SPECTROSCOPY OF 1D MATERIALS IN SINGLE-WALLED CARBON NANOTUBES

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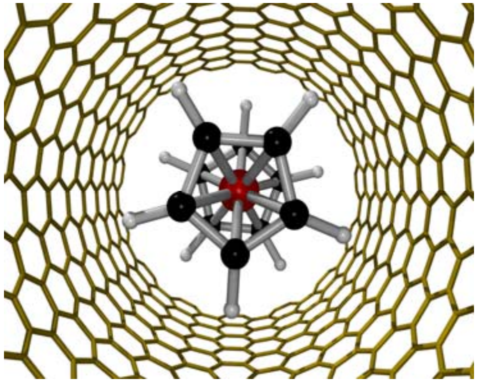
Content

THE SQUEEZED SPACE INSIDE
Filling the tubes

MAGNETIC PEAPODS
ESR, rotor state,
tuning the pea distance

DOUBLE-WALLED CNTs:
Pair spectra, catalytic growth

^{13}C SWCNT: NMR, spin gap,
Tomonaga-Luttinger behavior



$FeCp_2$@(10,10)

Co-operations

U Wien
TU Budapest
Oxford U
IFW Dresden
AIST Tsukuba
U Erlangen
U Paris Sud
MPI Dresden
U Sofia
U Bologna

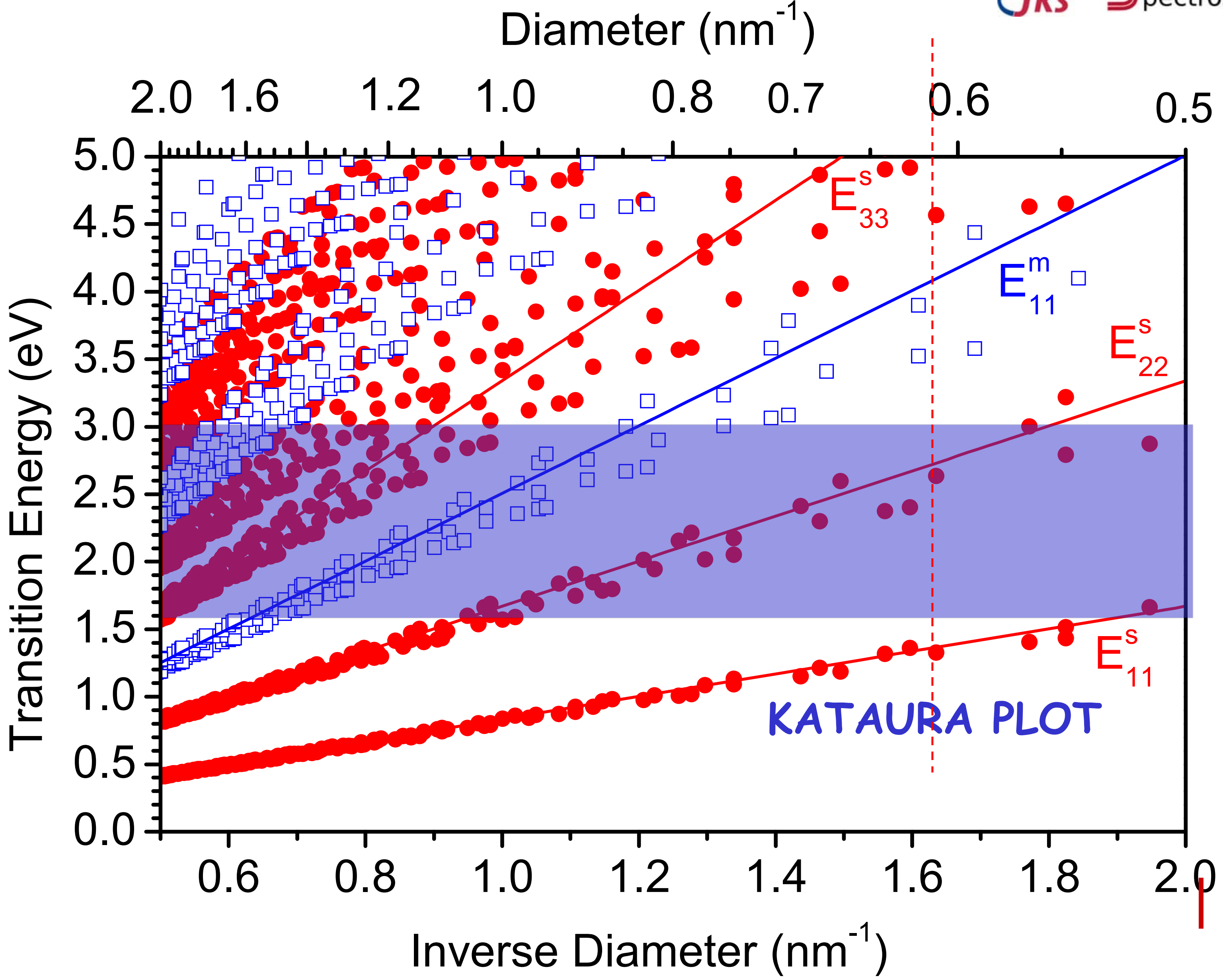
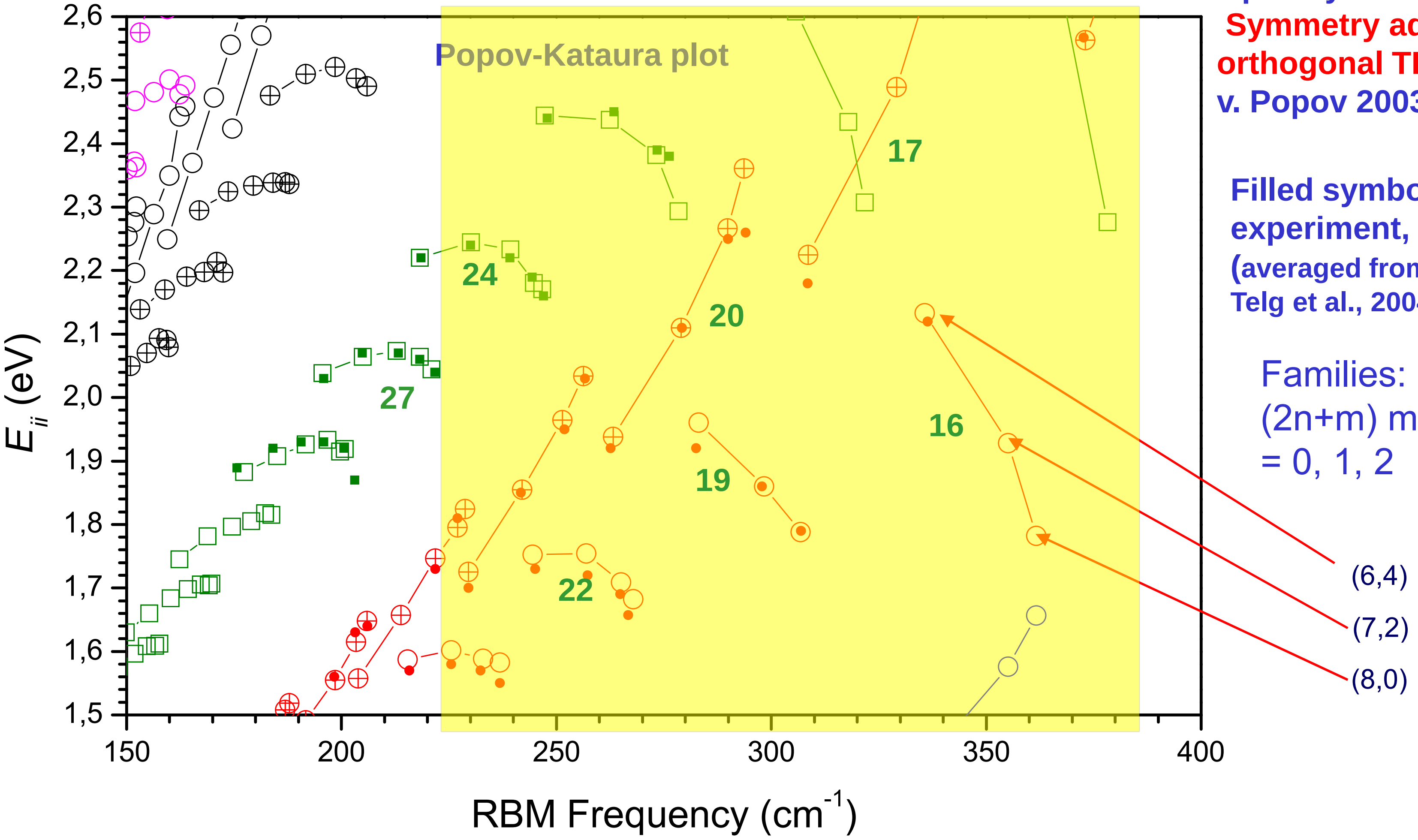

Diameter (nm^{-1})
2.0
1.6
1.2
1.0
0.8
0.7
0.6
0.5
Transition Energy (eV)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
E^s_{33}
E^m_{11}
E^s_{22}
E^s_{11}
KATAURA PLOT
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Inverse Diameter (nm^{-1})

Fig. 6.12

The squeezed space inside

FAMILY BEHAVIOR FOR RBM RAMAN RESONANCES



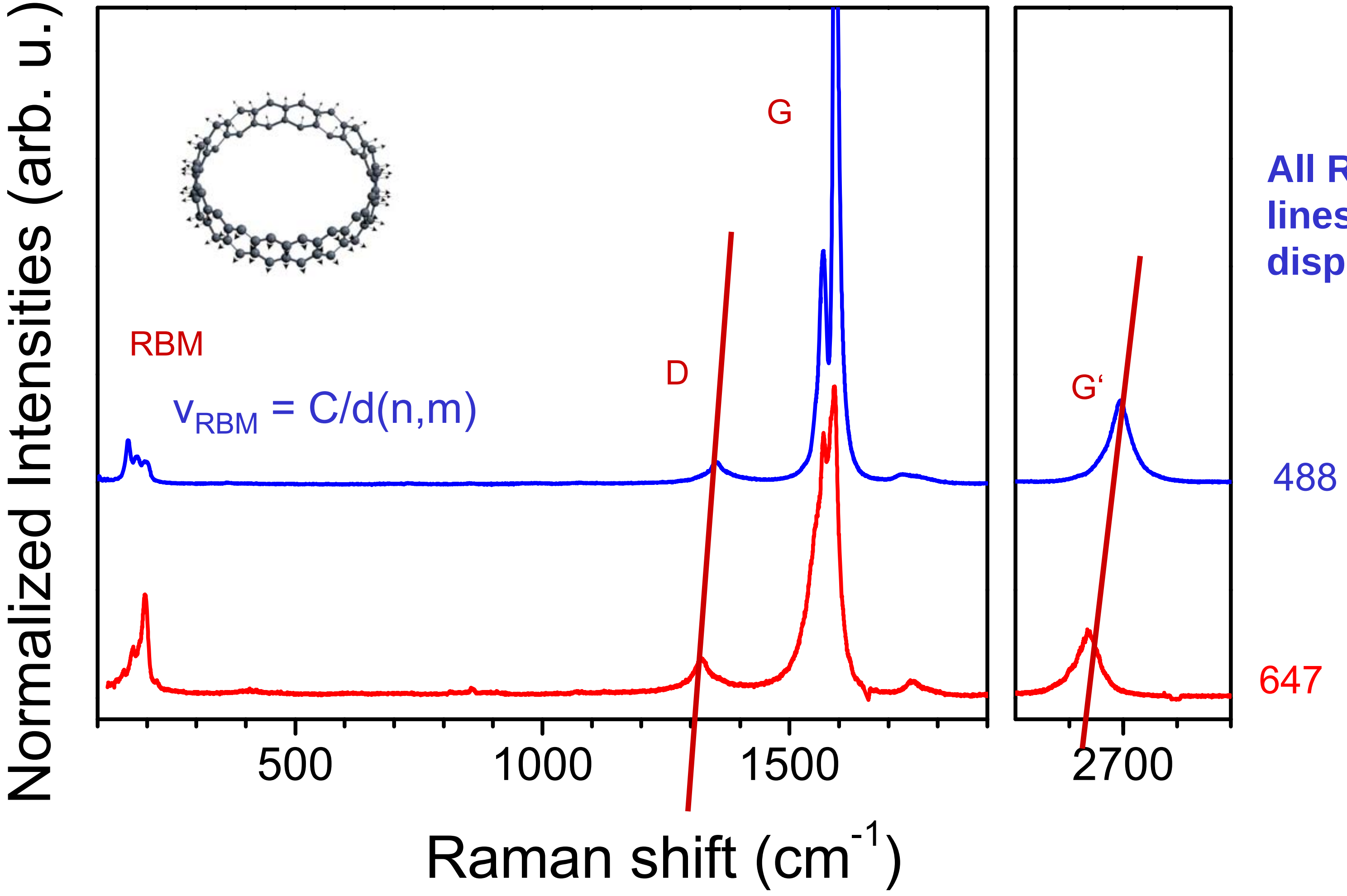
Open symbols:
Symmetry adapted non orthogonal TB
v. Popov 2003 +corrections

