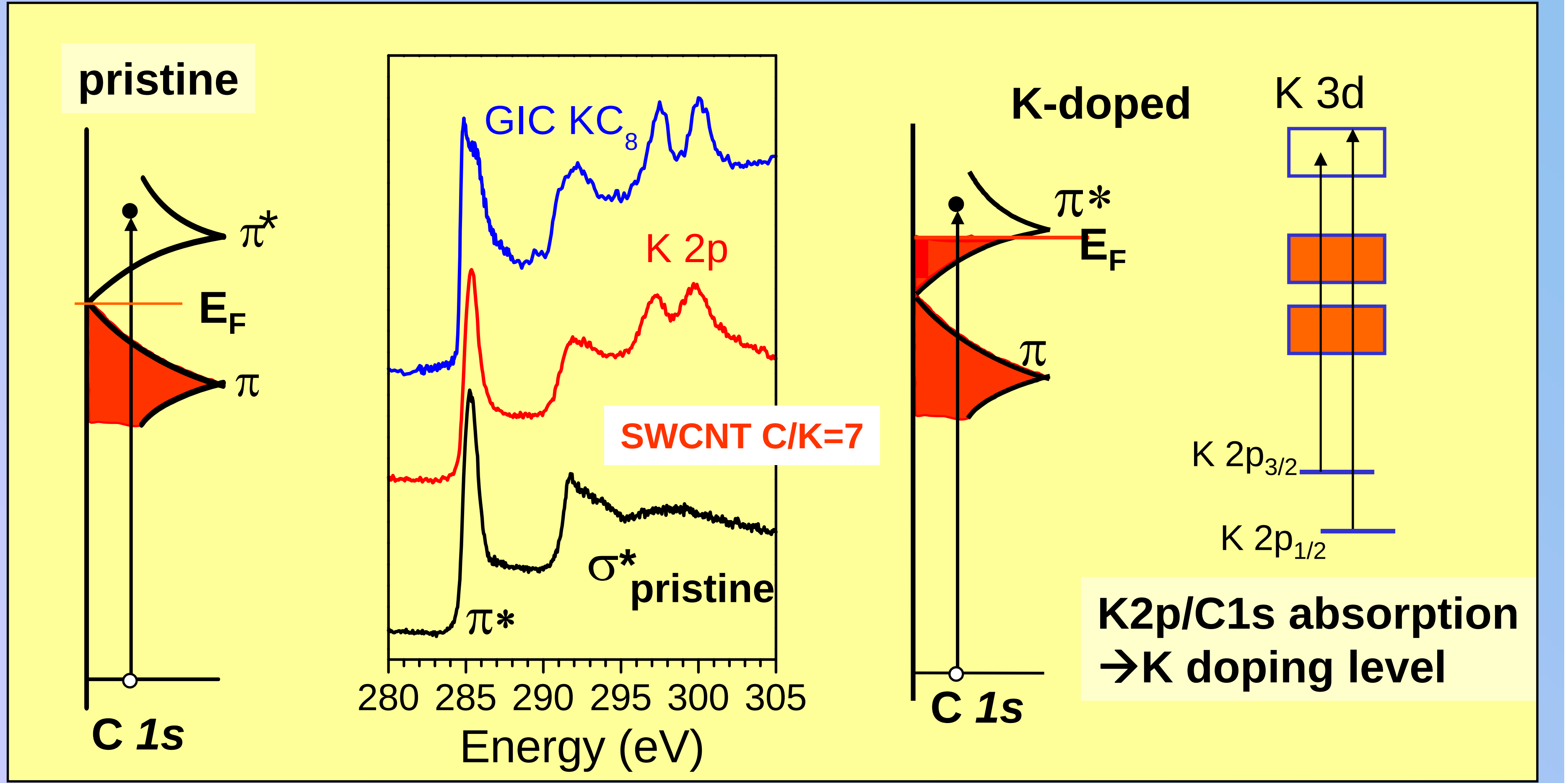
d=1.37nm

(Å)	Na	K	Rb	Cs
Ionic radius:	**0.95,**	**1.33,**	**1.48,**	**1.69**
Expansion:	**0**	**1.1**	**1.7**	**2.7**

alkali intercalates between the SWCNT lattice expansion depends on doping level, diameter & size of dopant. No staging

T. Pichler et al. SSC 109, 721 (1999);
X. Liu et al. PRB 67, 125403 (2003)
X.Liu et al. PRB 70, 245435 (2004)

Intercalation: C,K edge excitations (alkali-metal doping)

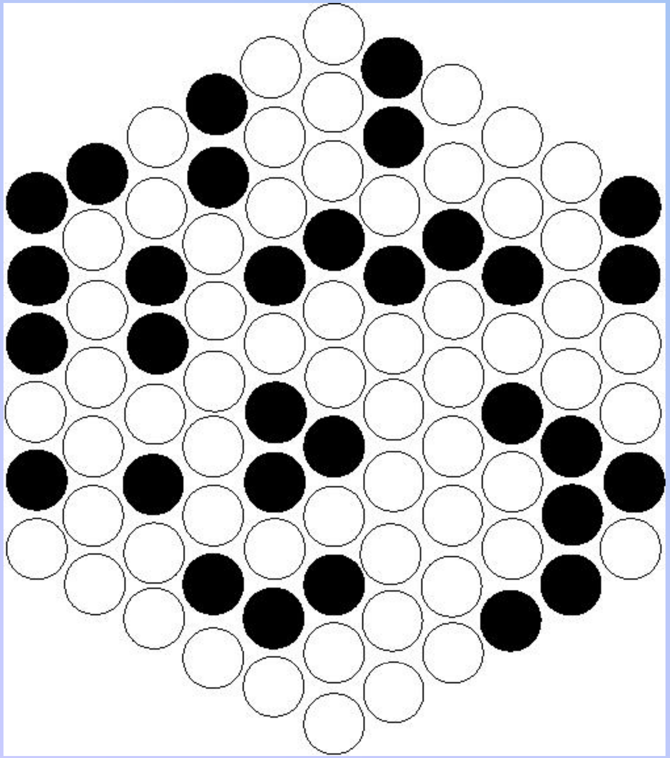


K2p/C1s absorption
→K doping level

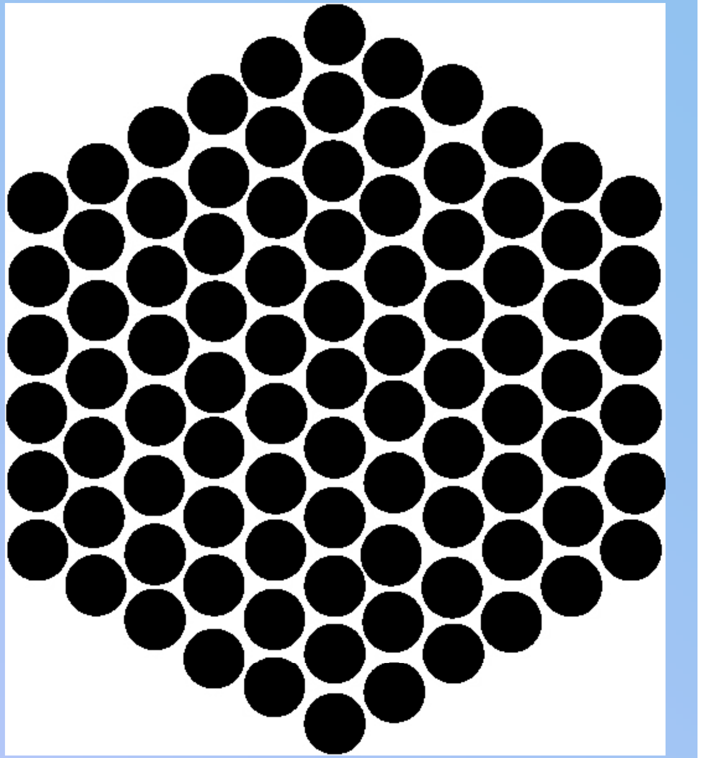
Ratio C1s/K2p edges:
Maximum intercalation ratio C/K=7
Ionic charge transfer, π^* resonance decreases by 15%

T. Pichler et al. SSC 109, 721 (1999), X. Liu et al. PRB 67, 125403 (2003)

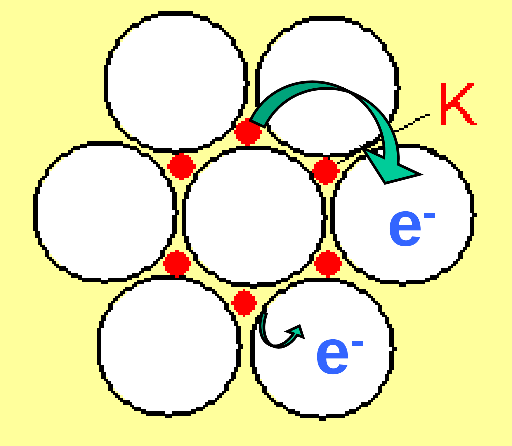
Intercalation: what happens at low doping?



doping

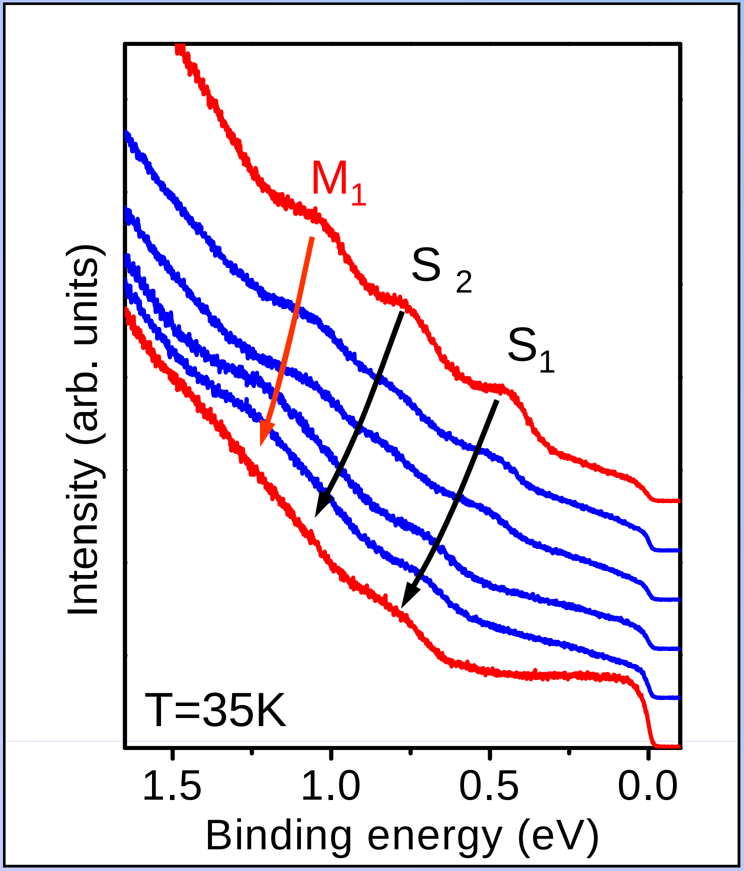


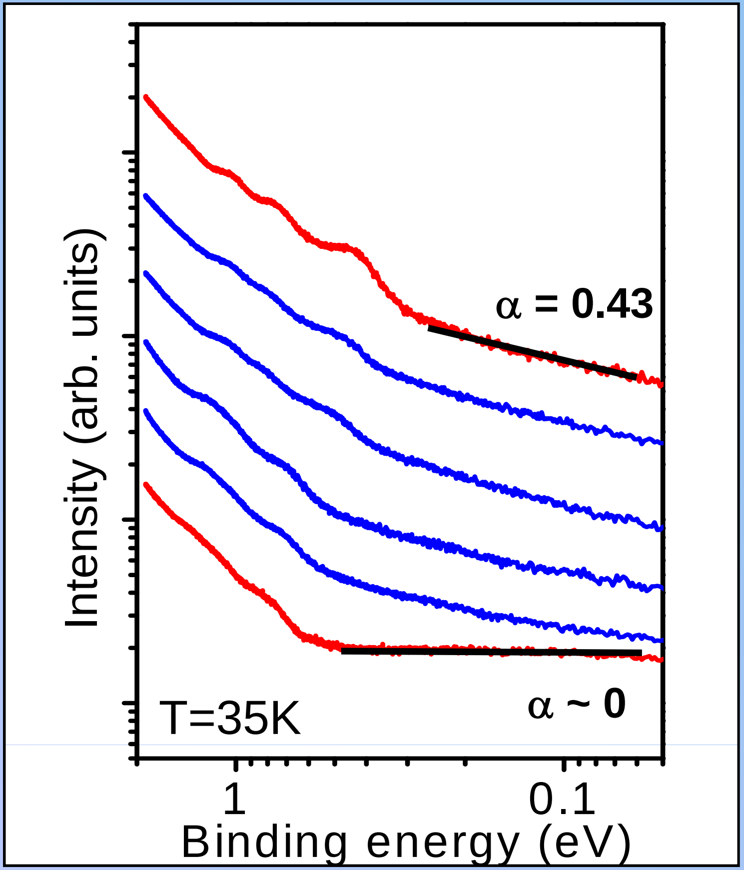
○ semiconducting
● metallic

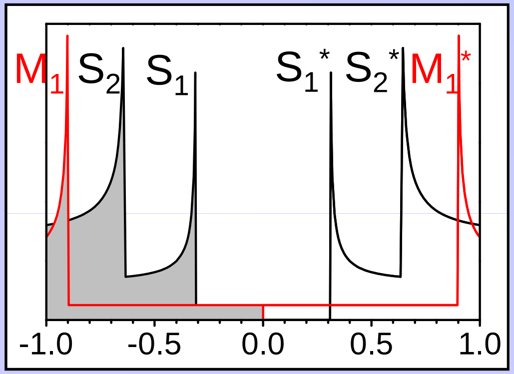


Is a bundle of metallic tubes a
normal Fermi liquid or a Luttinger liquid?

Rigid band shift

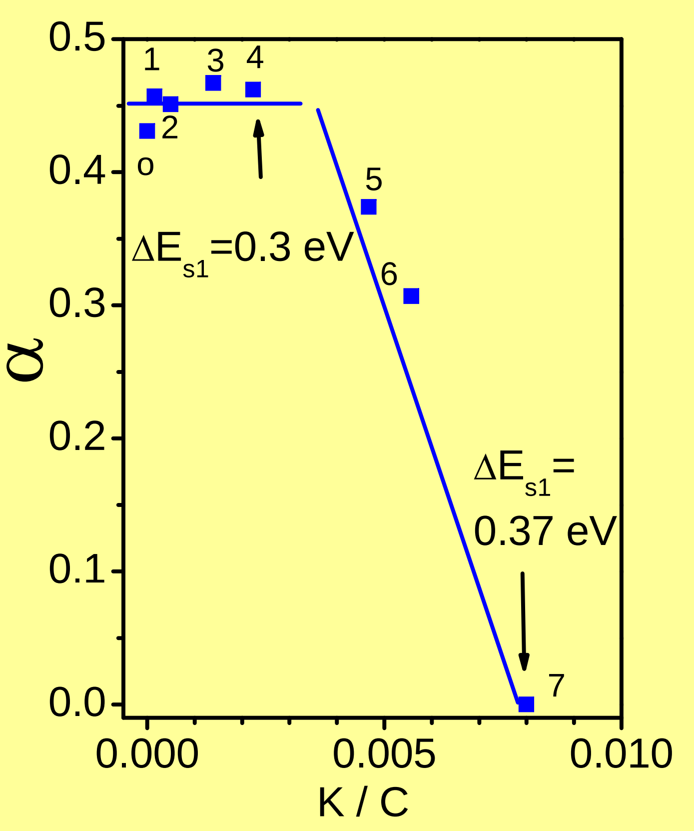


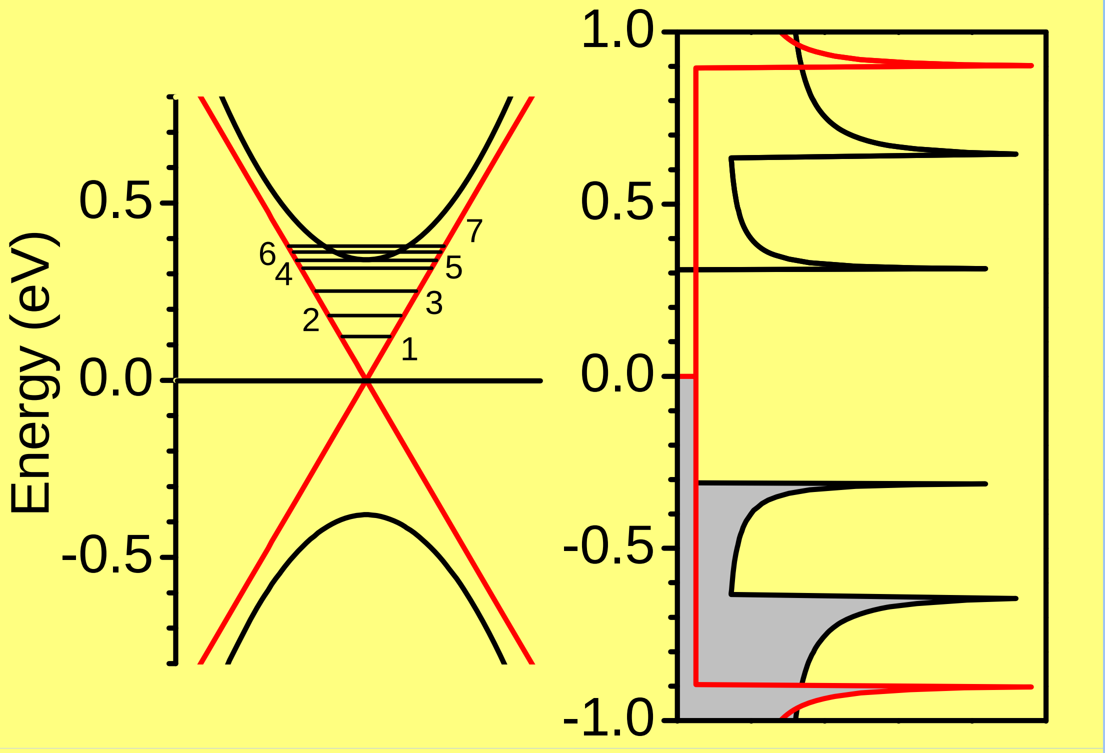




- S_1, S_2 and M_1 shift to higher binding energies
- power law behavior at first stable
- abrupt change at K:C = 1:125, $\Delta E(S_1)$ = 0.37eV