Filled symbols: experiment, HiPco (averaged from Fantini et al., Telg et al., 2004)

Families:
(2n+m) mod 3
= 0, 1, 2

RAMAN SCATTERING FROM SWCNTs

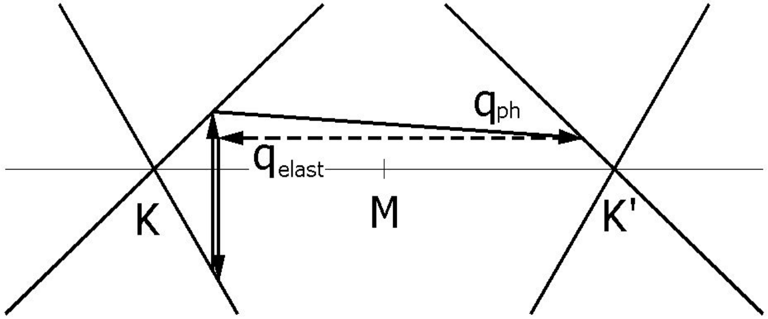
14 Raman active modes (8 for zig-zag, armchair)



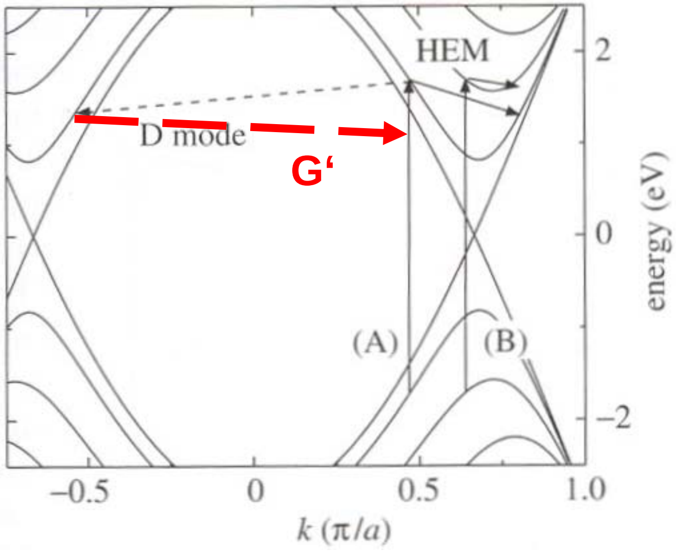
All Raman lines disperse!

DOUBLE RESONANCE SCATTERING FOR D-LINE AND G'-LINE

Double resonance for graphite

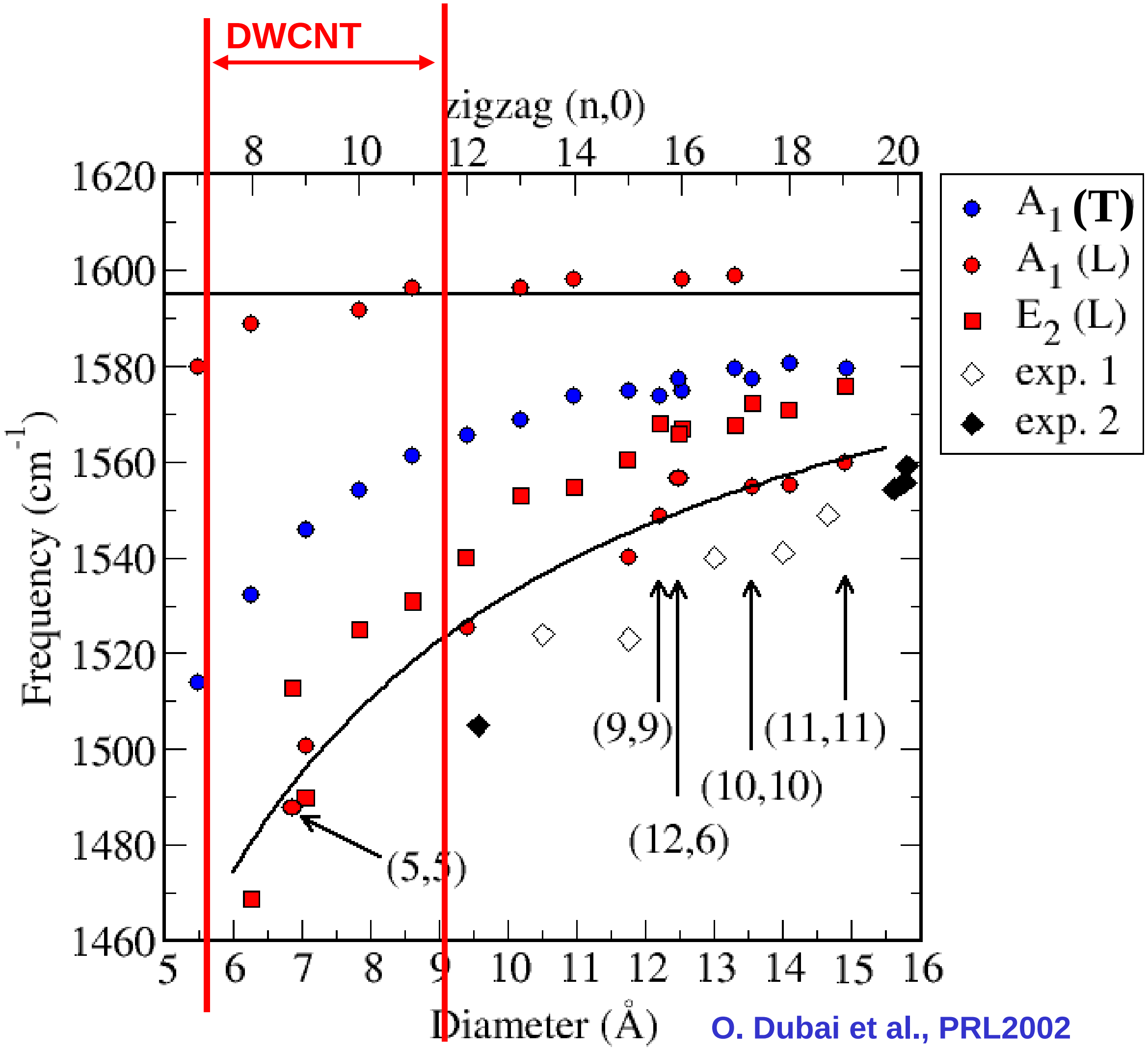


Triple resonance for nanotubes



DISPERSION OF G-LINES

Vienna **A**b initio **S**imulation **P**ackage, VASP



O. Dubai et al., PRL2002

Disp

Filling SWCNTs

FILLING SINGLE_WALLED CARBON NANOTUBES

A Opening the tubes

exposure to air at 450-650 0C, 2 h
re-closing is possible by heating in vacuum at 800 0C, 6 h

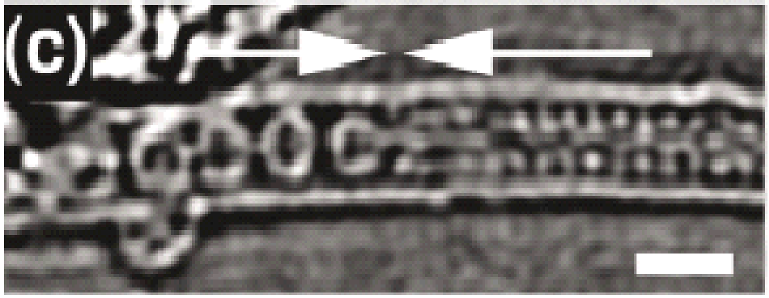
B The filling processes

Filling from	**Process characterization**	**Examples**
Vapour phase	Clean but thermal stability of filler is required	C60, C70, metallofullerenes
Liquid phase (melt)	Simple if melt exists Medium filling temperature	Alkali halides, ferrocene
(Solution)	Low temperature but solvent may also enter	Fullerenes, N@C60, C59N
Supercritical CO_2	Clean, low filling temperature but needs special equipment to handle sc CO_2 , long filling times	Functionalized fullerenes

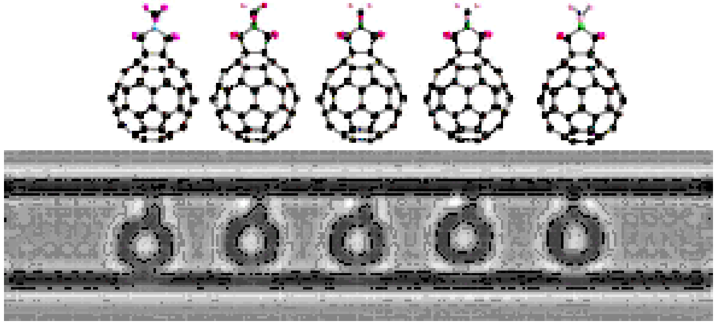
1D MATERIALS @ SWCNTs

Classical peapod

Hybride filling: C60-FeI$_2$

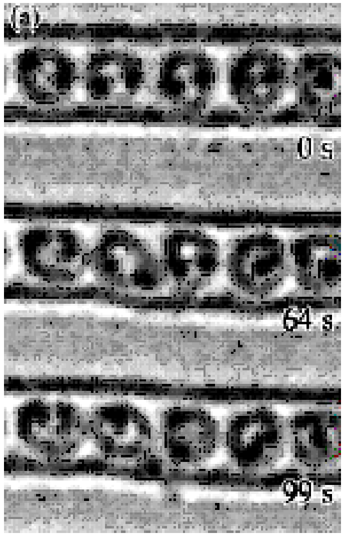


J. Sloan (2002)



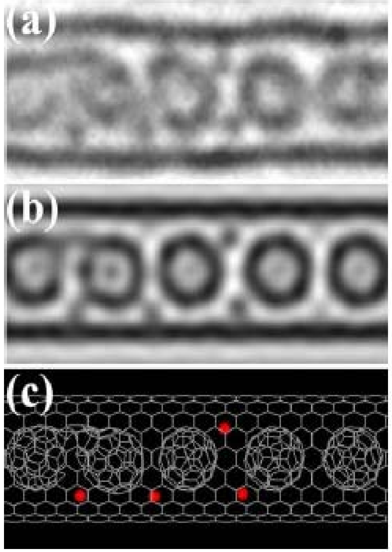
K. Suenaga IWEP2006

Metallofullerenes

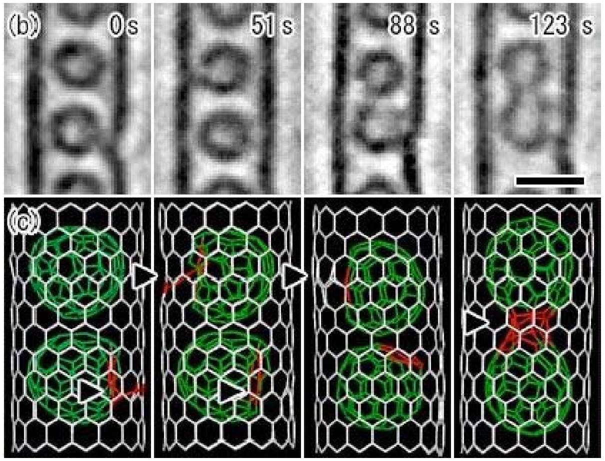


T. Okazaki (2005)

Doped Peapod



S. Iijima (2004)

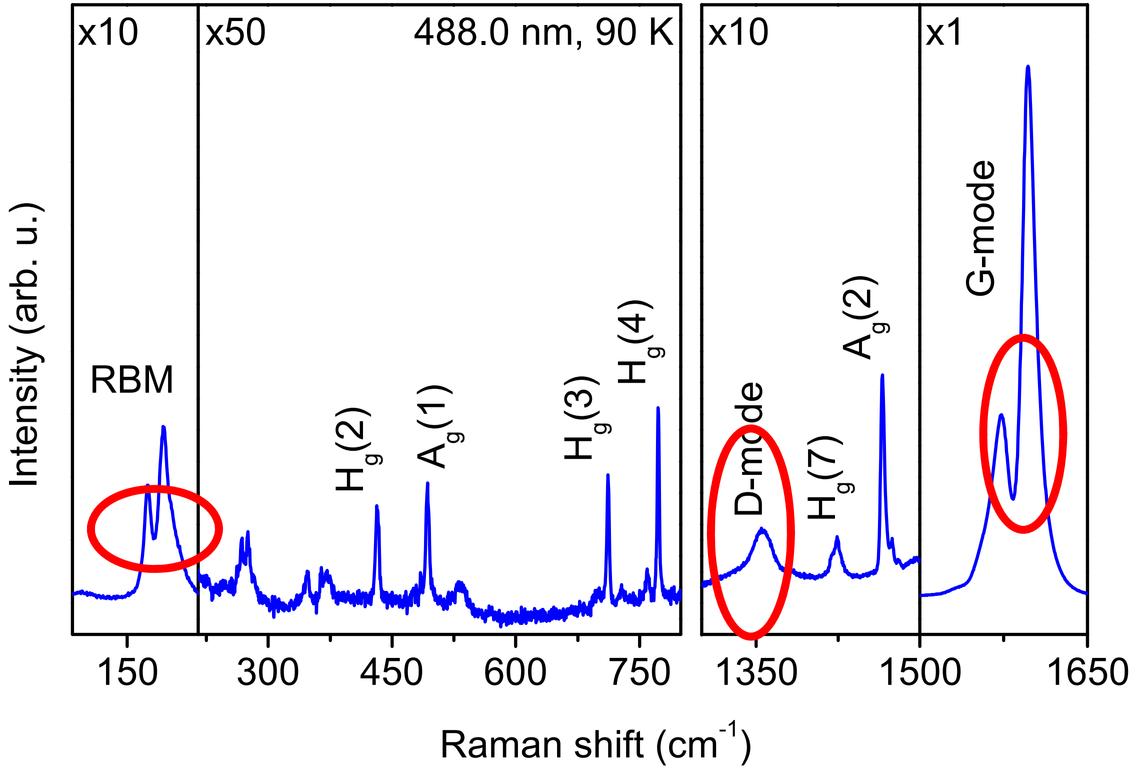


K. Suenaga
WONTON
2005

Fig.6.32

EXPERIMENTAL OBSERVATION OF PEAPODS

Raman scattering



Filling with magnetic peapods (N@C_{60}, C_{59}N)

Transformation to DWCNT

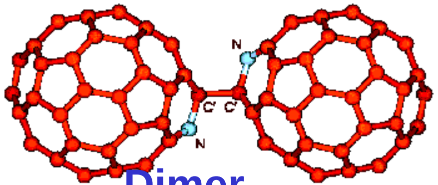
R. Pfeiffer, 2003

Fig. 6.31

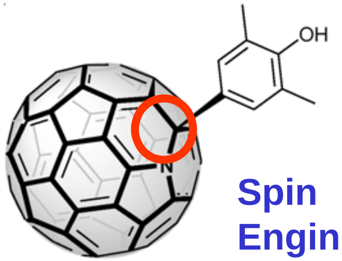
Magnetic peapods

LINEAR SPIN CHAINS WITH $C_{59}N$@SWCNTs

for $C_{59}N$:
S=1/2
I = 1

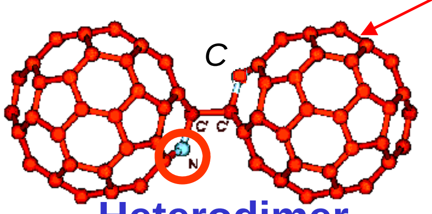


Dimer

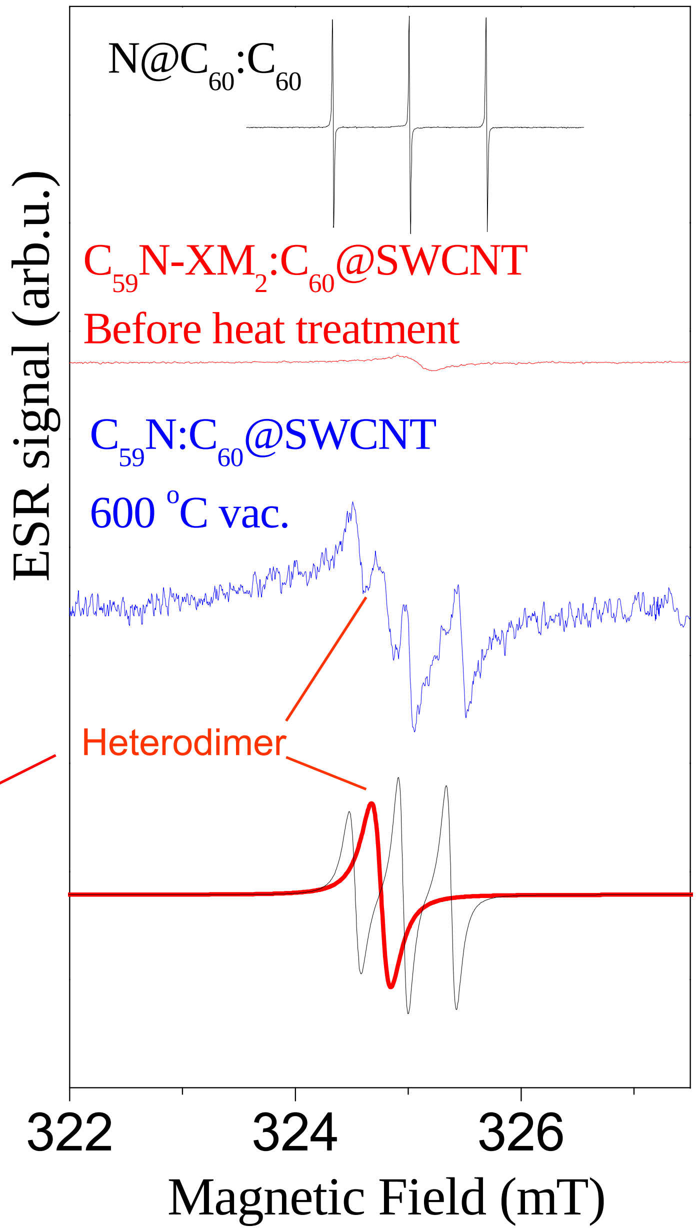


Spin Engineering

$C_{59}N$-XM_2



Heterodimer



Spinconcentration is only about 10^{-6}

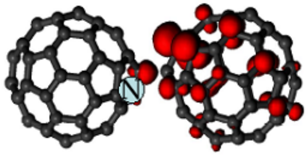
Spinconcentration zero

Spinconcentration is only about 10% of $C_{59}N$-XM_2 concentration!

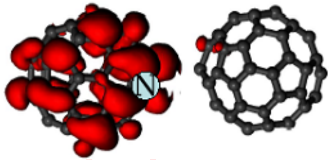
F. Simon et al., PRL 2006

DYNAMICS OF THE SPIN CARRYING STATE

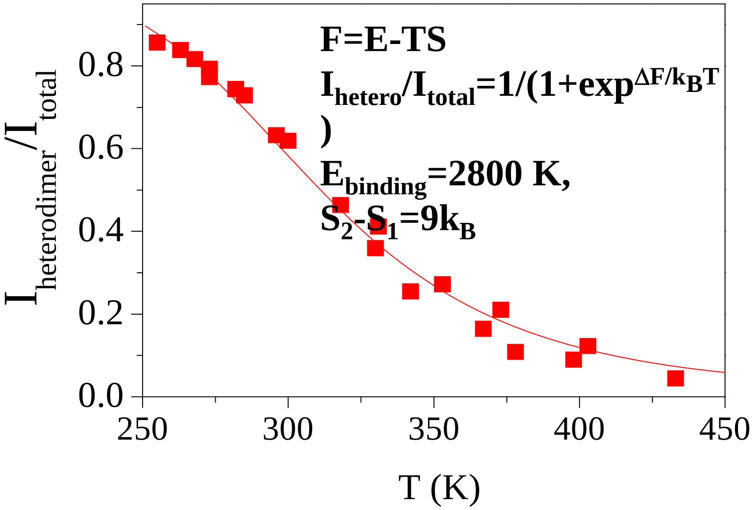
Heterodimer/monomer

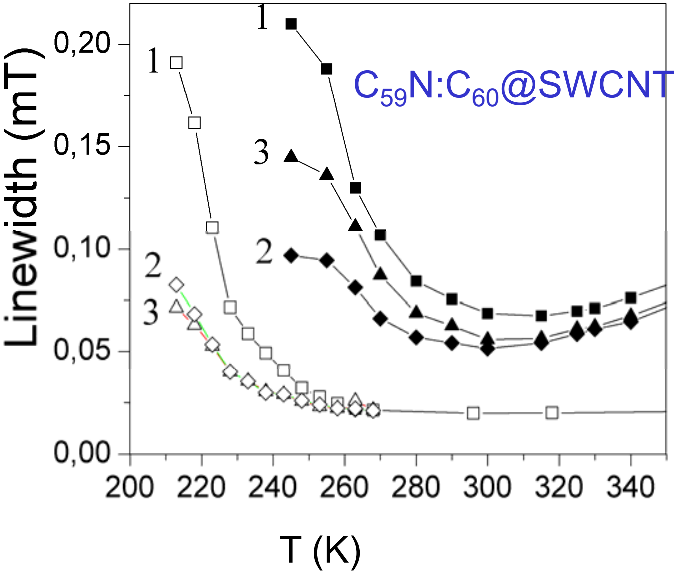


Ground state: spins at C

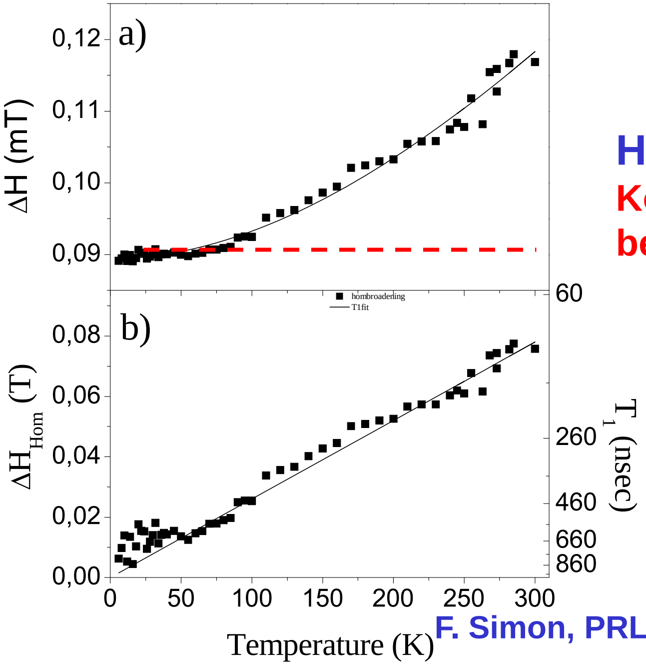


Excited state: spins at $C_{59}N$
-> hyperfine triplet





Monomer:
motional narrowing!