Doping dependence of the LL parameter α





Power law scaling vs. intercalation:

α= const. up to K/C=1/500, ΔE_{S1}=0.25 eV

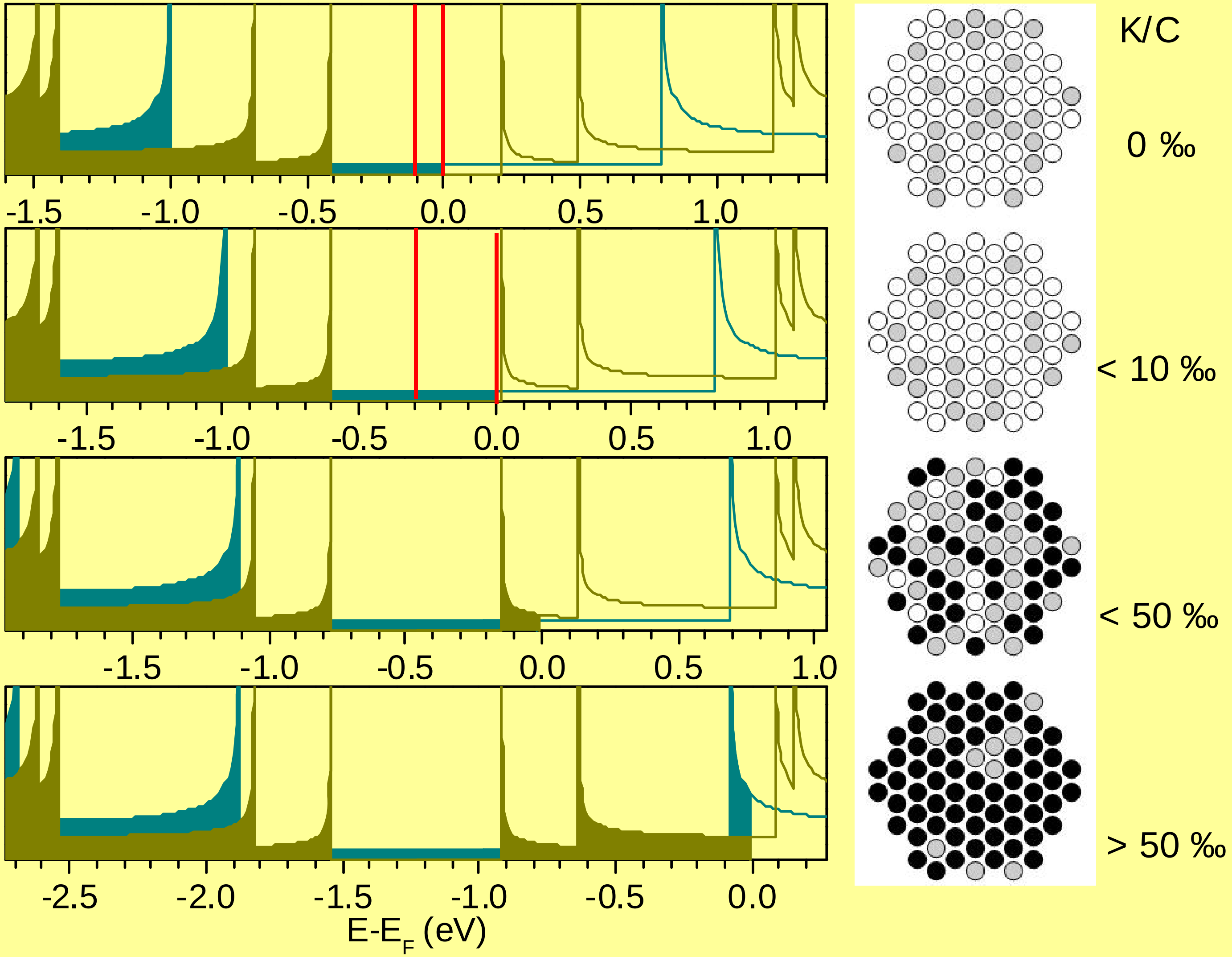
α=0, g=1 above K/C=1/150, ΔE_{S1}>0.35 eV

⇨ a bundle of only metallic tubes is a normal Fermi liquid!

H. Rauf et al. PRL 93, 096805 (2004)

Electronic structure of doped SWCNT bundles: 4 regions

ΔE_F=0.1 eV (Calc. A. Rubio)



pristine

s/m

low

s/m

intermediate

M/m

high

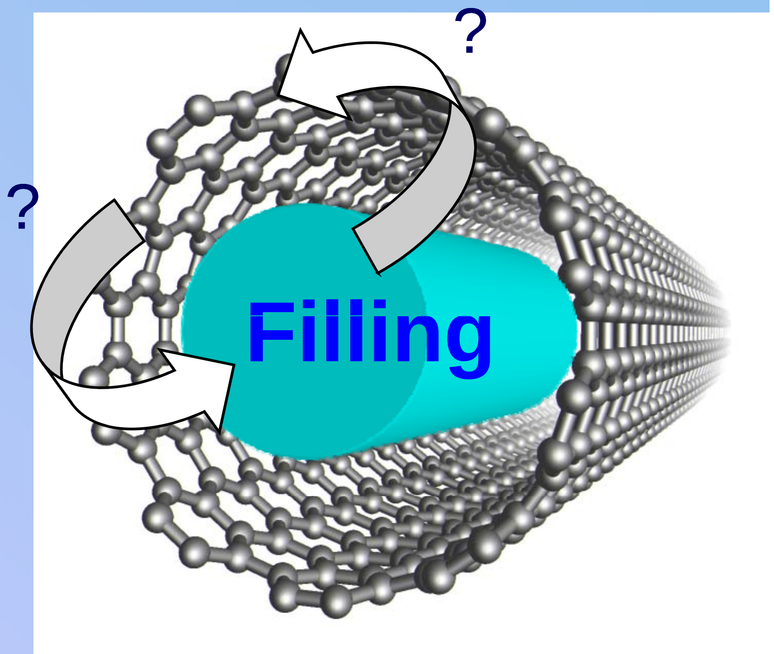
M/M

C. Kramberger et al. PRB, 79, 195442 (2009)

Filling of the inner space of SWCNTs with molecules

Filling@SWCNT

so-called “peapod”



- Modified electronic properties?

What happens upon the formation of the peapods?

Charge transfer, chemical bonding

or orbital hybridisation?

Conversion to double-wall carbon nanotubes (DWCNT)?

- Potential applications

Carrier tuning of SWCNT, protection for molecules and even drugs, stabilizing reactive compounds and nanocrystals, chemical reaction inside a 1D confined nano reaction tube, 1D spinchain for spin electronics, …

Examples

- Fullerenes@SWCNT

C_{60}@SWCNT :

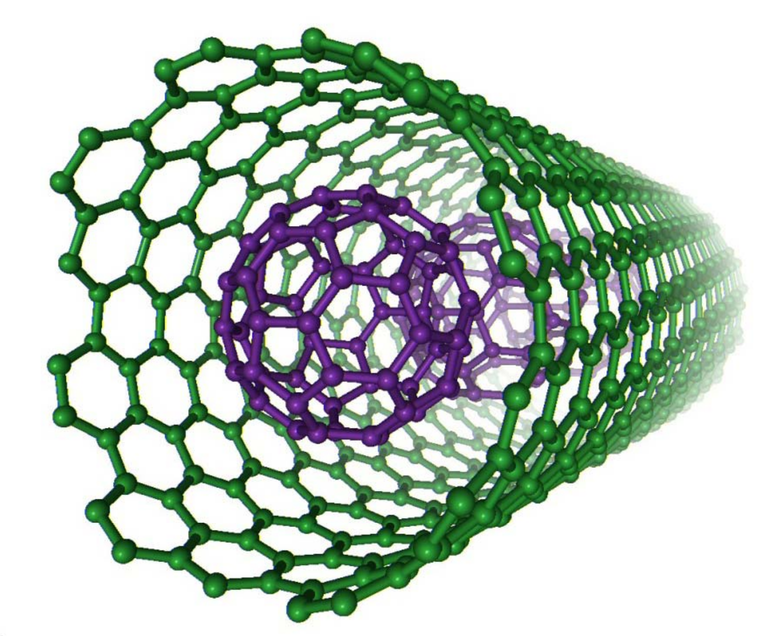
1D C_{60} chain inside SWCNT (TEM,Raman)

Gd@C_{82}@SWCNT :

Band gap modulation (STM,STS)

Dy_3N@C_{80}@SWCNT :

Charge transfer (PES)



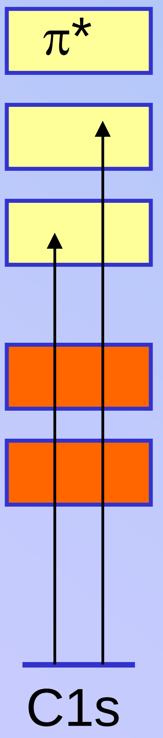
C_{60}@SWCNT

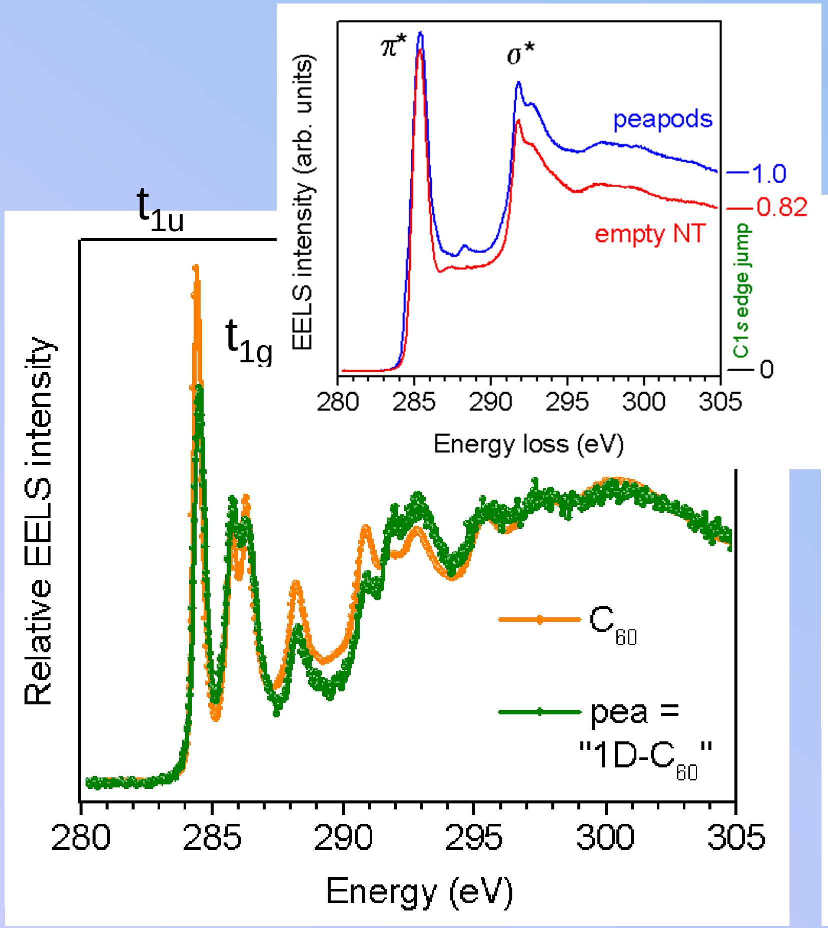
Conversion to DWCNT(TEM, Raman)!

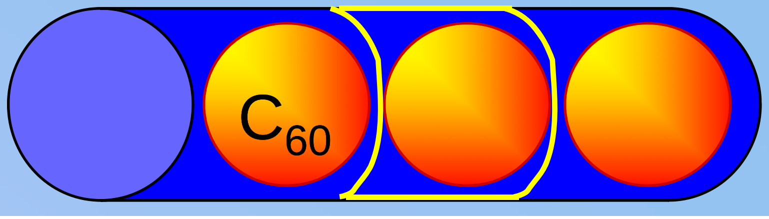
- Organic molecules @SWCNT

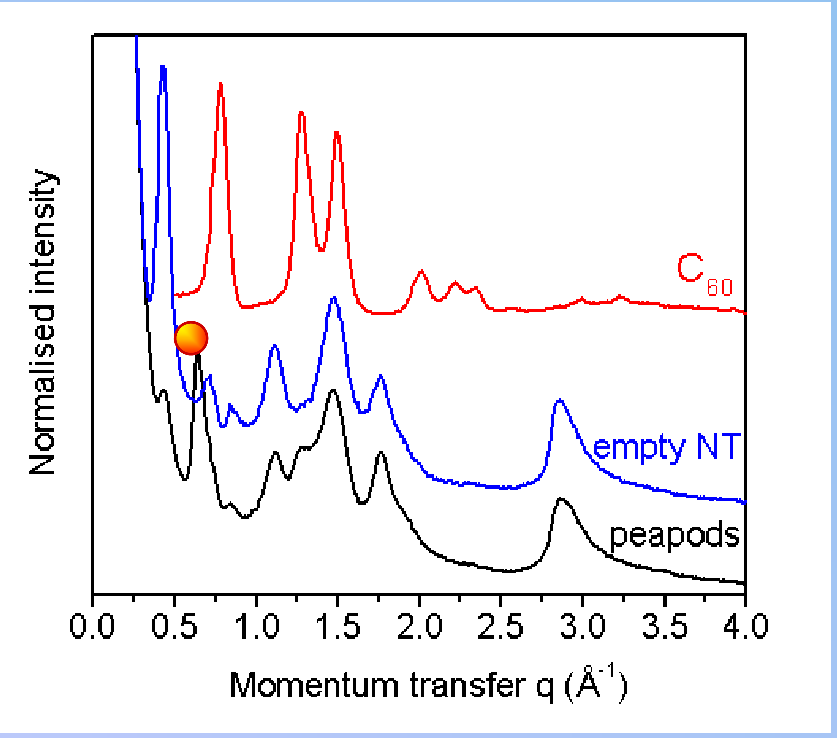
TCNQ, TDAE, Anthracene@SWCNT,
Metallocenes p- and n- type doping

Bulk filling ratio, structure in peapods







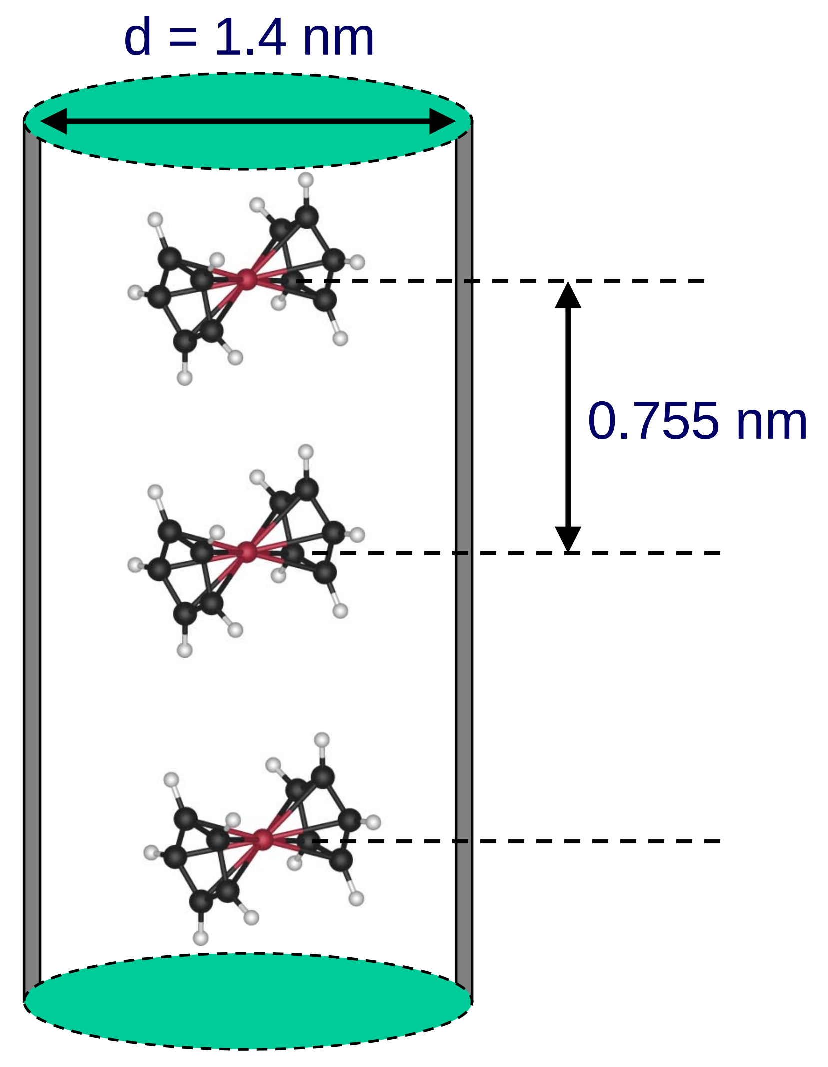


Maximum filling ratio with C_{60}: 100%
no charge transfer to C_{60}

C_{60} - C_{60} distance 9.7 Å
→ no C_{60} polymer in SWCNT

X. Liu et al., Phys. Rev. B 65, 45419 (2002), Synth. Met. 135-136, 715 (2003)

Metallocene filling: Filling factor



Assuming a 1D ferrocene chain inside SWCNT (d =1.4 nm) with adjacent ferrocene distance ~ 0.755 nm