Heterodimer:
Korringa behavior

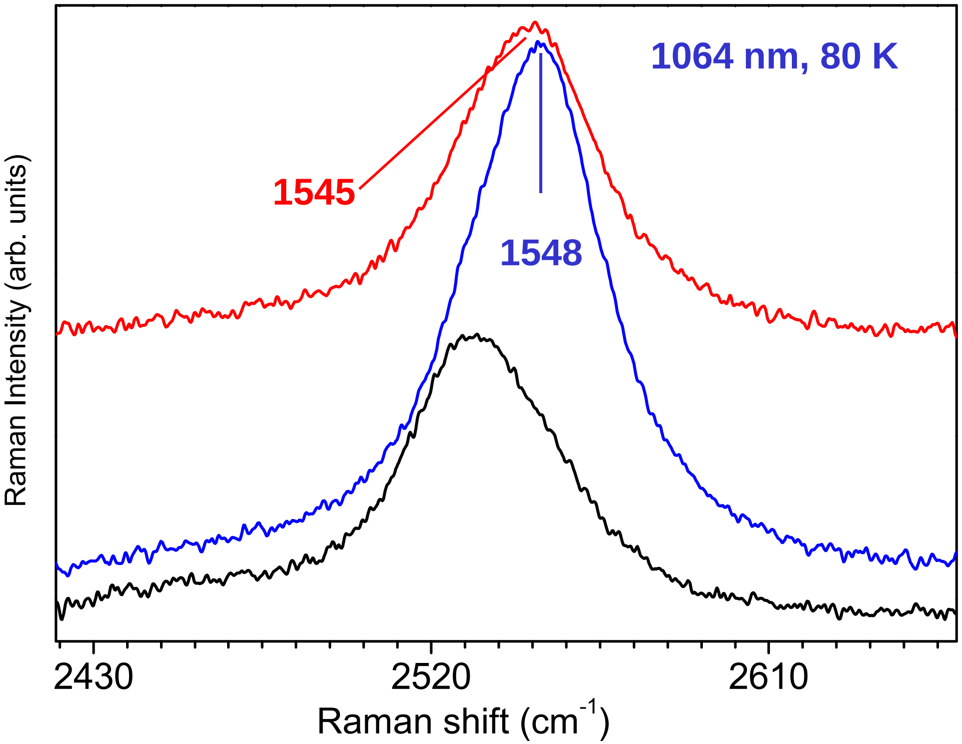
F. Simon, PRL 2006

ON TRANSFORMATION TO DWCNT: IS N INSERTED INTO THE INNER-SHELL TUBE?

expected:
0.14% line shift

RBM: 0.5 cm^{-1}
2D: 3.5 cm^{-1}

observed:
2D: 3 cm^{-1}



Red: DWNT transformed from $(C_{59}N)_2$@SWNT

Blue: DWNT transformed from $(C_{60})_n$@SWNT

Black: SWNT

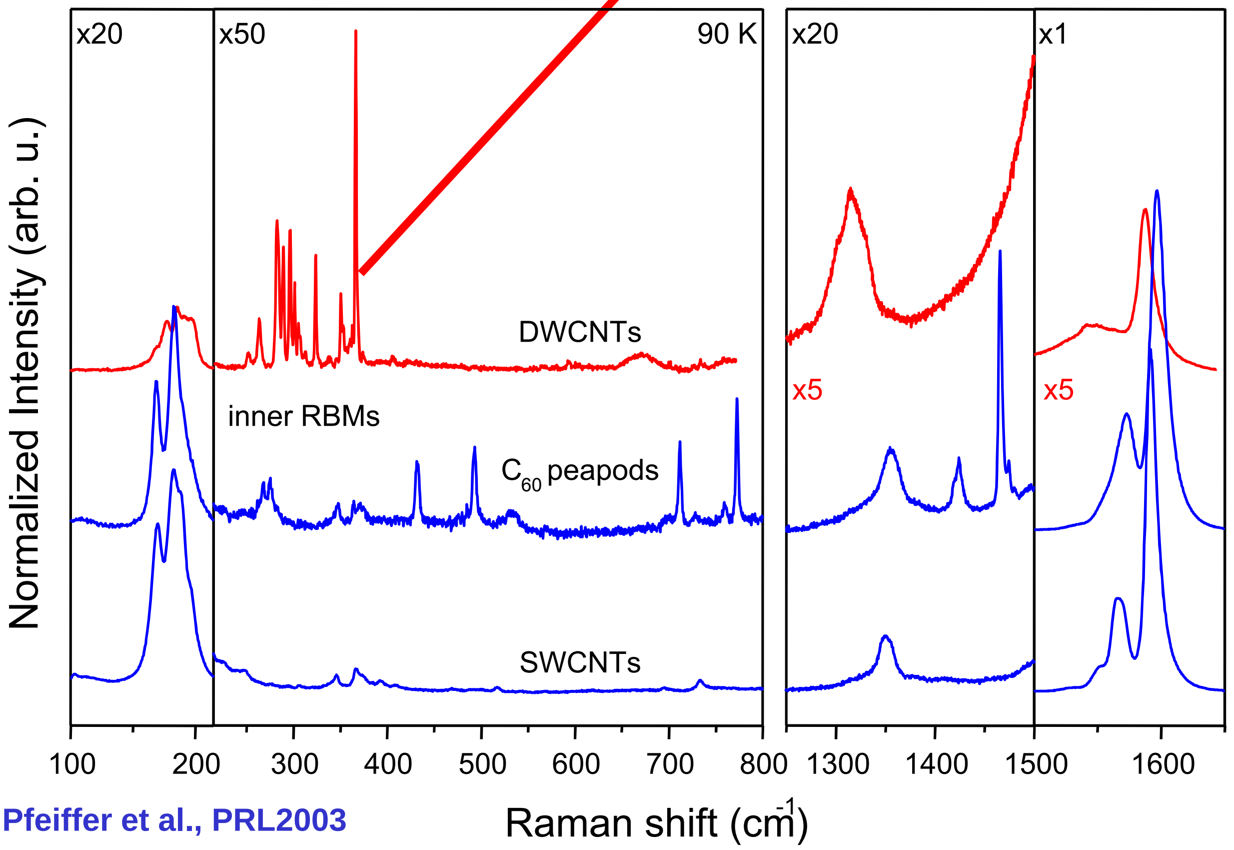
Double-walled carbon nanotubes, pair spectra

GROWING DWCNTs FROM PEAPODS

Linewidths down to 0.4 cm^{-1} 10x more narrow than for standard tubes

The interior is a Nano-cleanroom

RAMAN

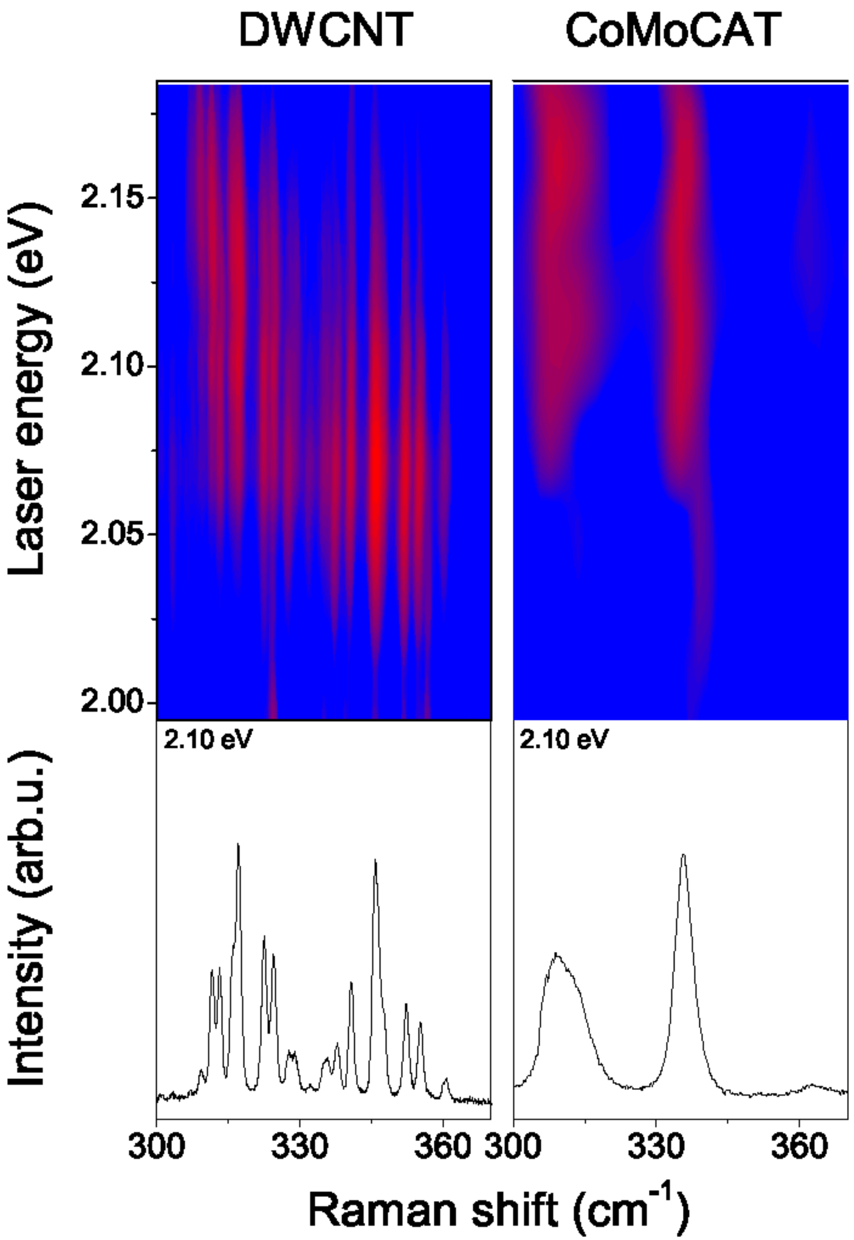


There are too many lines!!

Pfeiffer et al., PRL2003

RAMAN MAP

RBM RAMAN LINES DWCNT vs CoMoCat

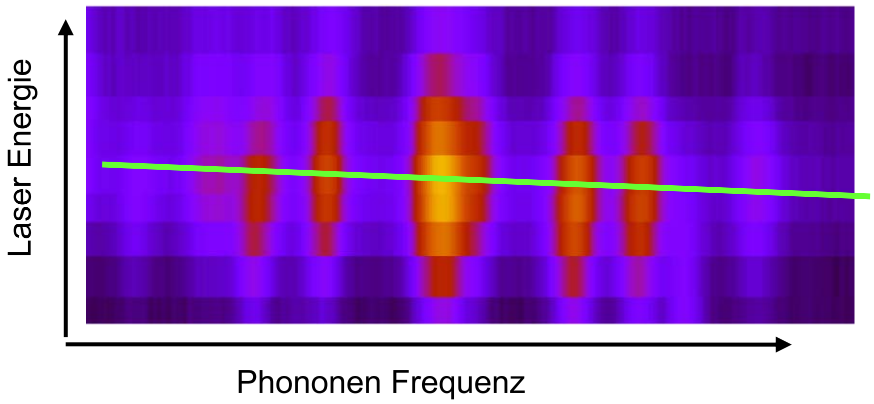


The two cluster of lines originate from the same inner tube **((6,5), (6,4))**

RESONANCE PROFILE OF CLUSTER COMPONENTES

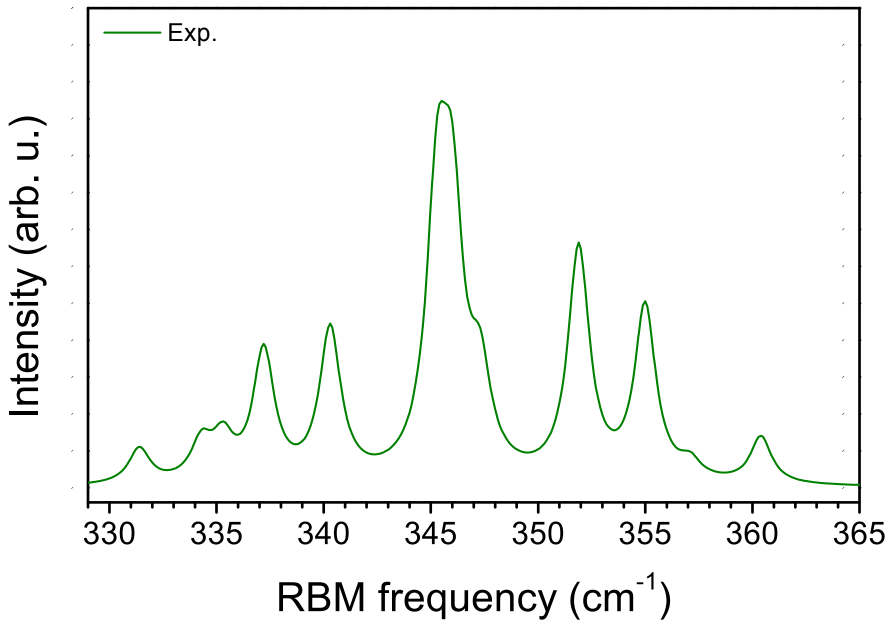
Color code:
Raman Intensity

All lines in the in the cluster come from the same inner but different outer tubes.



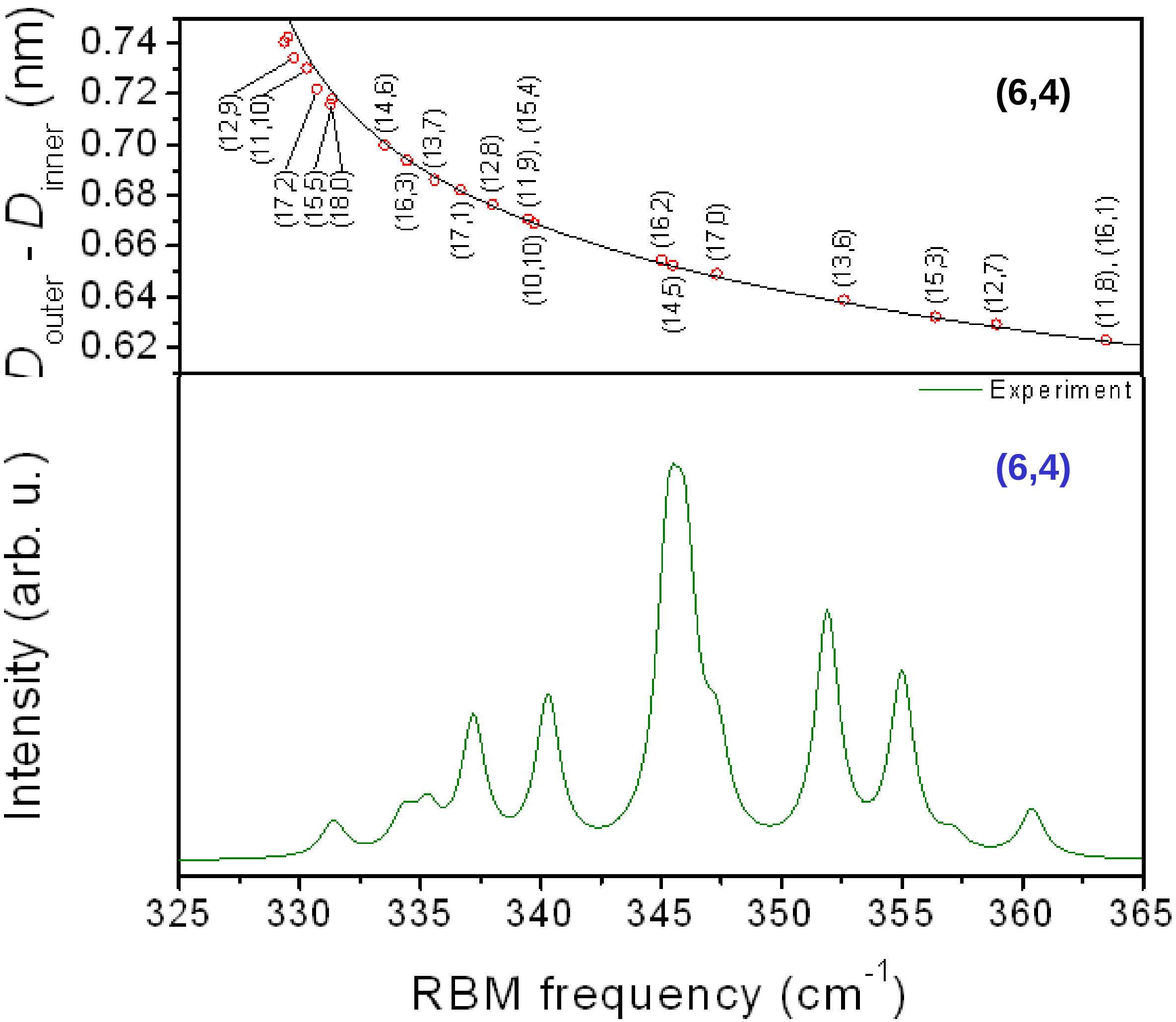
-2 mV/cm^{-1}

R. Pfeiffer et al
PRB 2005



Exp: intensity normalized by cross section

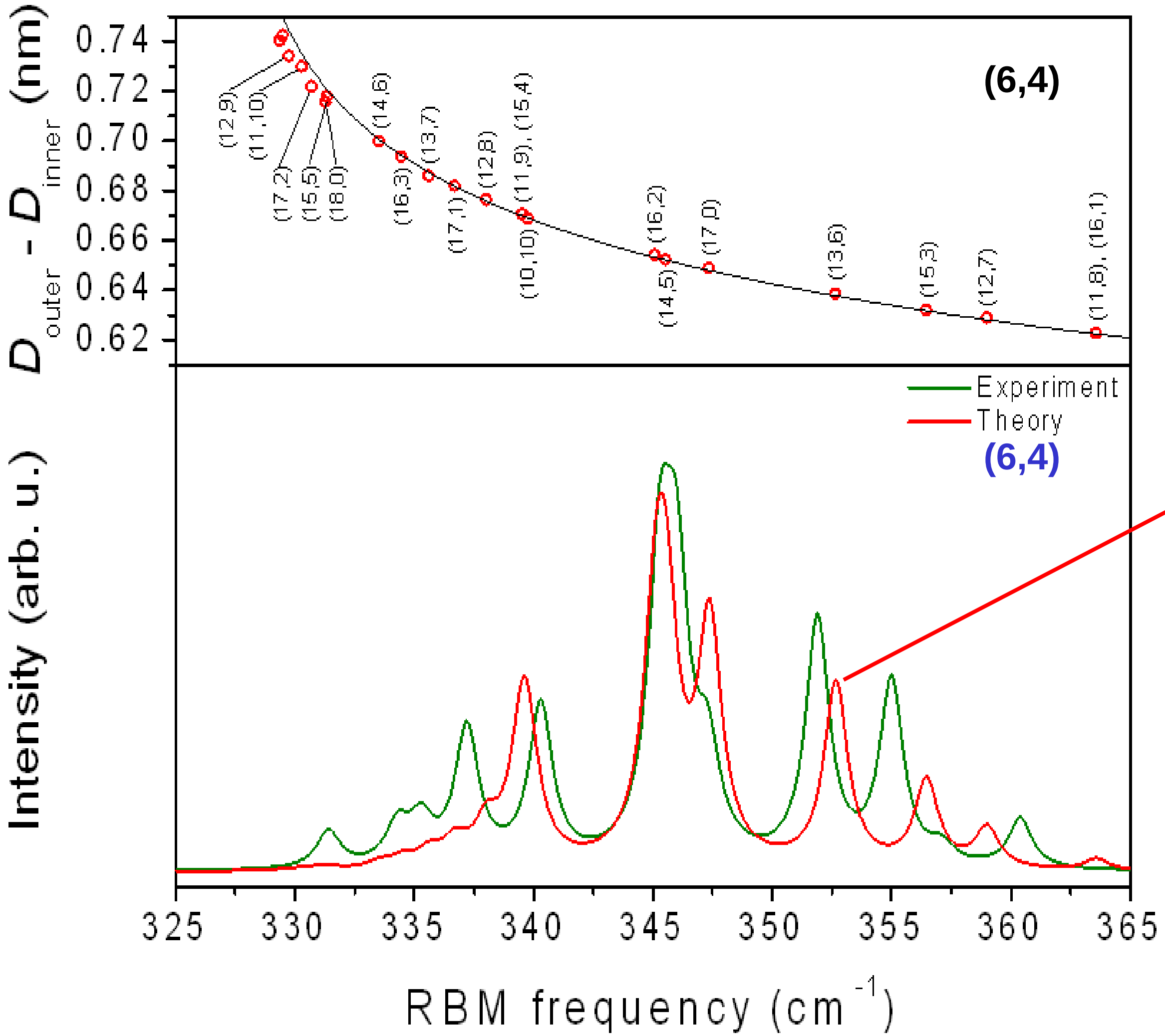
COMPARISON OF CLUSTERED LINES WITH CALCULATION



V. Popov, 2005
Continuum model

Exp: intensity normalized by cross section

COMPARISON OF CLUSTERED LINES WITH CALCULATION



V. Popov, 2005
Continuum model

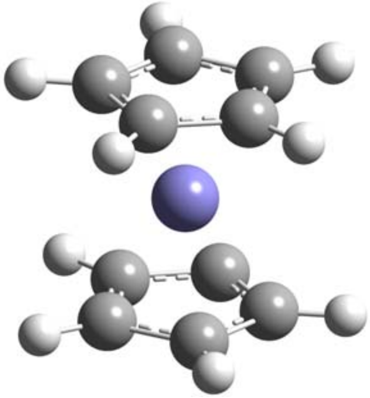
Calculatd with Gaussian profil
Pair spectra