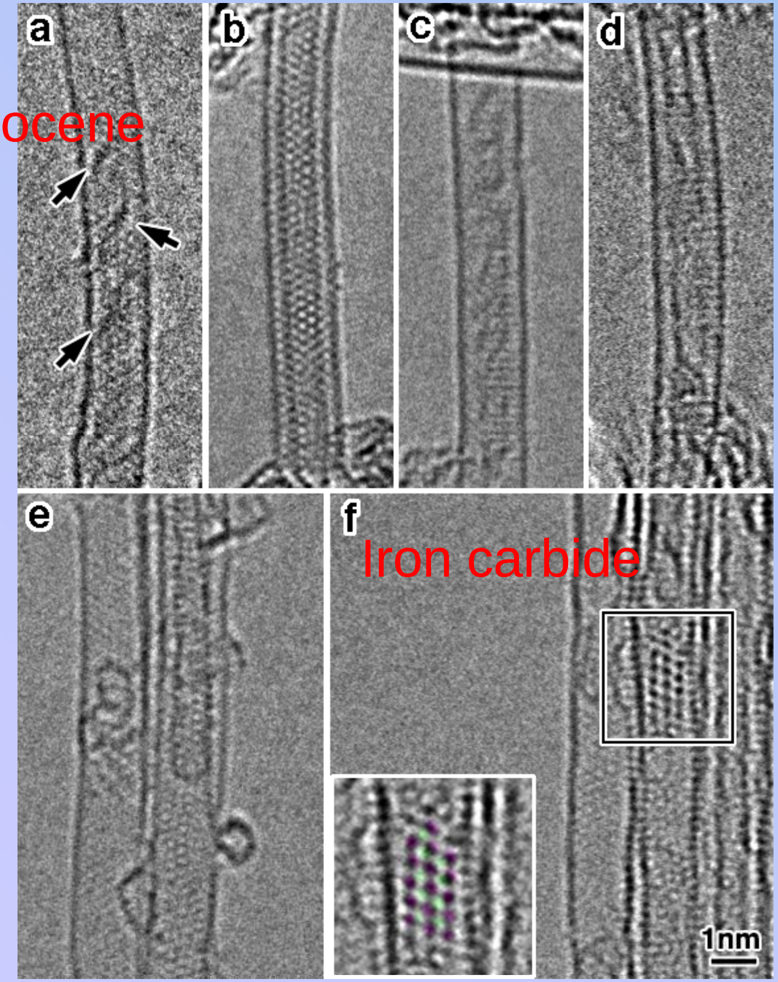
Fe/C ratio ~ 0.003

⇩

Filling factor ~ 35 %

Nanochemistry in 1D: Gain from TEM

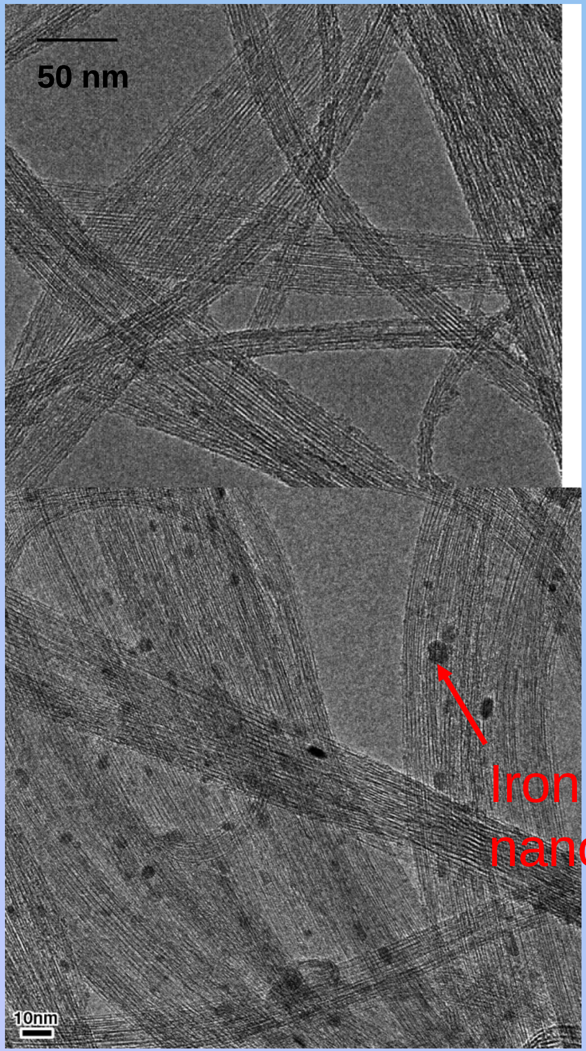
High resolution



Ferrocene

Iron carbide

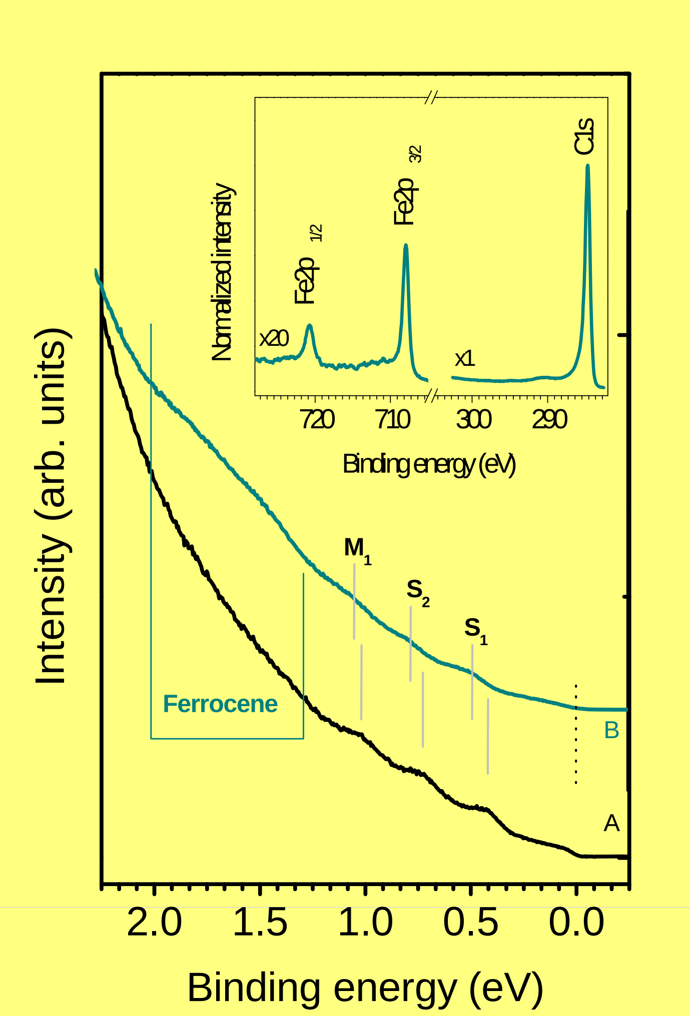
Overview

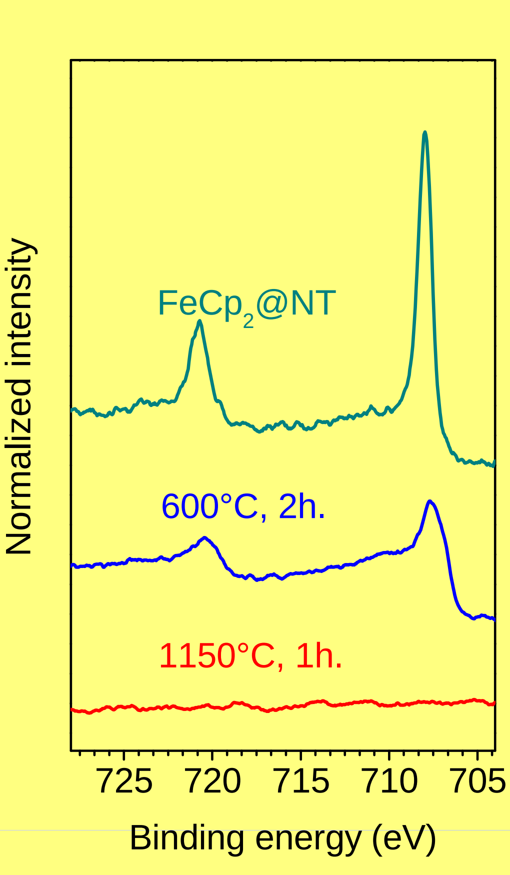


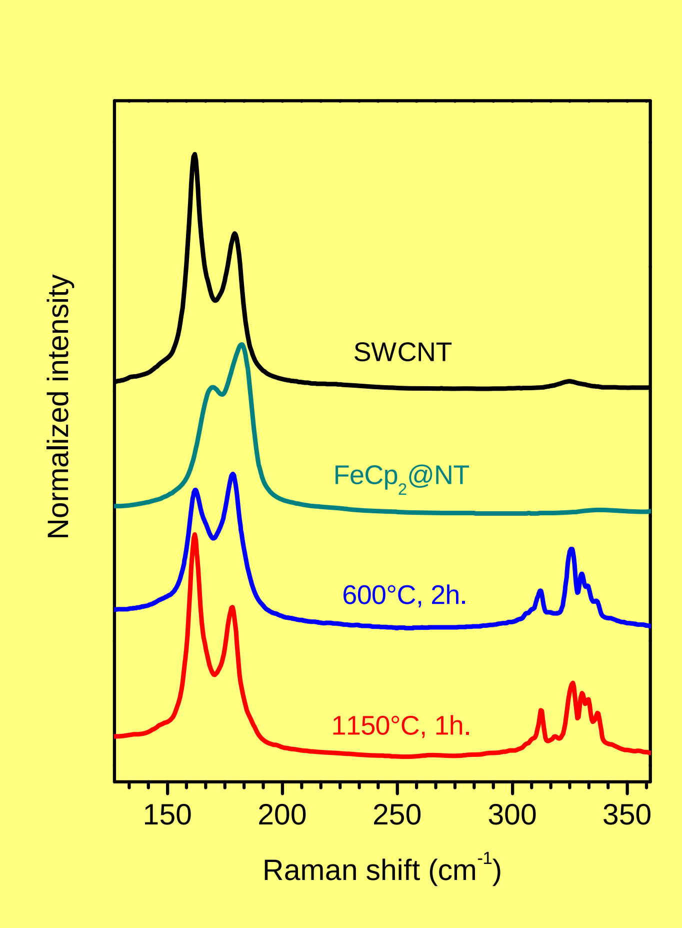
Iron oxide nanocrystals

H. Shiozawa et al. Adv. Mat. (2008)

Ferrocene filled SWCNT and growth of DWCNT



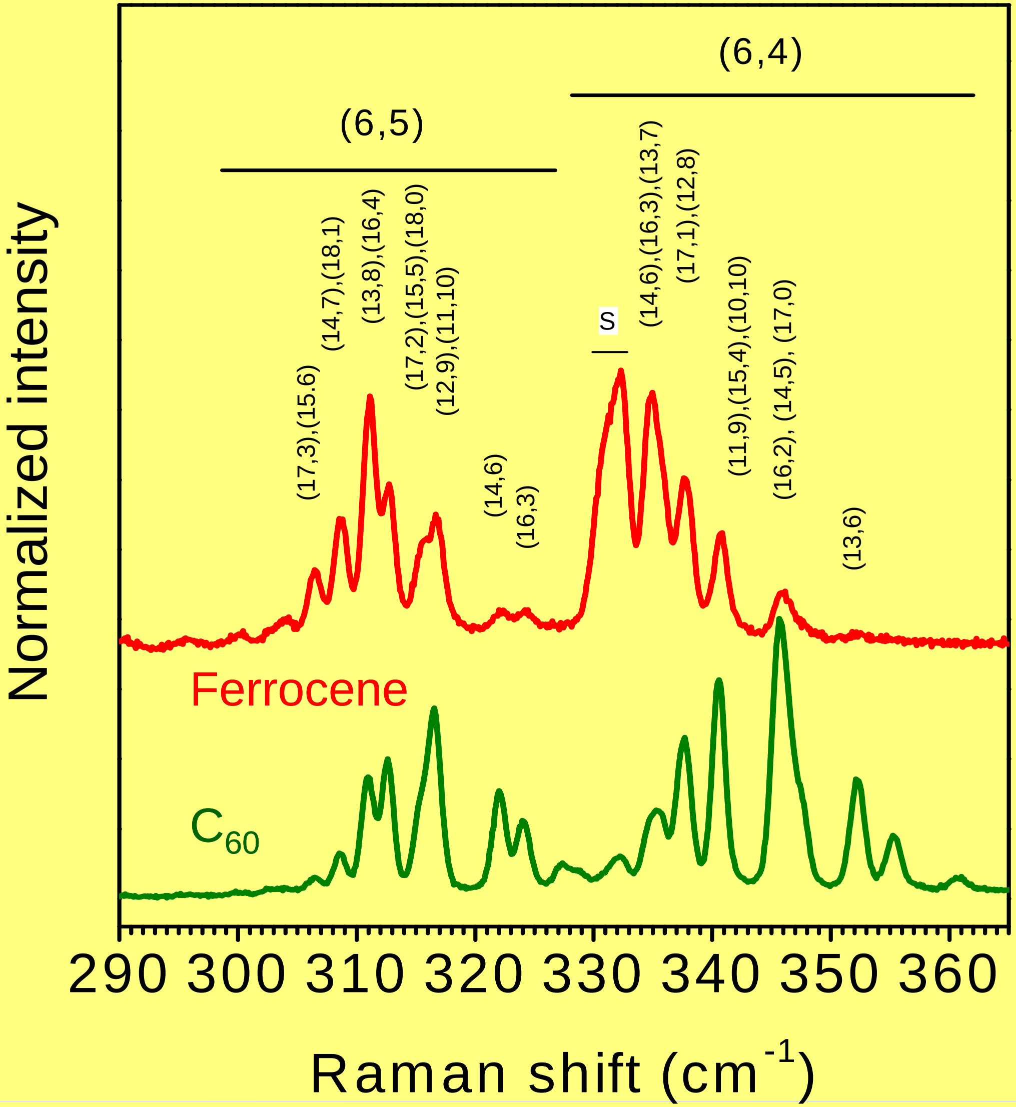


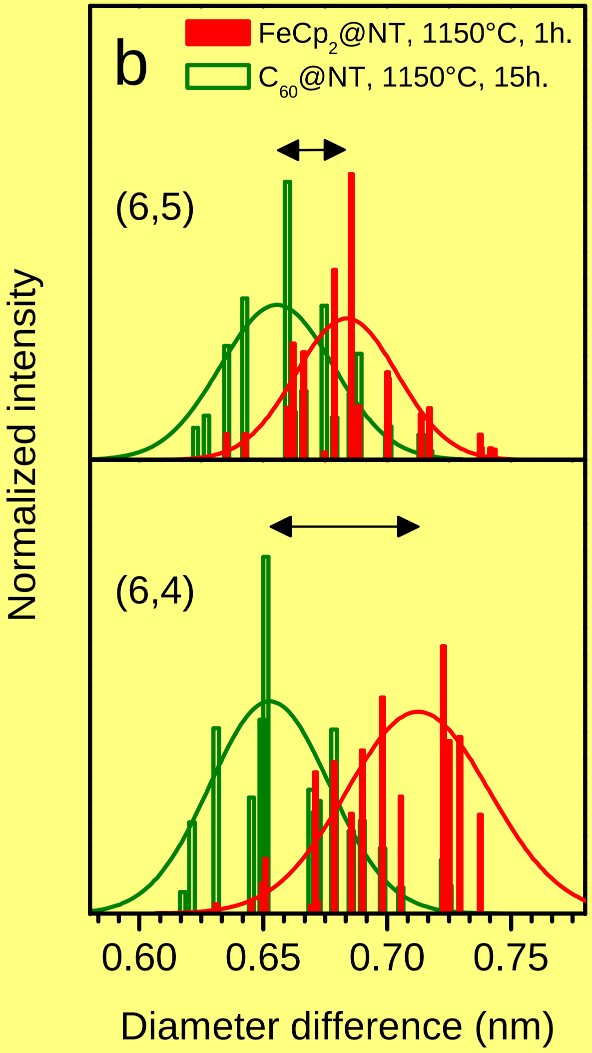


- Charge transfer ΔE_F=0.1 eV, ~0.2 e^- per ferrocene
- Power law behavior α =0.55
- growth of inner tubes at ~ 600 ° C

H. Shiozawa et al.
Adv. Mat. (2008);PRB (2008)

DWCNT/Inner tubes: Gain from high resolution Raman

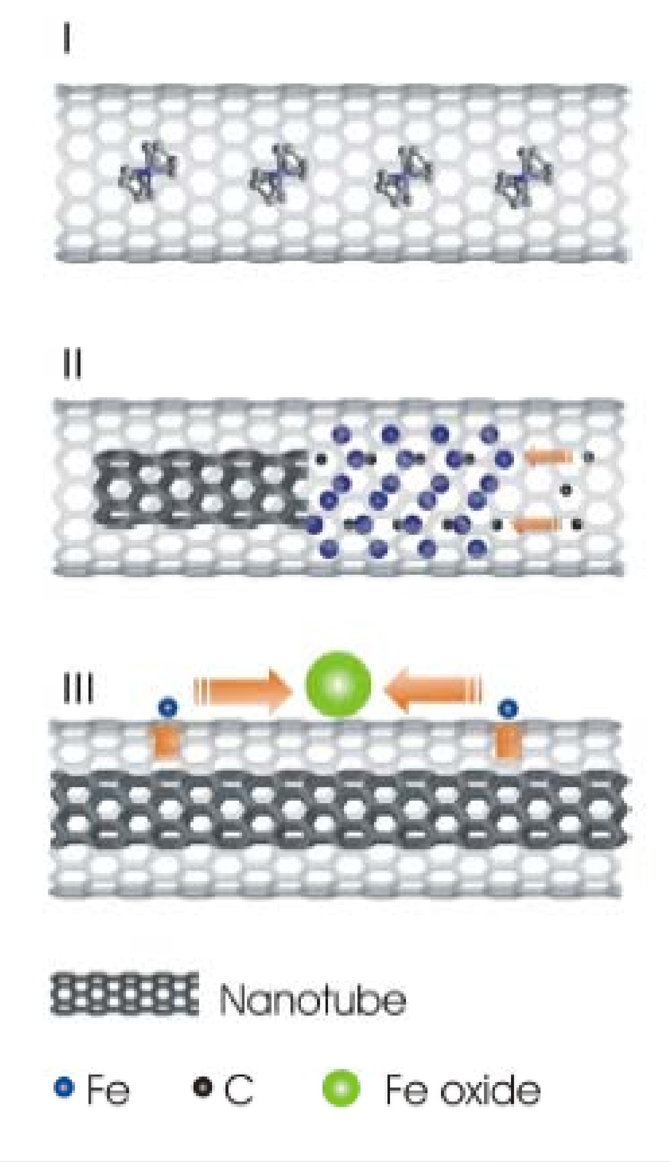




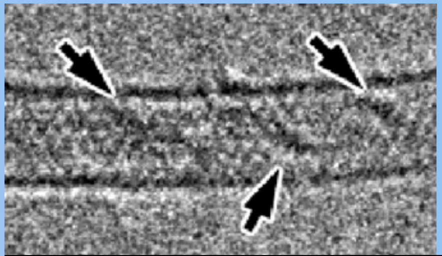
Catalytic growth of inner DWCNT differs from non-catalytic!

H. Shiozawa et al. Adv. Mat. (2008)

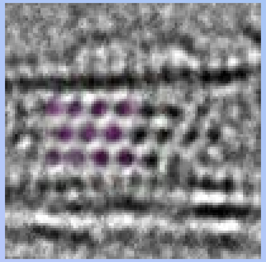
Temperature induced chemical reaction in a SWCNT nanoreactor

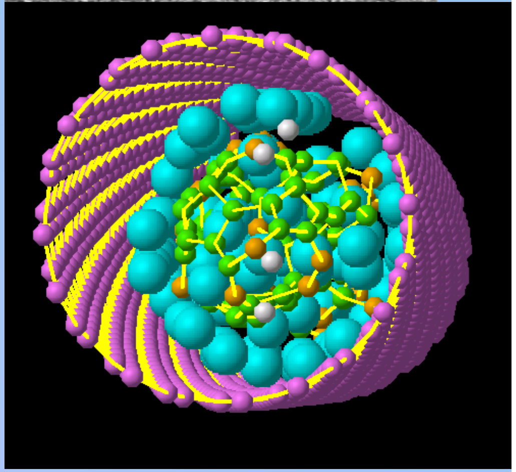


1. Ferrocene filling



2. Catalytic growth from Iron carbide particles





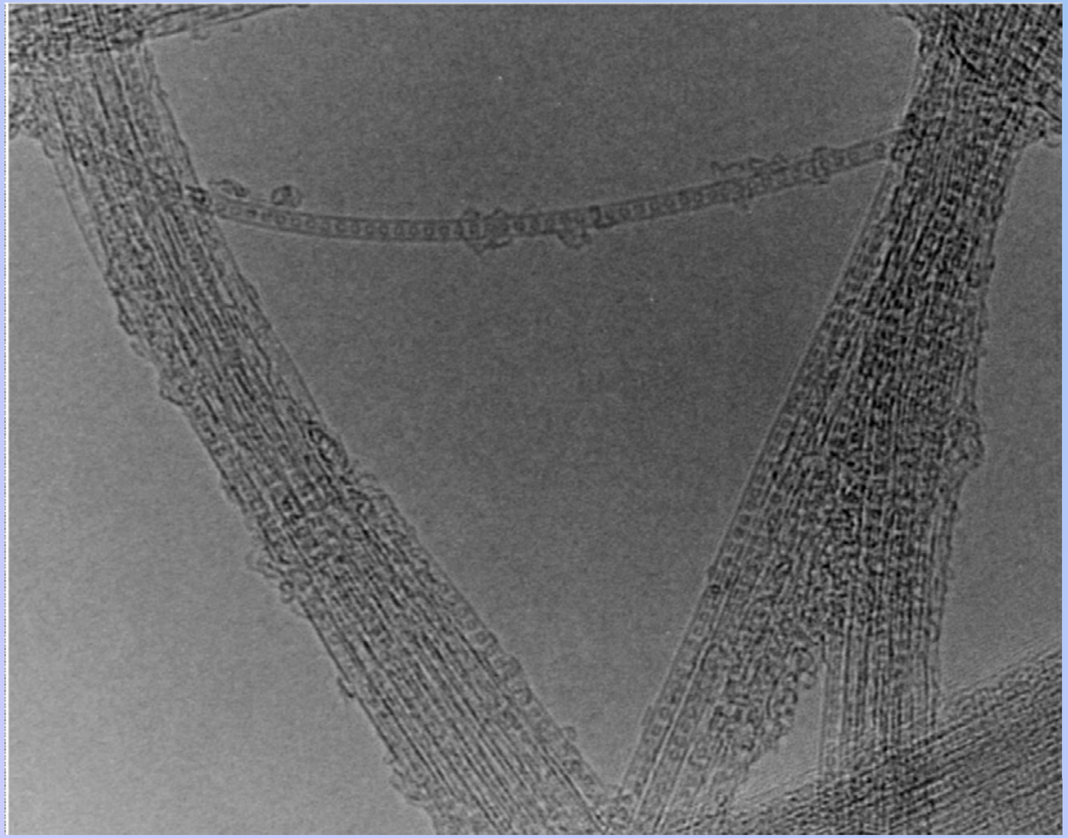
MD simulation
from S. Maruyama

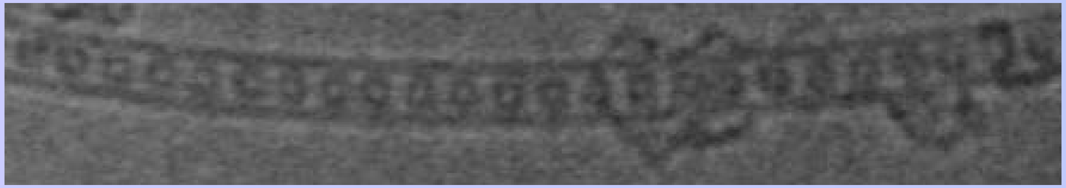
3. Iron release via defects Iron oxide nanocrystals

H. Shiozawa et al.
Adv. Mat. (2008); PRB (2008)

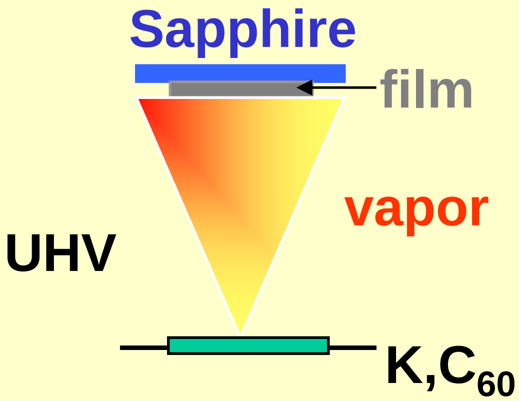
Combinational doping: Intercalation of peapods

Peapods: e.g. C_{60} filled SWCNT



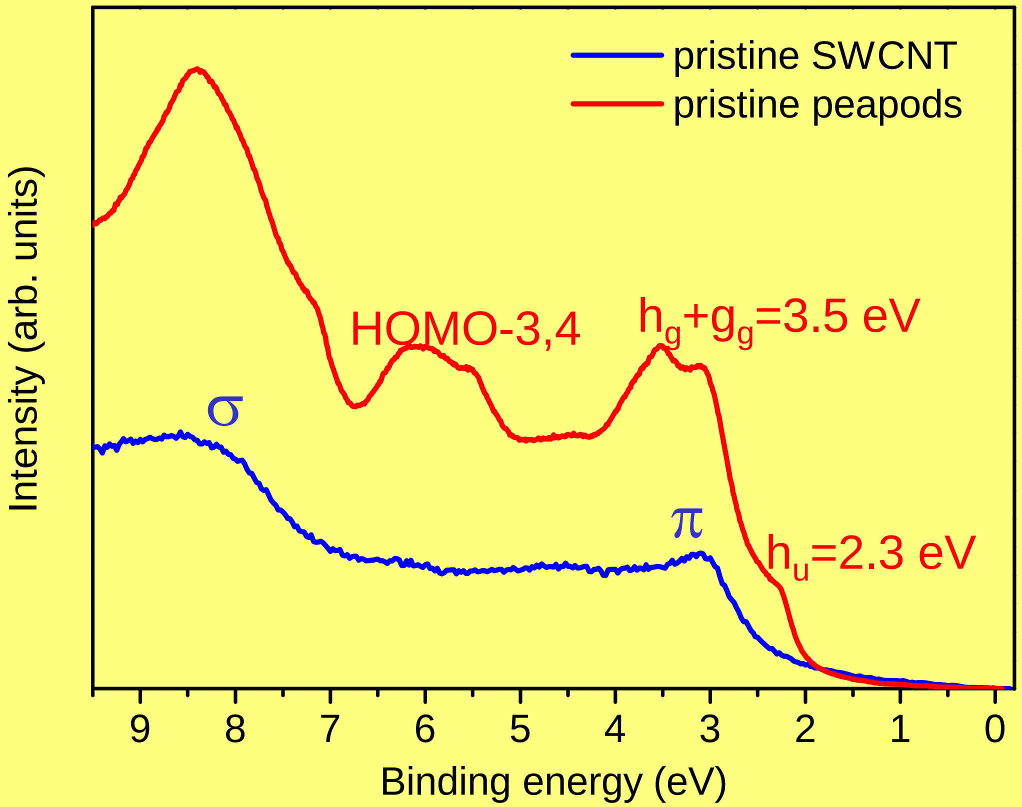


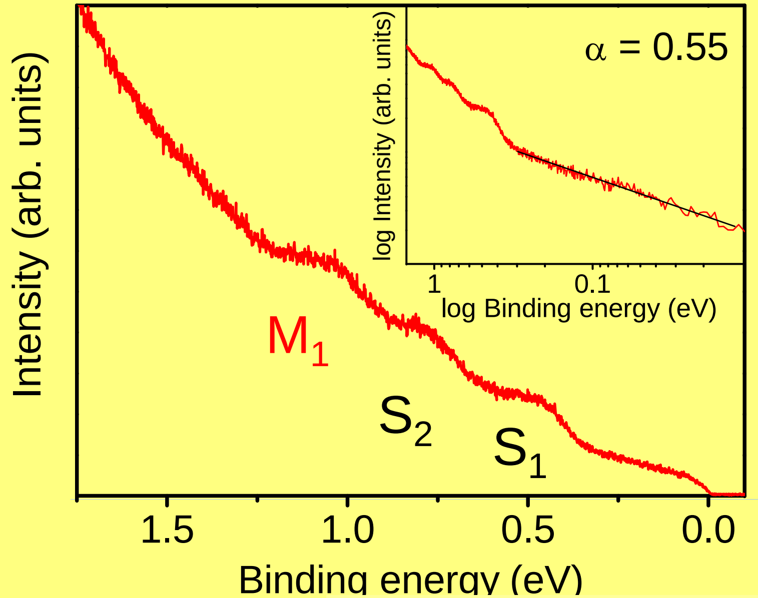
Filling/Intercalation

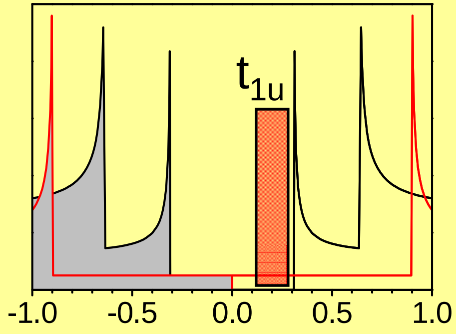


***in-situ* filling:**
UHV evaporation
($5x10^{-10}$ mbar)
K, C_{60} at 120/400 C
Equilibration 12 h
at RT/350 C
Annealing at
T=650 C