Exp: intensity normalized
by cross section

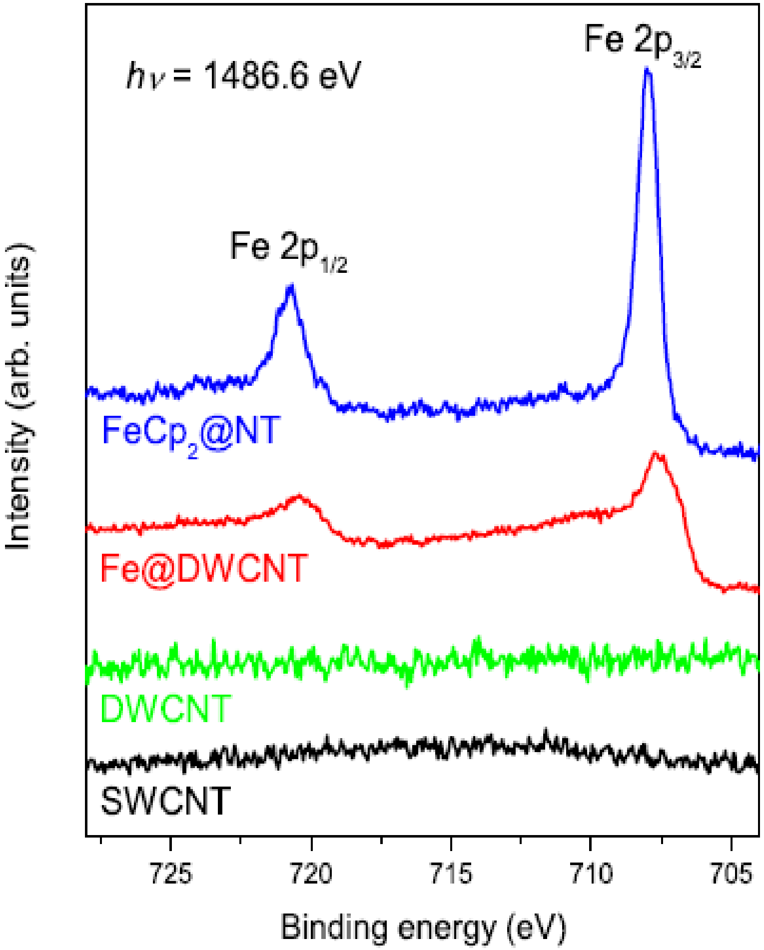
R. Pfeifferet al.
2005

FERROCENE IN SWCMTs

$FeCp_2$



No Raman spectrum could be observed after filling at 100 ^{0}C for several days



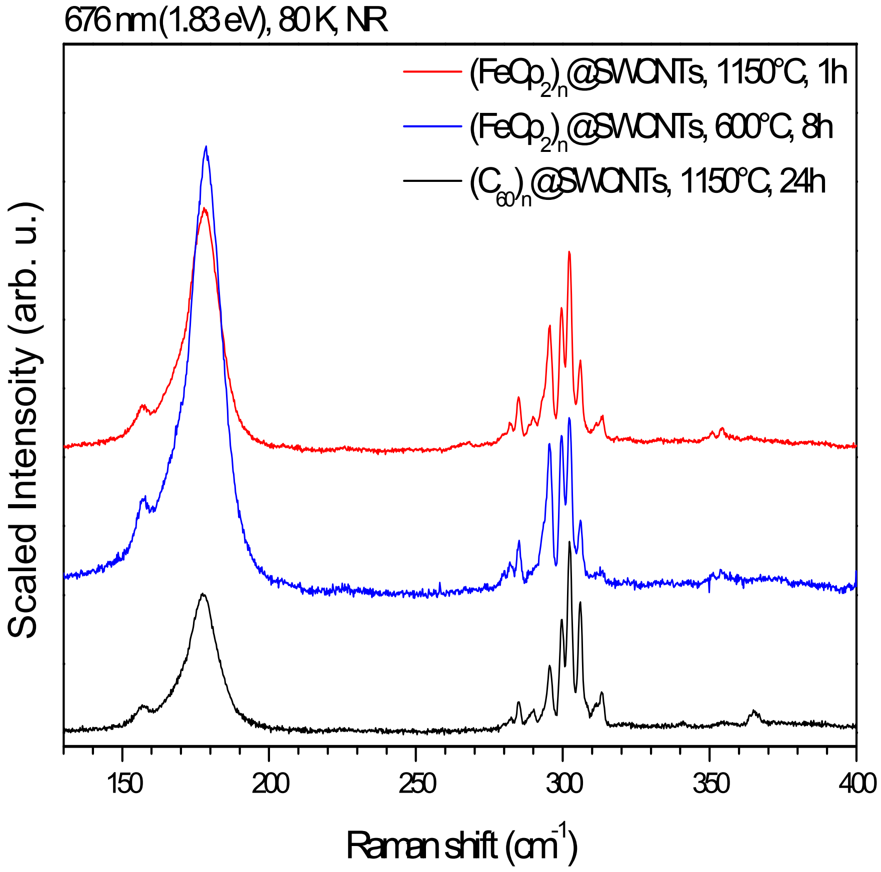
Photoemission spectroscopy

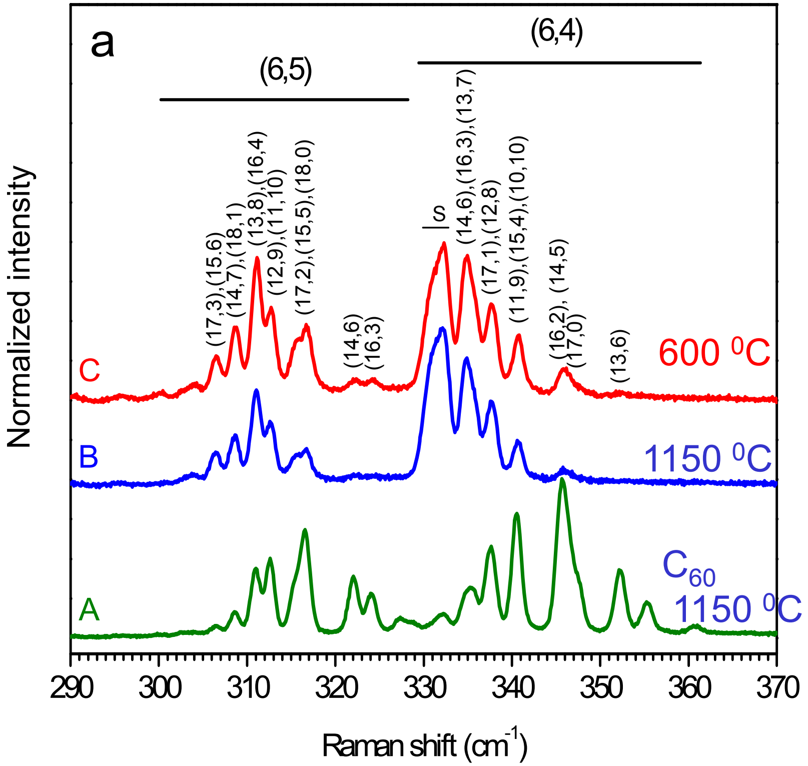
2 h, 600 ^{0}C

1 h, 1150 ^{0}C

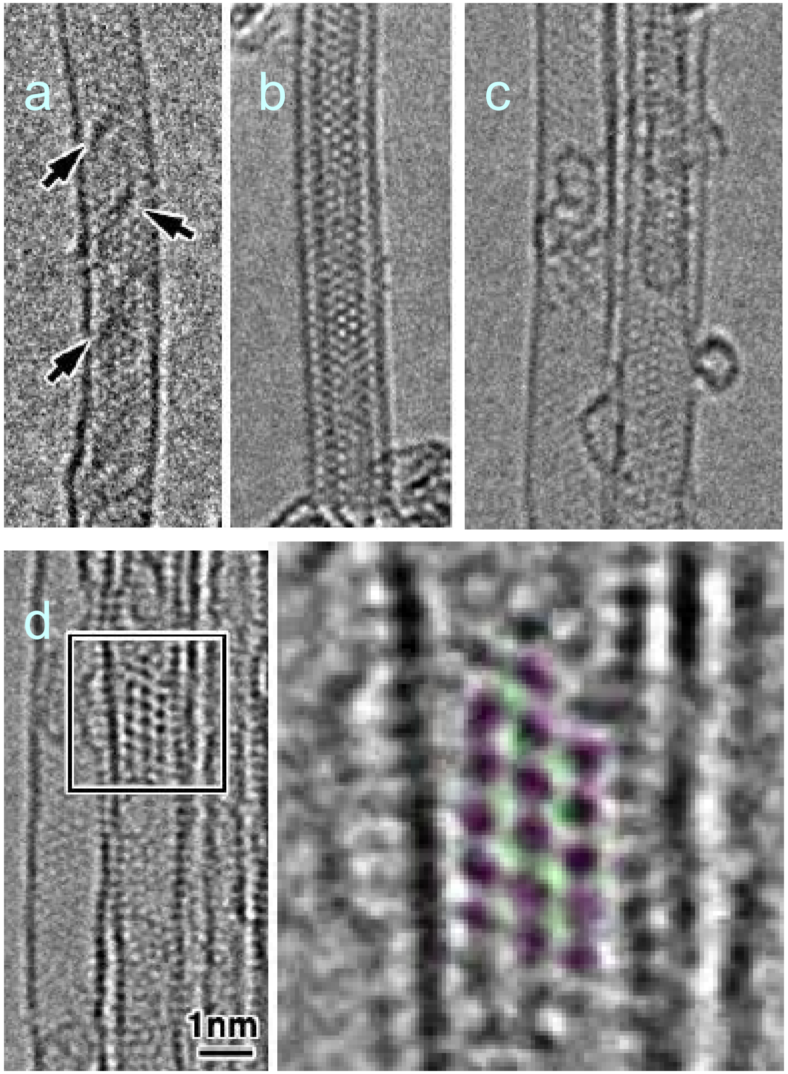
H. Shiozawa et al., 2007

RAMAN SCATTERING FOM FeCp2 AND C60 GROWN DWCNTs

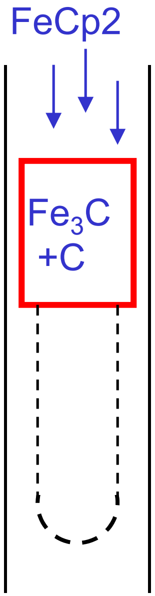




HR-TEM FOR FERROCENE FILLED SWCNTs



- a) As filled
- b) After heat treatment at 1150 ºC
- c) after heat treatment at 600 ºC
- d) Fe_3C particle with simulation