Electronic structure of C_{60} peapods







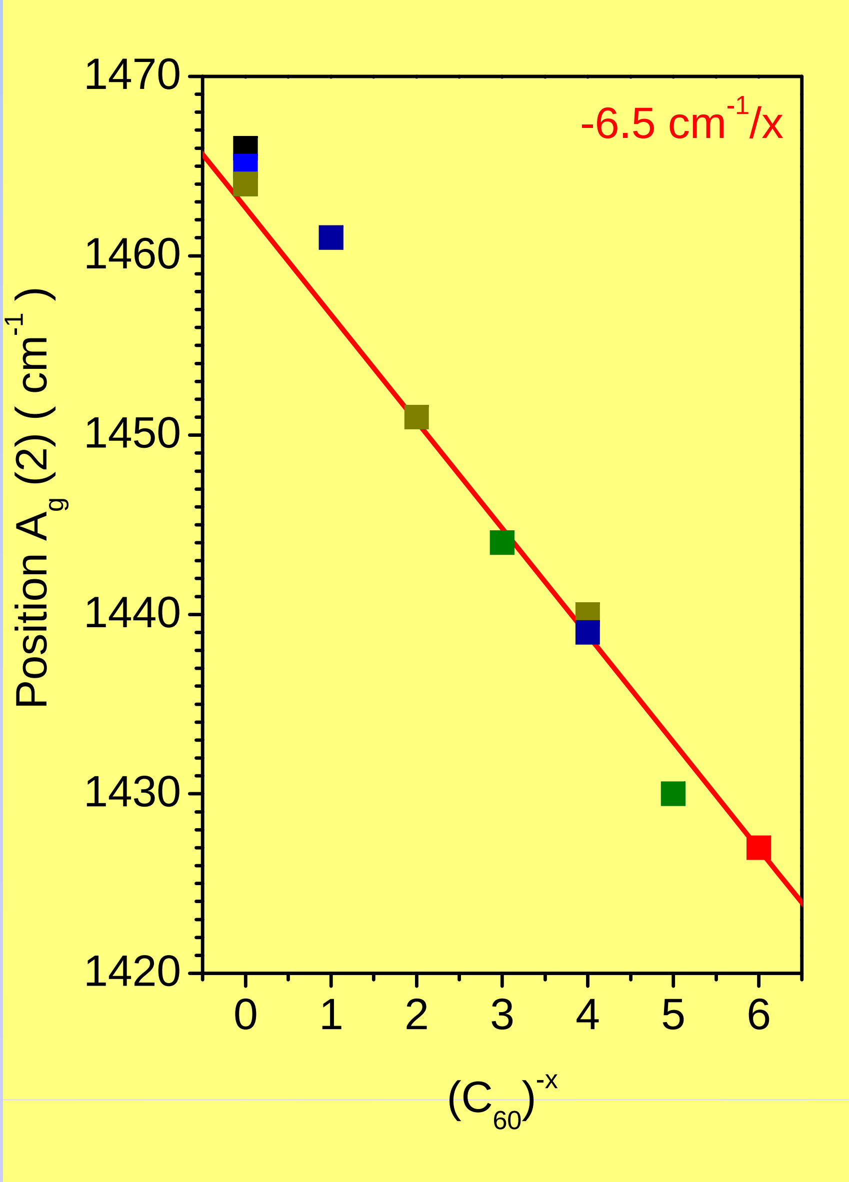
C_{60} derived molecular orbitals (Mos) observed

Binding energies as in bulk C_{60}, 100% filling

Power law α=0-48-0.55 → basically no increase !!!

H. Rauf et al., PRB 72, 245411 (2005)

Combinational doping: Intercalation of C_{60} peapods



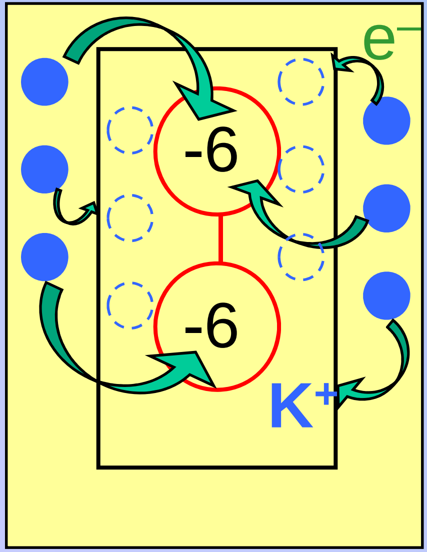
Competitive charge transfer to SWCNT and C_{60} peas !

Raman: $A_g(2)$ of C_{60}^{-x}:

- charge transfer up to C_{60}^{-6}
- no line phases:

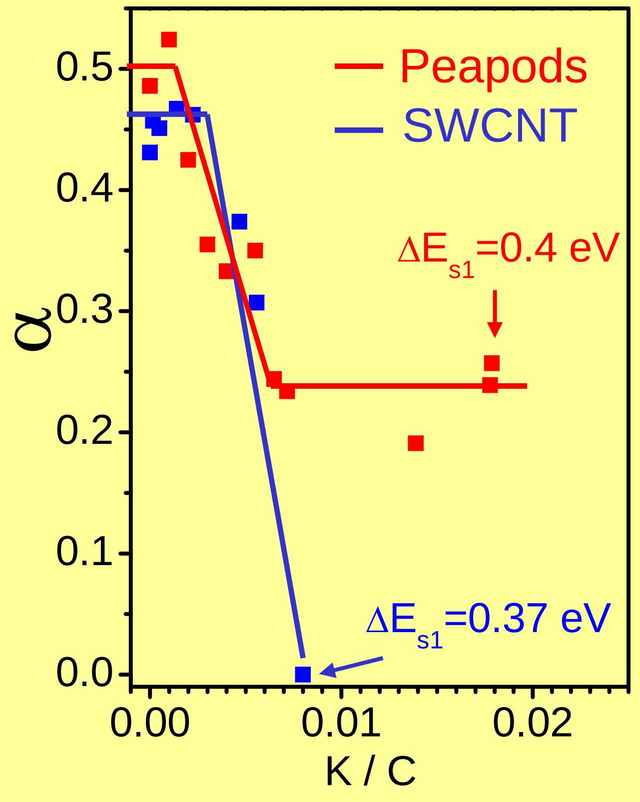
0.8 <x< 5.3 average charge transfer

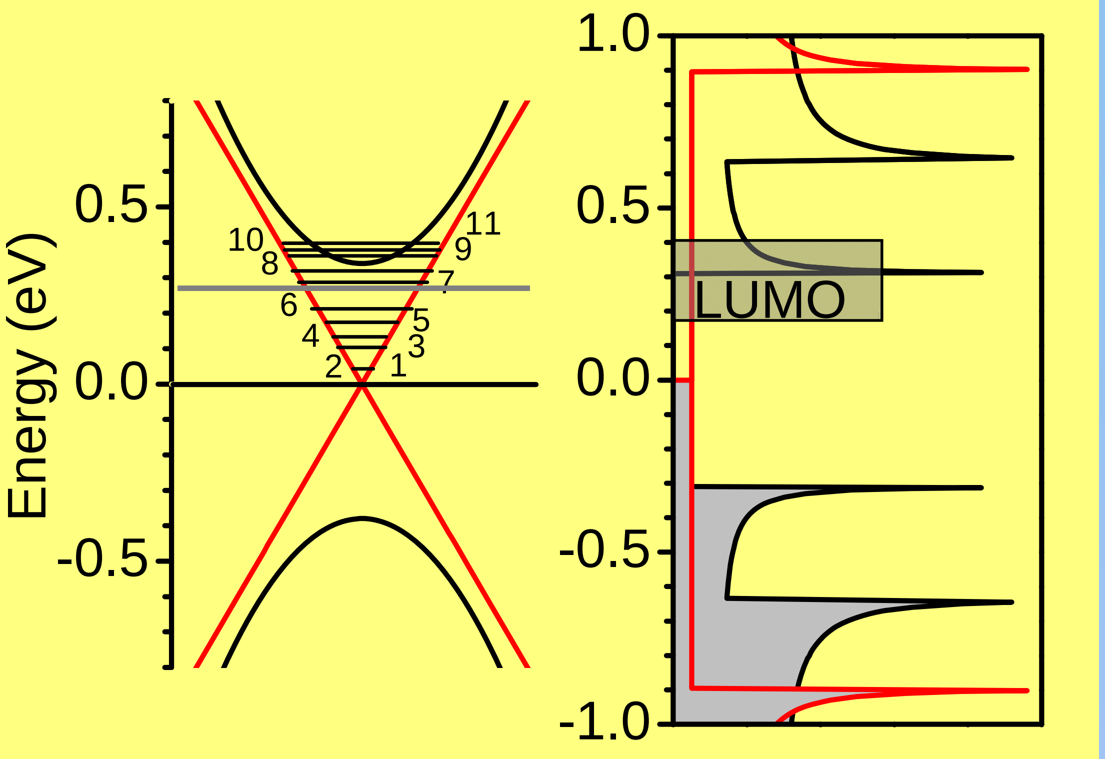
- charge transfer induced polymerization



T. Pichler et al.,
PRL 87, 267401 (2001),
PRB 67, 125416 (2003).

C$_{60}$ peapods at low doping close to E_F

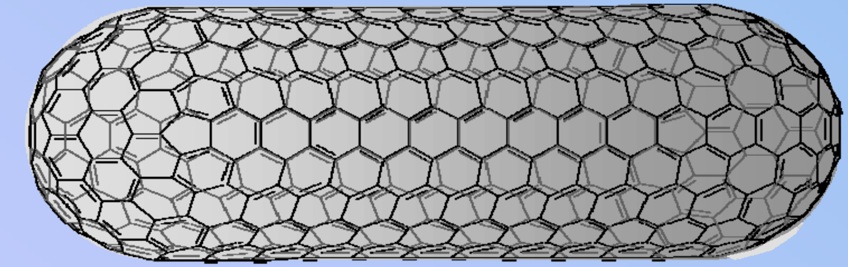




Second conduction channel in doped C$_{60}$ LUMO,
a bundle of metallic peapods is a Fermi liquid

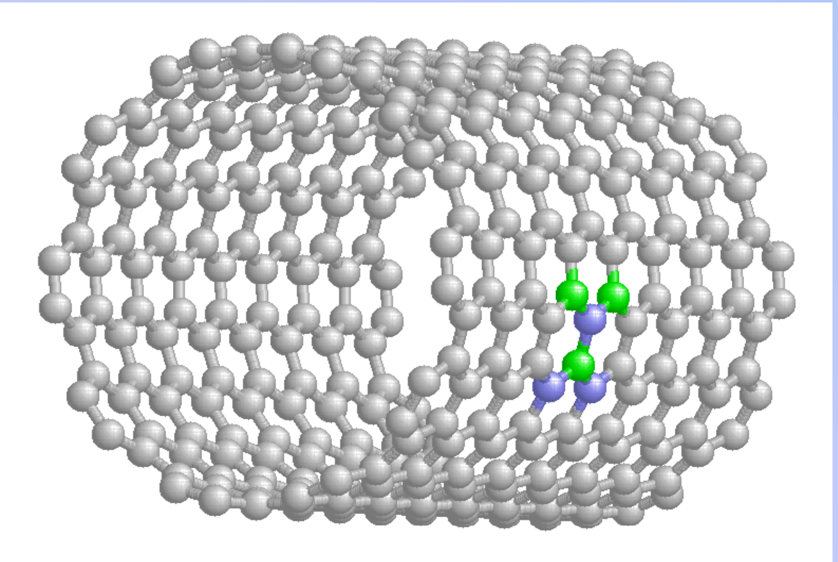
H. Rauf et al., PRL 93, 096805 (2004); PRB 72, 245411 (2005)

Substitution: Heteronanotubes



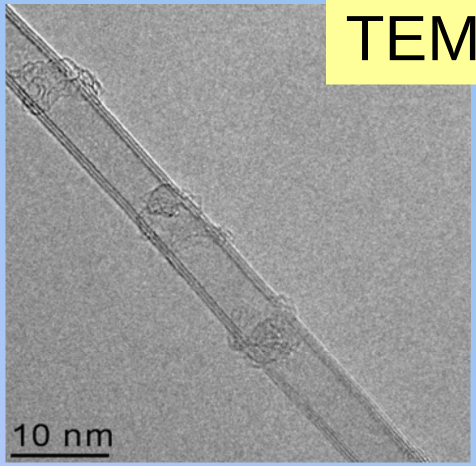
SWCNT

B,N Substitution

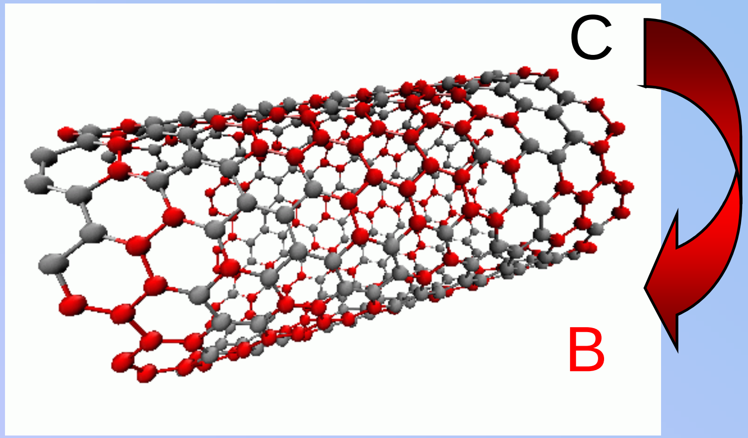


BCN-SWNT, MWBNT

TEM of DWBN-NT



B-SWNT, BC_3NT



E. Borowiak-Palen et al. Chem.Comm.1, 82 (2003), CPL, 387 , 516 (2003)
G. Fuentes et al. PRB 67, 35429 (2003), PRB 69, 245403 (2004)

Summary Part 3

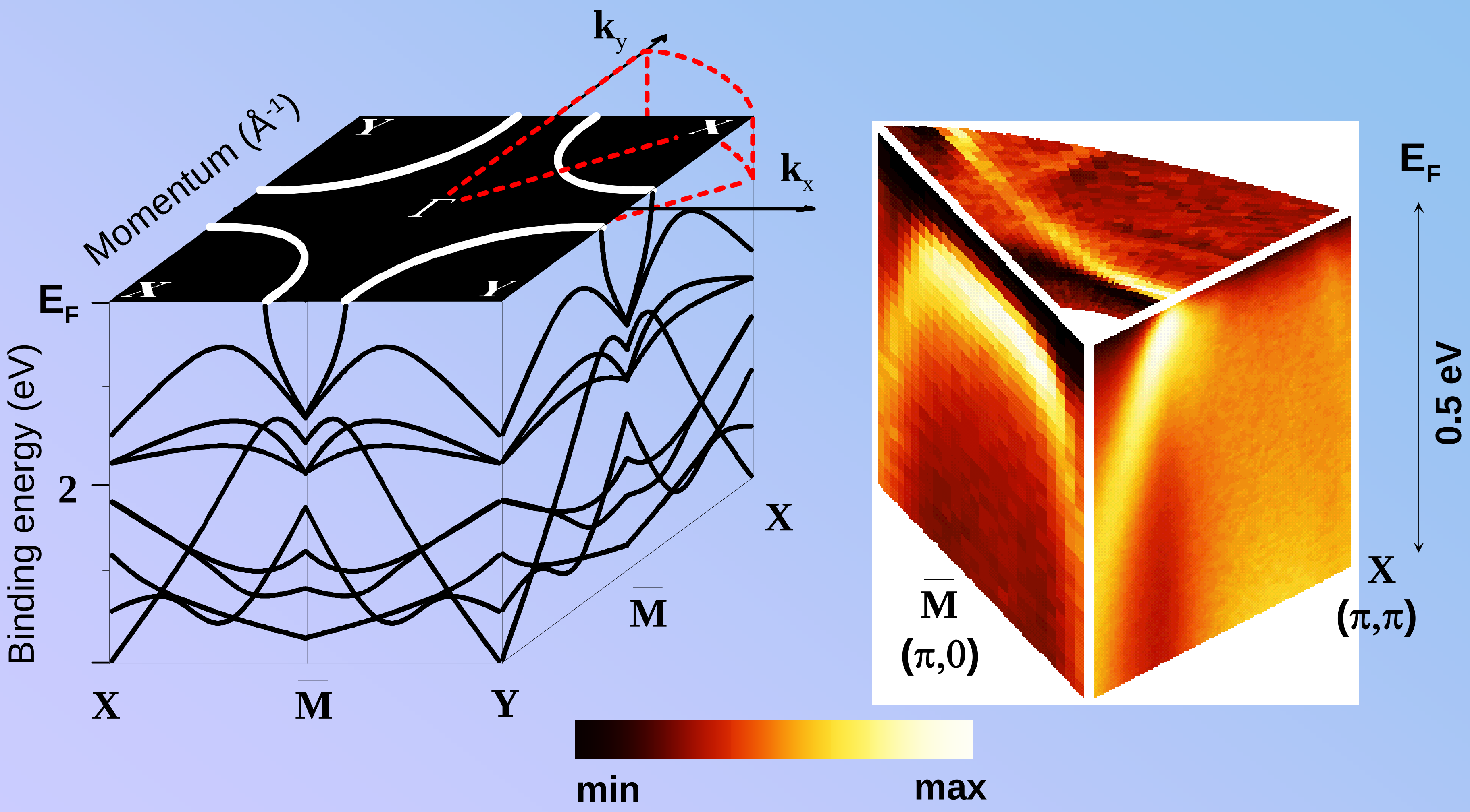
Tuning the electronic properties of SWCNT by functionalisation:

- p-, n- type intercalation of SWCNT bundles:
  - lattice expansion upon intercalation
  - direct measure of the doping level and charge carrier plasmon
  - Fermi level shift upon functionalization
  - interplay between charge transfer and hybridisation
  - Transition 1D-3D metal
- filled SWCNT, e.g. peapods:
  - bulk filling ratios, new chemistry inside a SWCNT nanoreactor
  - competitive charge transfer in intercalated peapods
  - Transition 1D-3D at higher doping compared to pristine SWCNT
- substituted SWCNT:
  - bonding environment
  - no ridged band shift upon doping
  - new BC_3 nanotubes

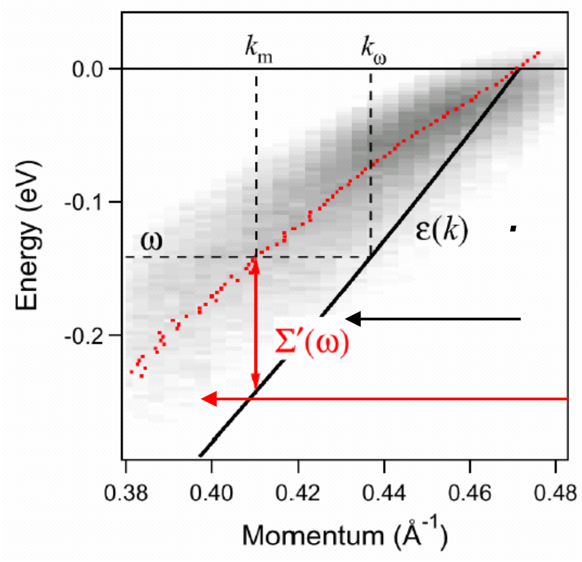
Outline

- Introduction/Motivation/Experimental
- Part 1: Angle resolved dielectric response of SWCNT
  - a) SWCNT bundles vs. individual SWCNT
  - b) Implications on excitation spectrum in 1D,2D
  - c) 1D „Drude“ plasmon in intercalated SWCNT?
- Part 2: Electronic structure of metallicity selected SWCNT
  - a) Textbook example for intrinsic XPS line shapes
  - b) Unravelling the 1D DOS in PES and XAS
  - c) Nature of metallic ground state in metallic SWCNT
- Part 3: Functionalized SWCNT:
  - a) Examples for intercalation, filling and substitution
  - b) Nanochemical reactions inside SWCNT
- Part 4: Electronic and phononic structure of graphene systems
  - a) Electron dispersion, phonon dispersion and EPC
  - b) GIC KC_8 revisited: A key to graphene
- Summary and outlook

ARPES: Experimental momentum-energy space „cake“

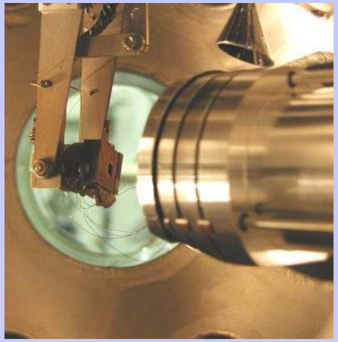


ARPES measures quasiparticle dispersion



Bare band dispersion

Quasiparticle dispersion



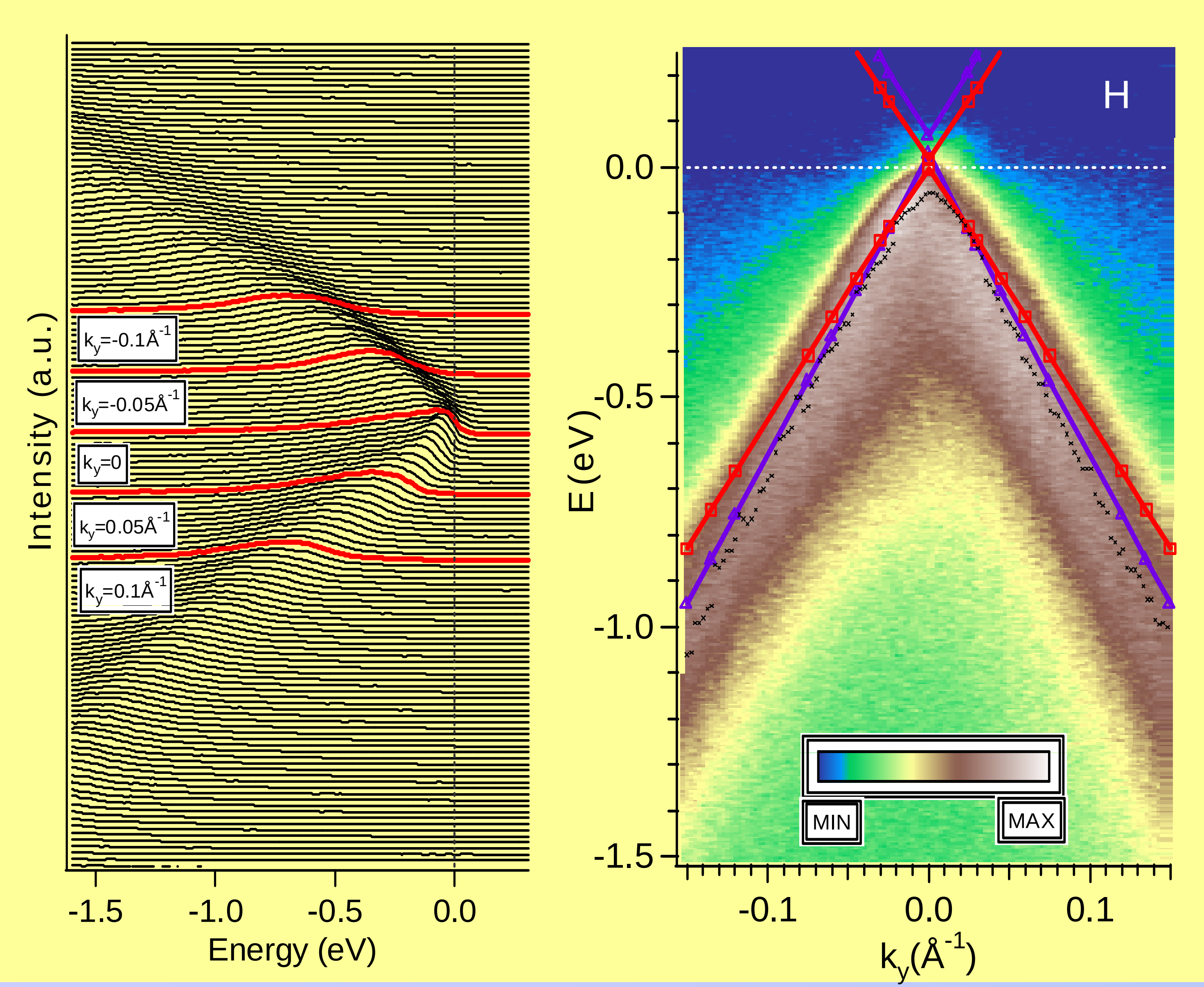
Single particle spectral function:

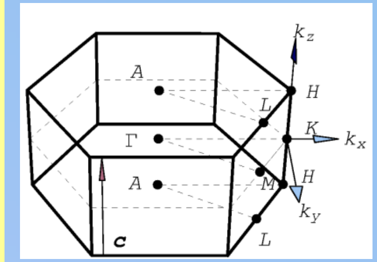
$$A(\mathbf{k},\omega) = \frac{\left|\operatorname{Im}\Sigma(\mathbf{k},\omega)\right|}{\left(\omega - \omega_b(\mathbf{k}) - \operatorname{Re}\Sigma(\mathbf{k},\omega)\right)^2 + \left(\operatorname{Im}\Sigma(\mathbf{k},\omega)\right)^2}$$

Self energy correction Σ depends on:

Electron-phonon, electron-plasmon,
electron-electron interactions,..

Electron-electron correlation in graphite





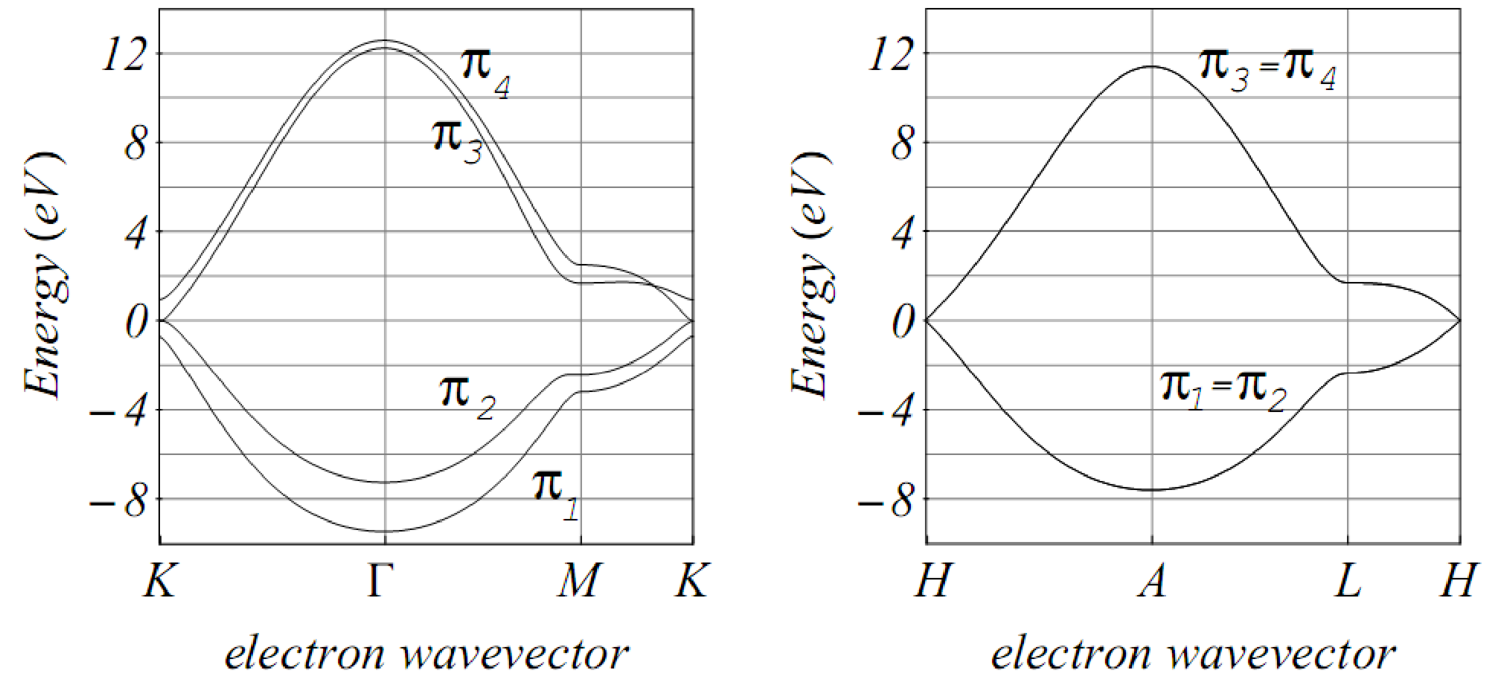
RED=LDA

BLUE=GW

BLACK DOTS
=MAX

A.Grüneis et al. Phys. Rev. Lett. 100, 037601 (2008)

K,H Point: New 3NN neighbor TB fit to GW



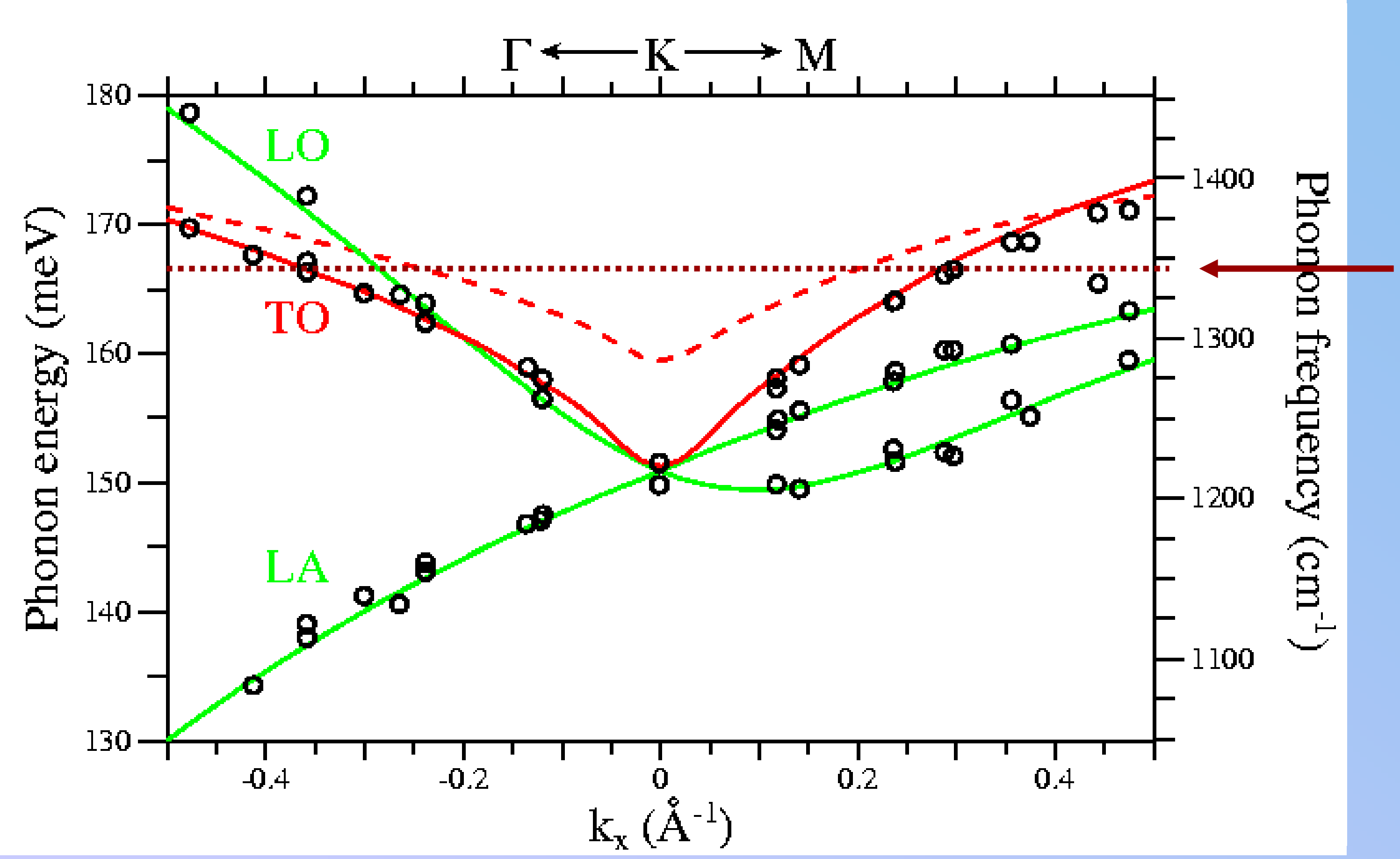
Method	γ_0'	γ_1'	γ_2'	γ_3'	γ_4'	γ_5'	E_0'	Δ'
TB-GW[a]	3.053	0.403	-0.025	0.274	0.143	0.030	-0.025	-0.005[b]
TB-LDA[a]	2.553	0.343	-0.018	0.180	0.173	0.018	-0.022	-0.018
EXP[c]	3.16	0.39	-0.02	0.315	0.044	0.038	-0.024	-0.008
LDA[d]	2.598	0.364	-0.014	0.319	0.177	0.036	-0.026	-0.013
EXP[e]	2.9	0.3	-	0.1	0.12	-	-	
KKR[f]	2.92	0.27	-0.022	0.15	0.10	0.0063	0.0079	-0.027

Point	Method	π_1	π_2	π_3	π_4
Γ	*GW*	-9.458	-7.257	12.176	12.541
	TB-*GW*	-9.457	-7.258	12.184	12.540
M	*GW*	-3.232	-2.441	1.655	2.491
	TB-*GW*	-3.216	-2.457	1.656	2.495
K	*GW*	-0.736	-0.025	-0.025	0.917
	TB-*GW*	-0.728	-0.024	-0.024	0.909
H	*GW*	0.020	0.020	0.025	0.025
	TB-*GW*	0.020	0.020	0.025	0.025

Very good agreement of the GW QP band structure to experiment

A. Grüneis et. al., PRB 78, 205425 (2008)

Assignment of the coupling phonons by IXS

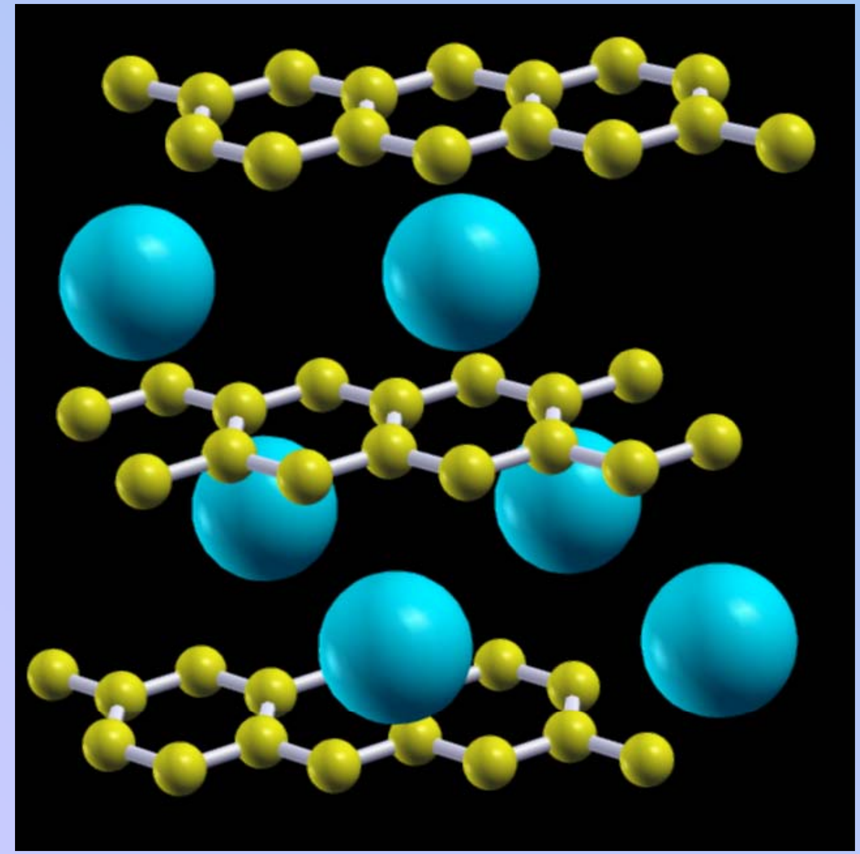


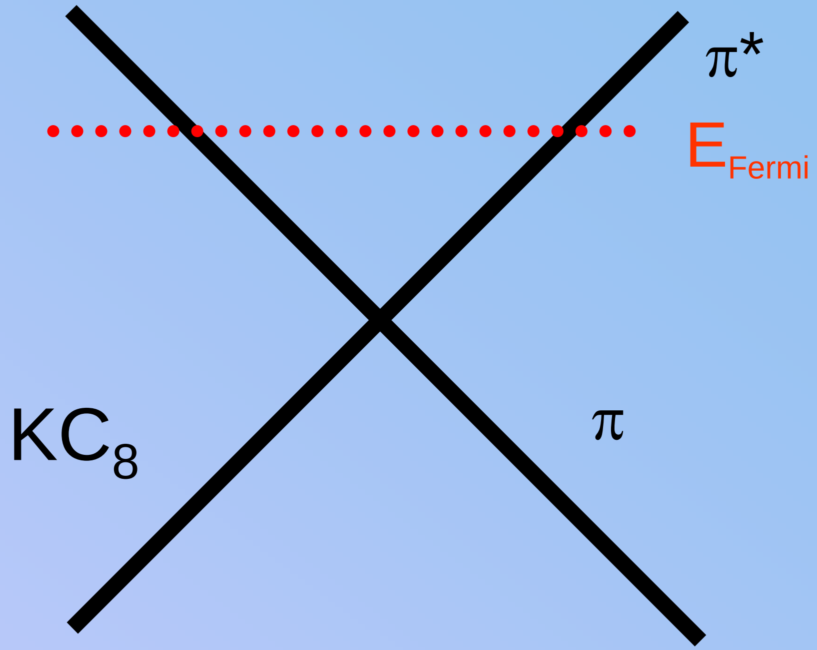
ARPES kink

First unambigous assignment of the TO/LO/LA branches,
Kohn anomaly at K using IXS.
First purely experimental EPC 166 (eV/A)^2

A.Grüneis et al. cond. mat. arXiv:0904.3205

KC_8 revisited: Interlayer decoupling by intercalation





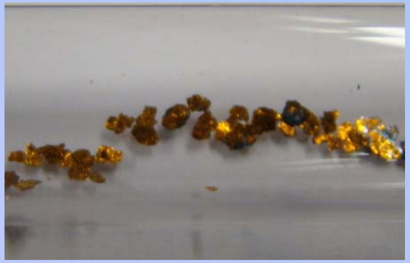
1) Interlayer distance increases from 0.335 nm to 0.535 nm.

2) Charge traransfer K 4s to C π

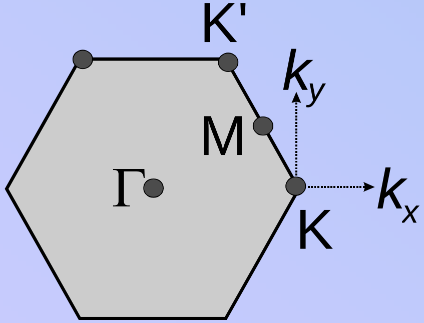
3) First description by 2x2 Hamiltonian from Blinkowski.

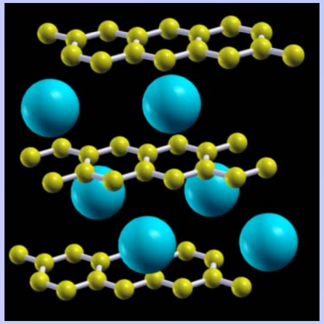
(J. Blinowski, N.H Nguyen, Rigaux, C., Vieren, J.-P., J. Phys. 41,47 (1980))

ARPES of KC$_8$ revisited

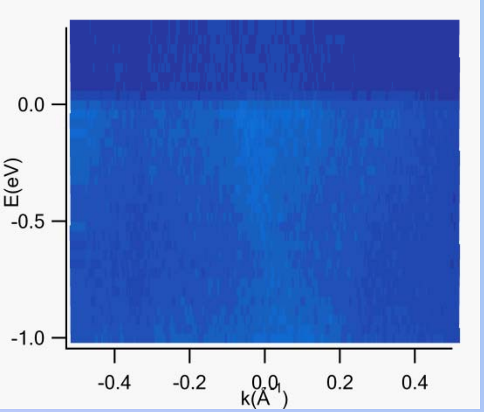


Golden KC$_8$.

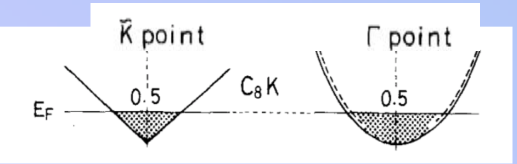




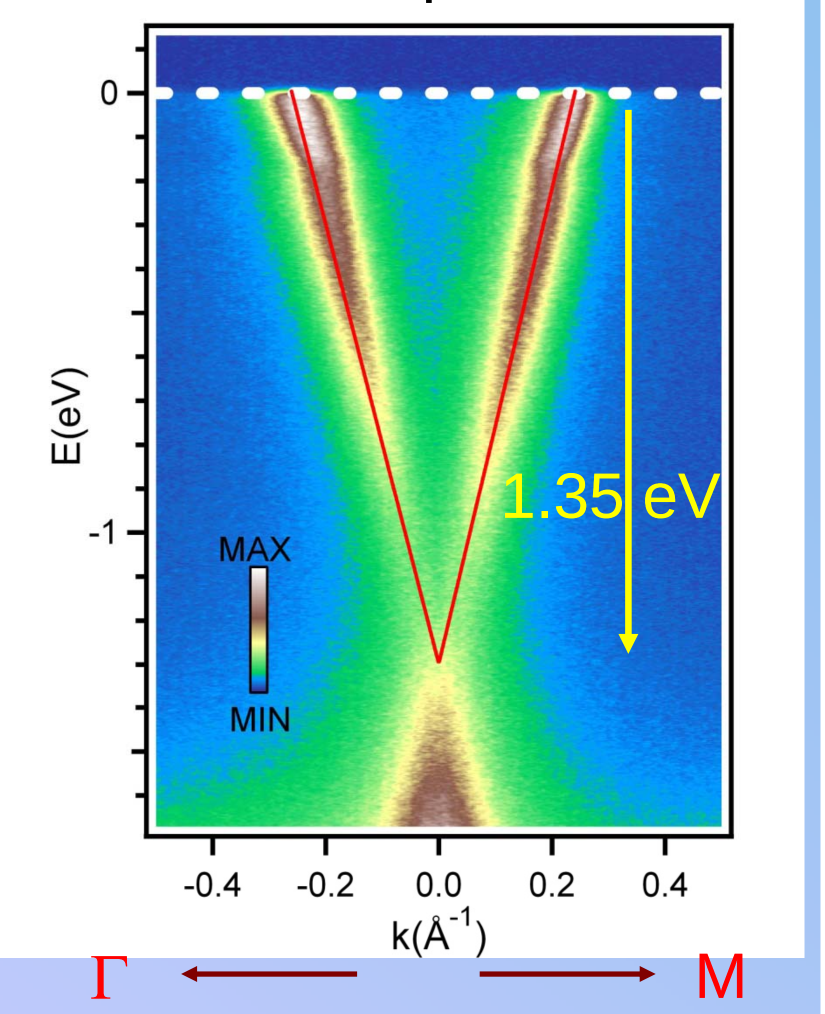
Γ point



Ionic charge transfer:
No 4*s*-like band

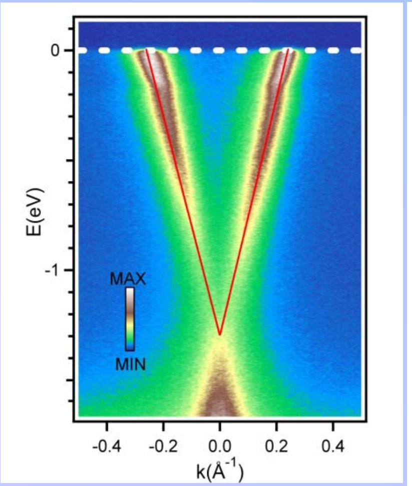


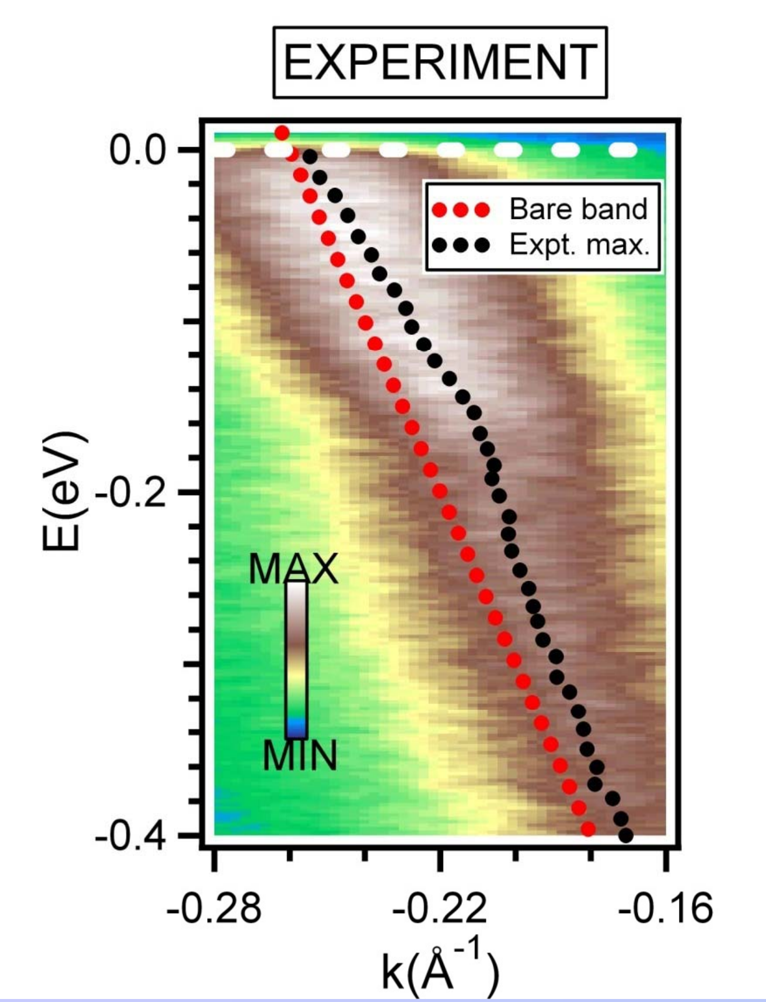
K point

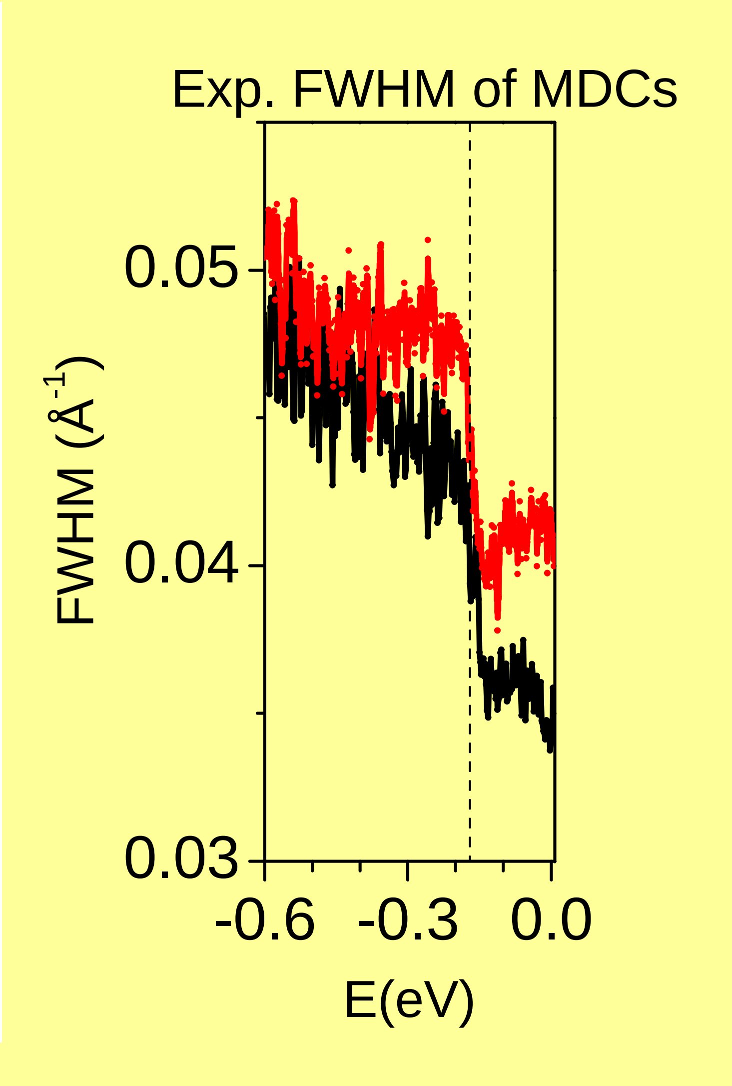


- Kink in QP dispersion at 166 meV
  → coupling to a bosonic mode
- Dirac point shifts by 1.35 eV: linear dispersion of Dirac Fermions