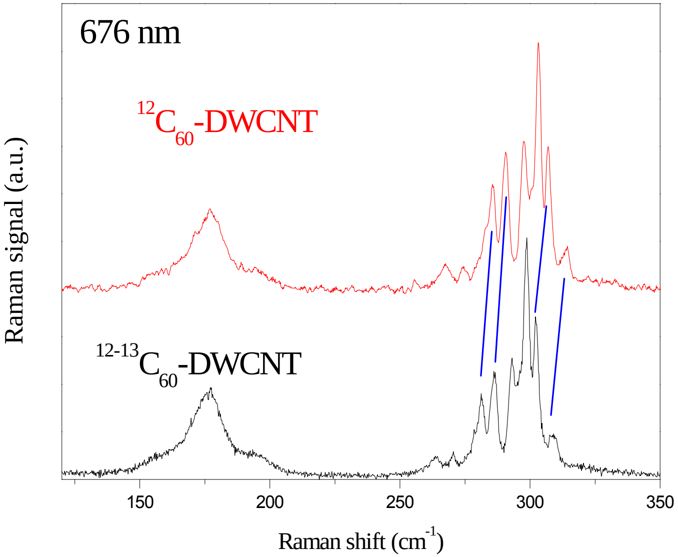
Growth from catalytic reaction

K. Suenaga, 2007

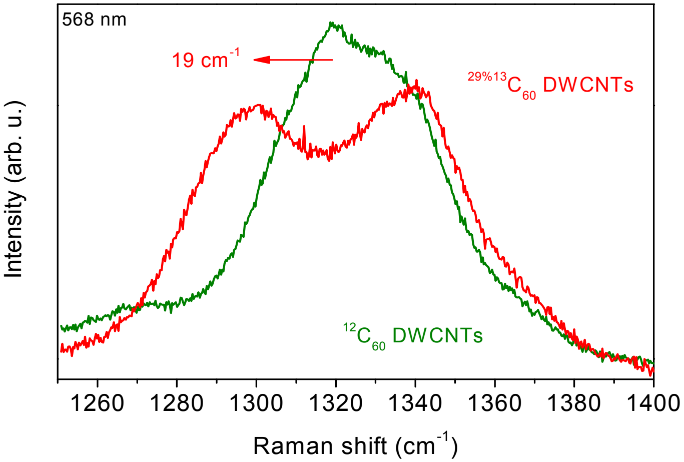
^{13}C precursor grown DWCNT

SPECTROSCOPY FOR ^{13}C-SWCNT

RBM line



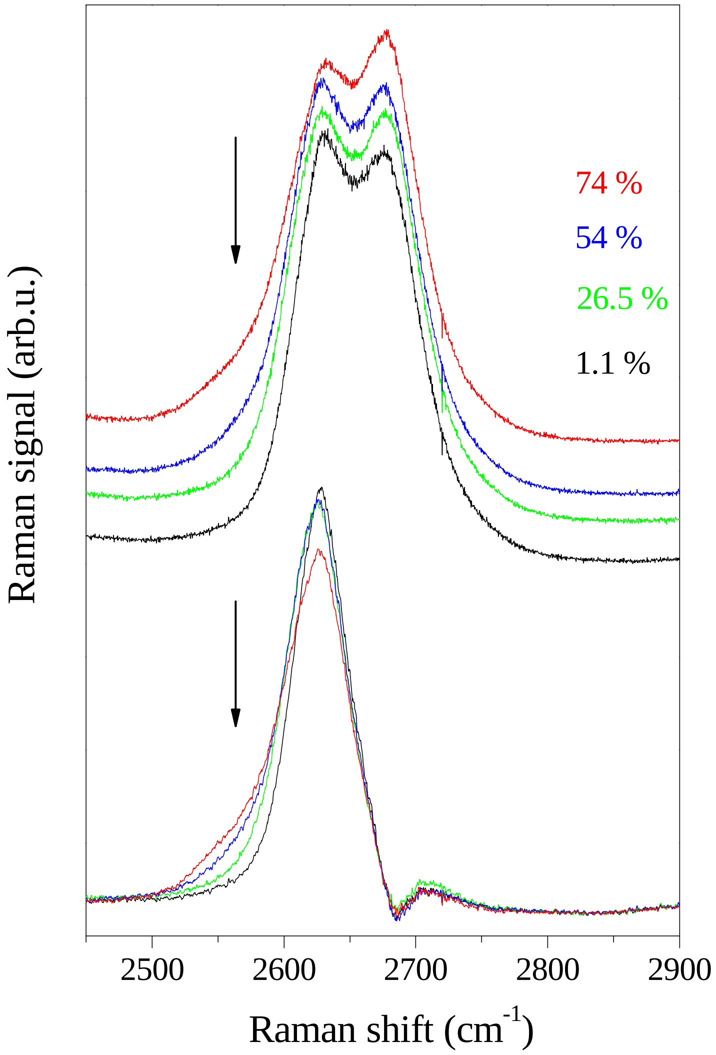
D line

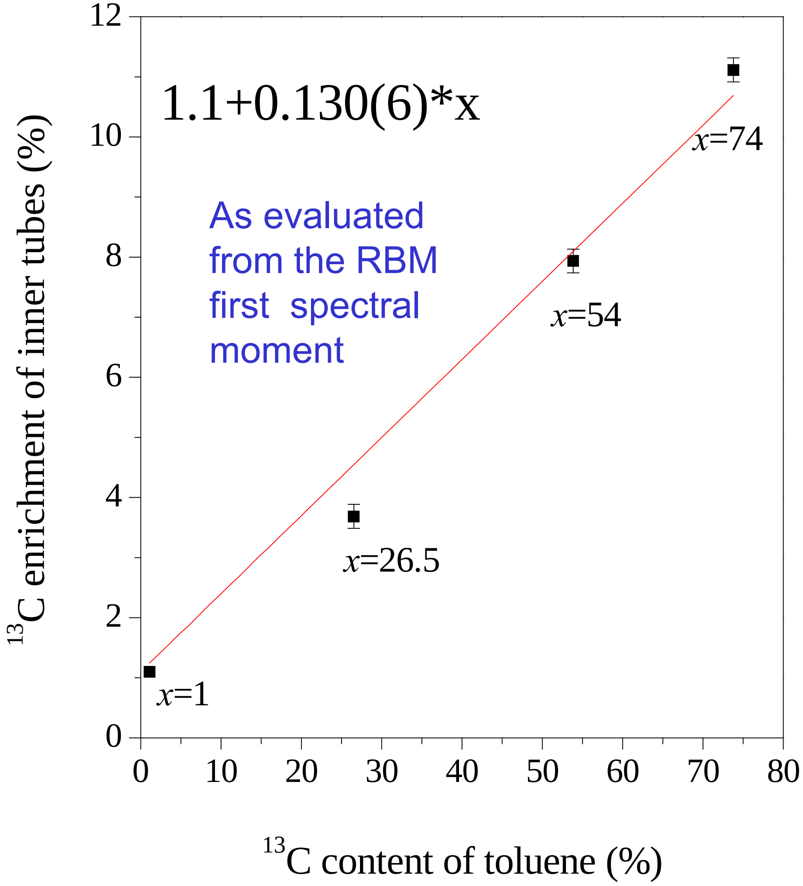


CHECKING THE ROLE OF TOLUENE

^{13}C enriched toluene+C_{60}

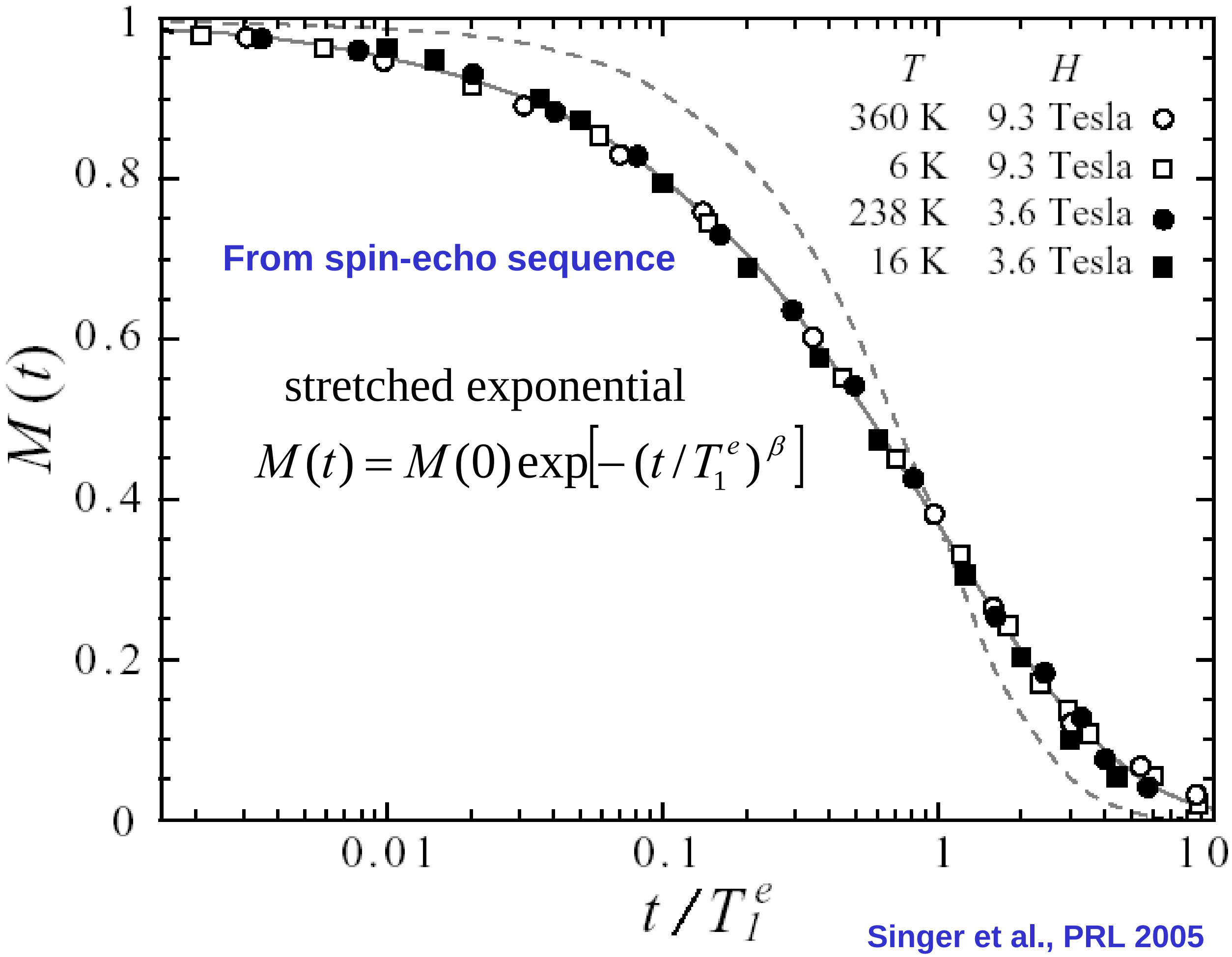
515 nm, RT




1.1+0.130(6)*x

As evaluated from the RBM first spectral moment

^{13}C-SWCNT@^{12}C-SWCNTs
RELAXATION OF MAGNETIC MOMENTS



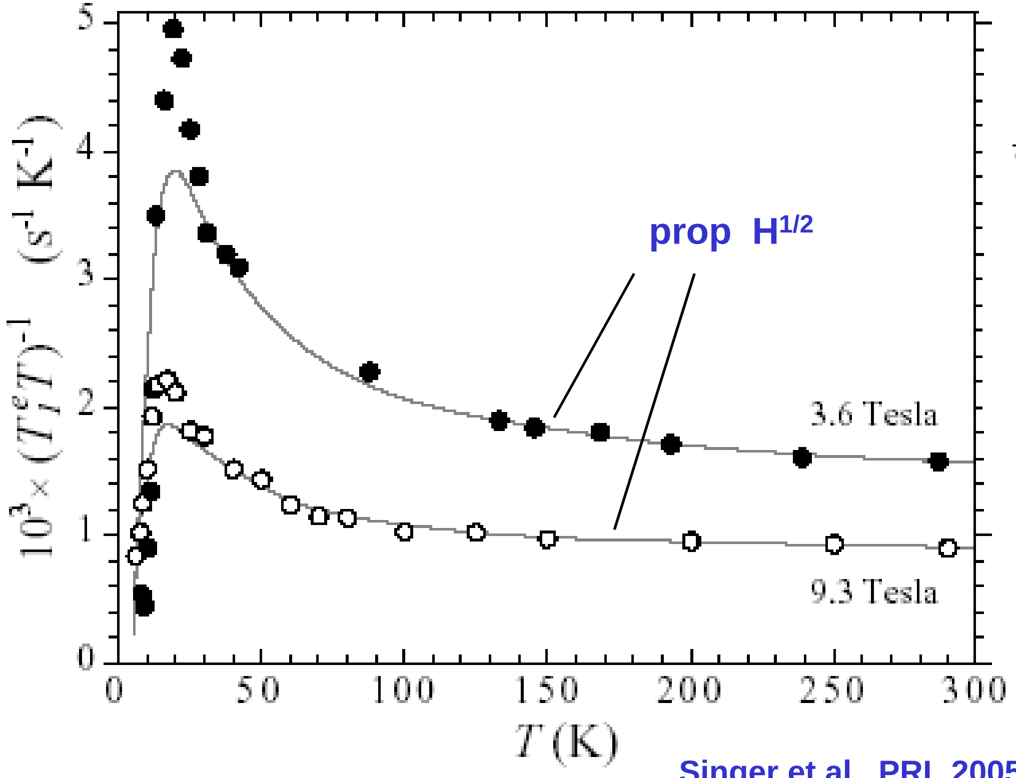
From spin-echo sequence

stretched exponential

$$M(t) = M(0)\exp\left[-(t/T_1^e)^\beta\right]$$

Singer et al., PRL 2005

LONGITUDINAL NUCLEAR SPIN RELAXATION T_1



prop $H^{1/2}$

$$\overline{n}(E) = \overline{n}(\epsilon_f)\frac{d\epsilon}{dE} = \overline{n}(\epsilon_f)\frac{E}{\sqrt{E^2-\Delta^2}}$$