Self consistent self-energy analysis of the „kink“



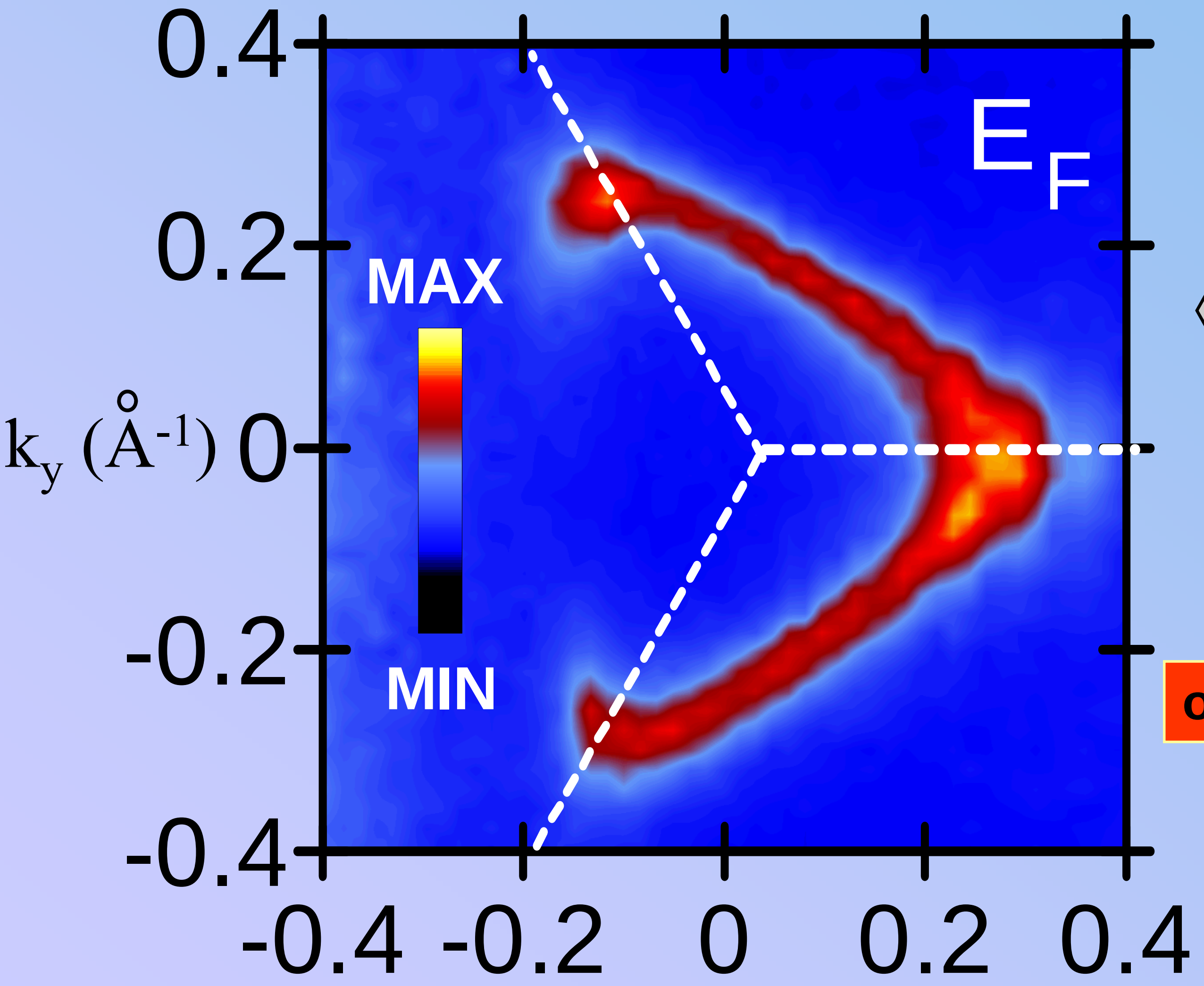


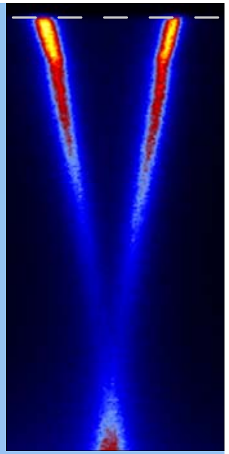


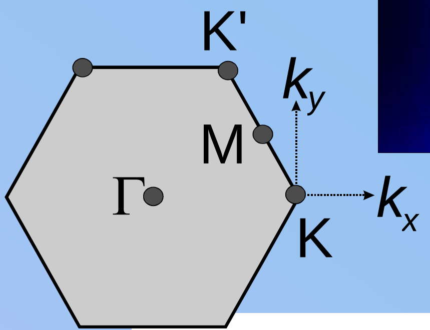
1) Strong el-ph. coupling to TO phonon at K point at 166 meV
2) Direction dependent el-ph coupling constant 0.3-0.6.

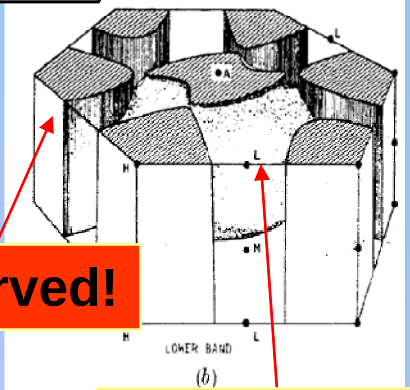
A. Grüneis et al. PRB 79, 205106 (2009)

Fermi surface of KC_8









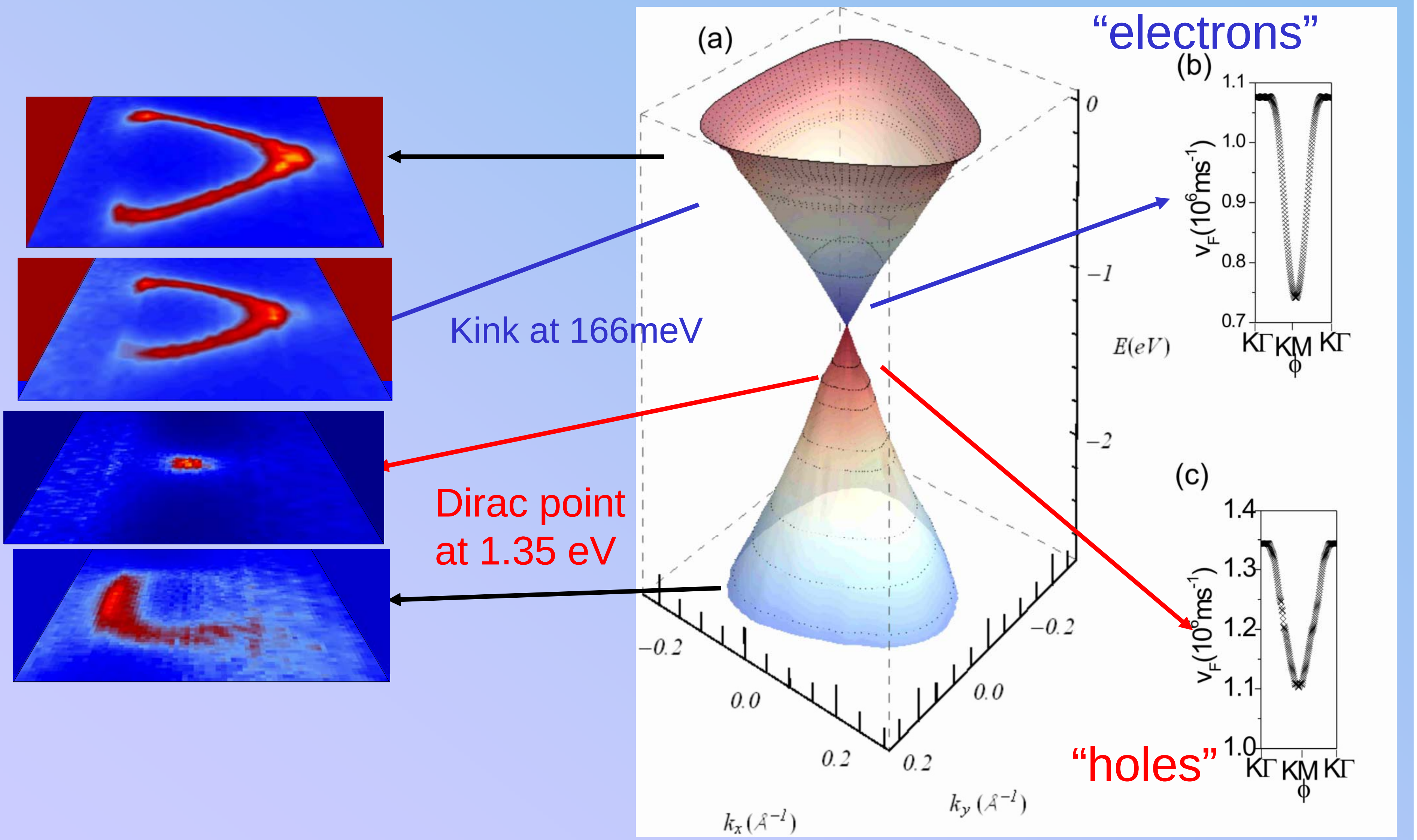
observed!

Not observed!

1) Fermi surface only around K point.

2) n=**7 x 10 ^{21}** electrons per cm^3.

Experimental Dirac cone and Fermi velocities of doped graphene



“electrons”

Kink at 166meV

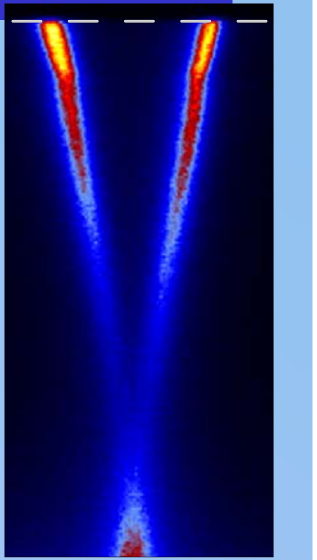
Dirac point
at 1.35 eV

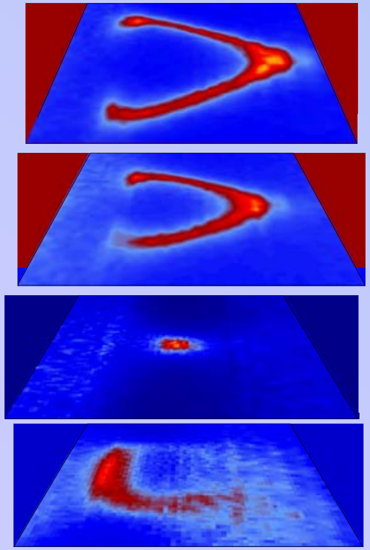
“holes”

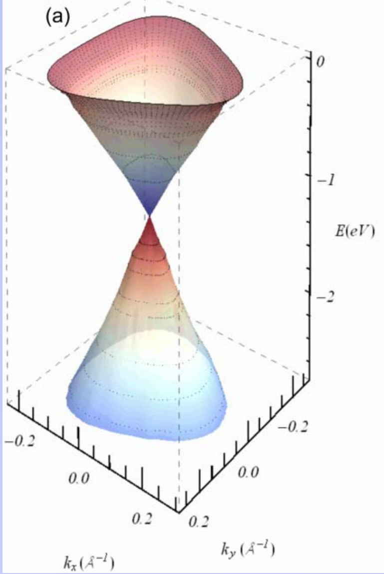
A. Grüneis et. al., cond-mat. arXiv:0808.161; cond-matt. arXiv:0808.1467

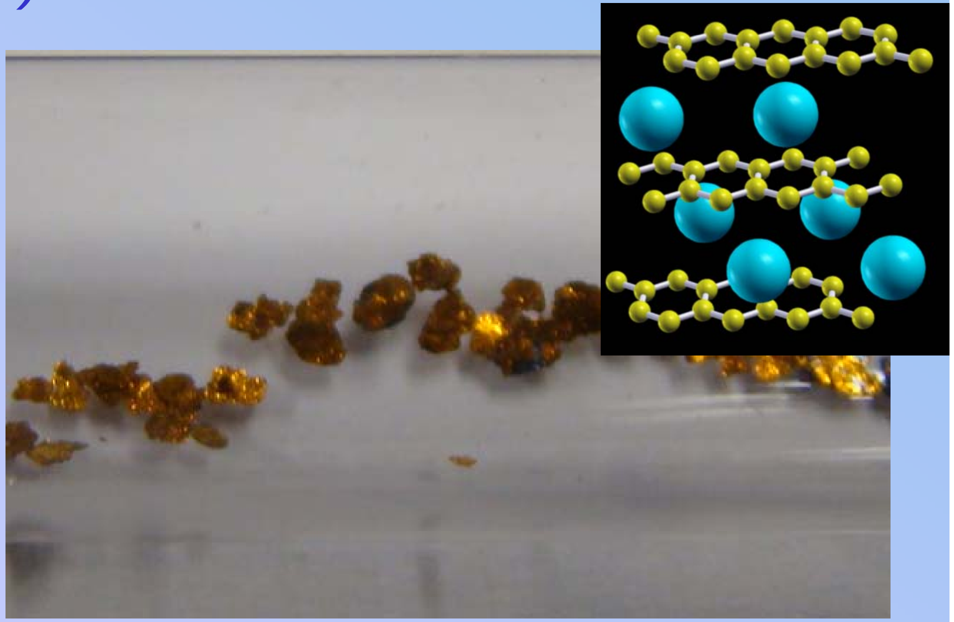
Summary Part 3:

- **Gain from GIC KC_8**
  1.Charge transfer is completely ionic AA stacking and decoupled layers
  2. ***K*** point TO phonon at 166 meV mediates superconductivity.
  3. ***Purely experimental Dirac cone!***
- ***Gain from Graphite IXS, ARPES:***
  1. el.el. Correlations important
  2. optical K *point phonons disentangled*
  3. experimental EPC=166 $(eV/A)^2$









A. Grüneis et. al., cond-mat. arXiv:0808.161; cond-mat. arXiv:0808.1467
C. Attaccalite et al. cond-mat. arXiv:0808.0786, PRB 78, 205425 (2009)

Outlook some open problems

- Low dimensional carbon systems:

  - The role of instabilities in 0D, 1D, 2D systems:
    - Mechanical stability of low D systems
    - Growth of low D systems
    - Chemistry inside 1D and 2D confinement
  - The role of basic correlation effects:
    - Electron-phonon (e.g. superconductivity)
    - Electron-electron (e.g. quasiparticle dispersion, TLL)
    - Electron-hole (e.g. Exciton, size, life time, binding energy)
    - Spin-spin (e.g. spin coherence, spin lifetimes in 1D)
  - Tunable electronic and optical properties:
    - Key to engineer new molecular solids with novel electronic transport, optical, and magnetic properties
    - Interplay charge transfer vs. hybridization in functionalized metallicity selected SWCNT
    - Nanochemistry inside metallicity selected SWCNT…..

New research group
in Vienna:

**LOW DIMENSIONAL
QUANTUM SOLIDS**

The beauty of instabilities…!!!

WANTED: *PhD student, postdoc eager to unravel the equilibrium ground state dressed by correlations……!*

Summary

- SWCNT are truly 1D regarding optical response:
  - 1D on axis Plasmons: linear dispersion
  - Nondispersive surface plasmon at circumference
  - Charge carrier Plasmon: Non-dispersive, not acustic??

    Implications for all metallic 1D,2D systems
- Metallicity selected SWCNT:
  - Truly 1D, vHs, Tomonaga-Luttinger liquid
  - Very good agreement to diameter cumulative DOS
  - Key to understand interactions in functionalized SWCNT

    Interplay between charge transfer and hybridization
- Electronic and vibronic structure of graphene systems:
  - Electron-Electron interaction important in graphene
  - Disentangeled quasidegenerate TO, LA, LO at K point.
  - Purely experimental EPC = 166 (eV/A)^2
  - Fully experimental Dirac cone!
  - TO branch couples in GIC! Implications for sc?