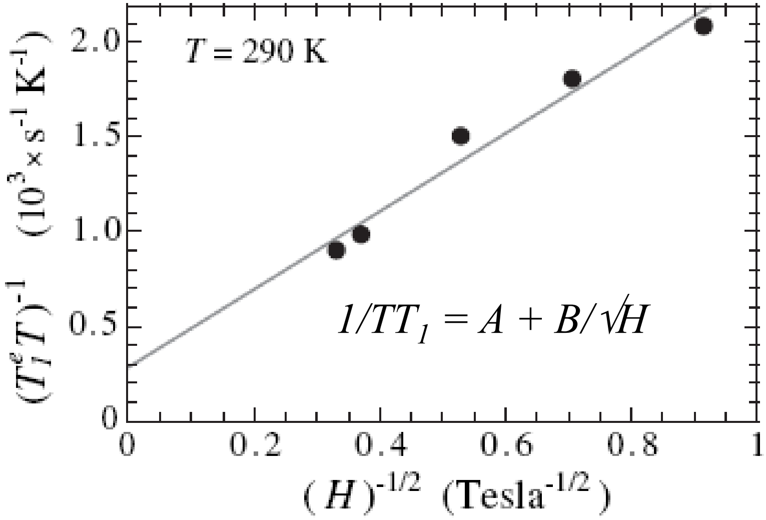
$$\frac{1}{T_1T} = \alpha \int_\Delta^\infty \overline{n}(E)\overline{n}(E+\omega_n)\left(-\frac{\delta f}{\delta E}\right) dE$$

Description by a gaped DOS

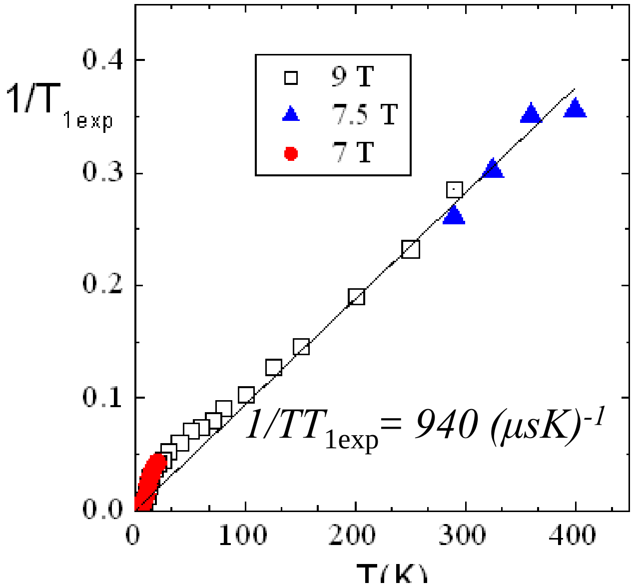
Singer et al., PRL 2005

DYNAMICS OF NUCLEAR SPINS

1D spin diffusion



Korringa relaxation



$$\frac{1}{T_1 T} = \frac{2\pi k_B}{\hbar} A_{dip}^2 \overline{n}(\epsilon_f)^2,$$

$$A_{dip} = \frac{2}{5}\gamma_e\gamma_n\hbar^2 \left\langle \frac{1}{r^3} \right\rangle,$$

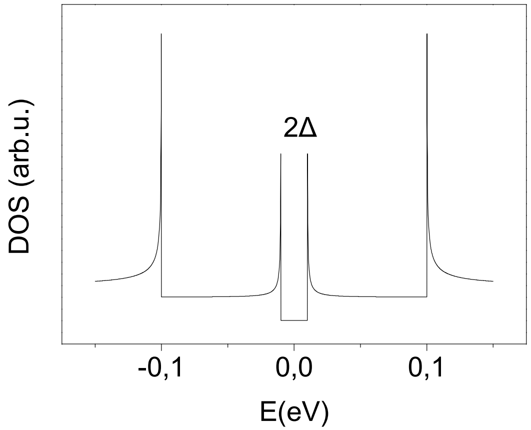
RESULTS FROM NMR RELAXATION

i) **High T: 1/TT_1 constant, independent from T**
for all tubes, Korringa behavior

ii) **T<150K: 1/TT_1 increases dramatically**

iii) **Below 20 K a spin gap appears**

Description with a gaped DOS, Δ = 20 K,



Origin of gap:

Not field-induced (independent of field

Not curvature-induced (100 meV expected)

Not longitudinal quantization (distribution expected)

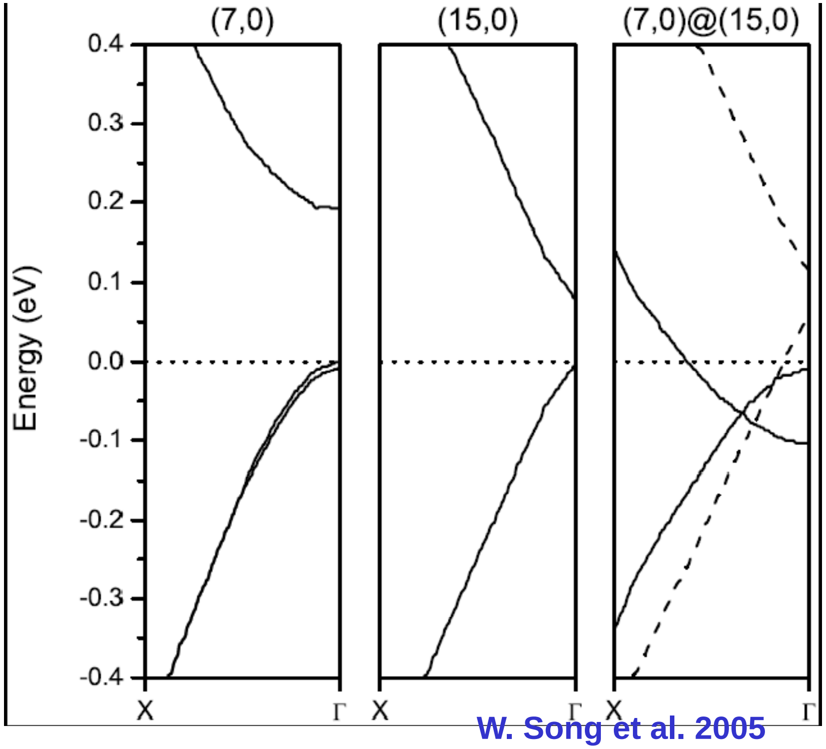
Possible: Peierls or spin-Peierls gap

Origin of metallization:

Intertube interaction

Charge tansfer

METALLIZATION FROM TUBE-TUBE INTERACTION



W. Song et al. 2005

From first principle calculations

(V. Zolyomi et al. 2007)

General: gap closes or at least gets reduced

TOMONAGA-LUTTINGER DESCRIPTION FOR T_1

For 1D electronic system a correlated ground state is expected ->

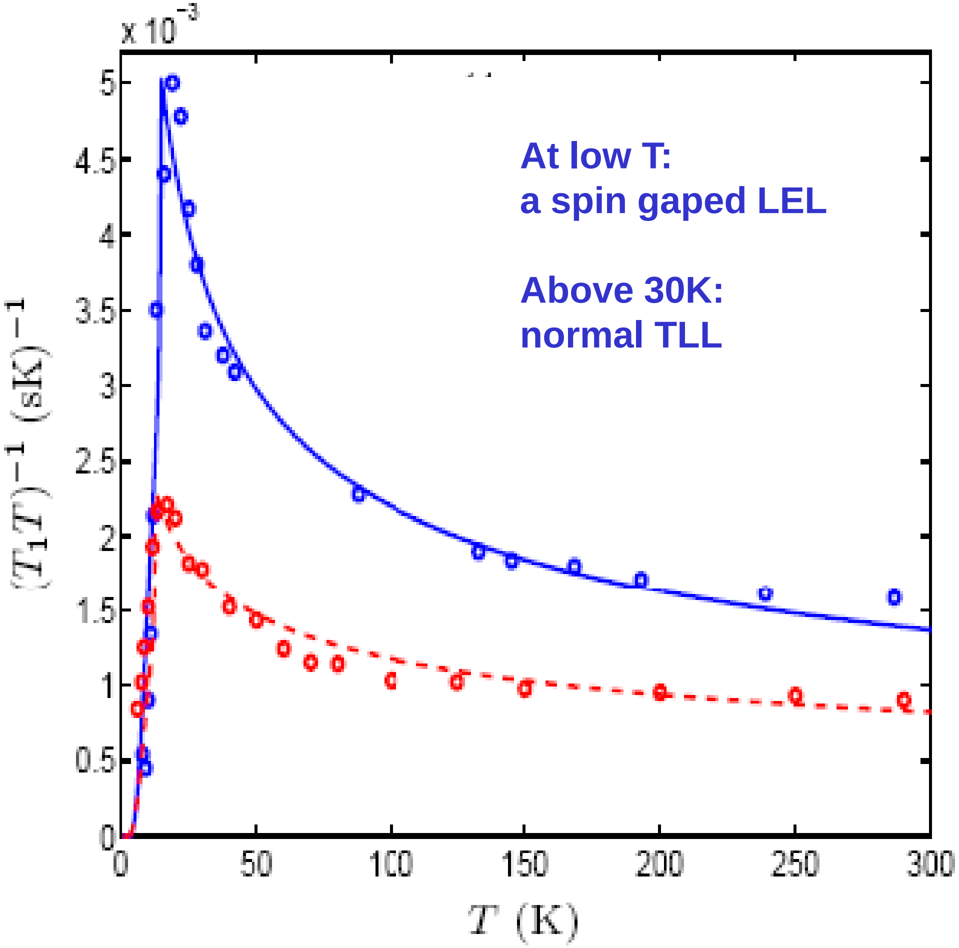
TL-liquid instead of Fermi liquid

H. Ishii et al., 2003 from PES:
α =0.46 (g=0.18)

TLL is described by bosonization of the fermions

The FL description above uses a gap already at room temperature wich violates $2\Delta/K_BT_c > 3.52$ rule (mean field not applicable)

Here: TLL (ungaped) and Luther- Emery (gaped) description were combined



At low T:
a spin gaped LEL

Above 30K:
normal TLL

B. Dora et al., PRL 2007

SUMMARY

The inside of SWCNTs: a narrow space for preparation of new structures.

1D materials from magnetic molecules can be prepared inside.

Nanotubes growth inside: clean room conditions

Raman line pattern of the RBM modes for DWCNTs: pair spectra

Catalytic reactions inside: tube growth at 600 ^{0}C

^{13}C DWCNTs: with inner tubes almost exclusively ^{13}C.
Raman: G’-anomaly
NMR: inner tubes: metallic, with a spin gap of 3.5 meV appearing at 20 K,
Best described by TLL and LE liquids

ACKNOWLEDGEMENT

Co-worker, in Wien

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W. Plank
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international

A. Janossy (TU Budapest)
V. Popov (U Sofia, Namur)
H. Alloul (U Paris Sud)
F. Singer (U Paris Sud)
K Suenaga (AIST, Tsukuba**)**
H. Kataura (AIST, Tsukuba)
A. Hirsch (U Erlangen)
H. Shiozawa (IFW Dresden**)**

Projects

FWF, Projekt 14893
Projekt 17345
Projekt 14386

EU, FUNCARS
PATONN
NANOTEMP
IMPRESS