NT06
June 18-23, 2006, Nagano, Japan

HR-TEM imaging of molecules and ions trapped inside carbon nano-spaces

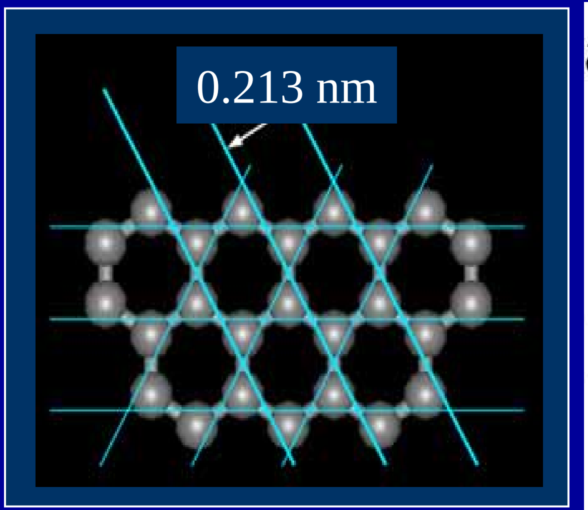
Kazu Suenaga
AIST, Tsukuba

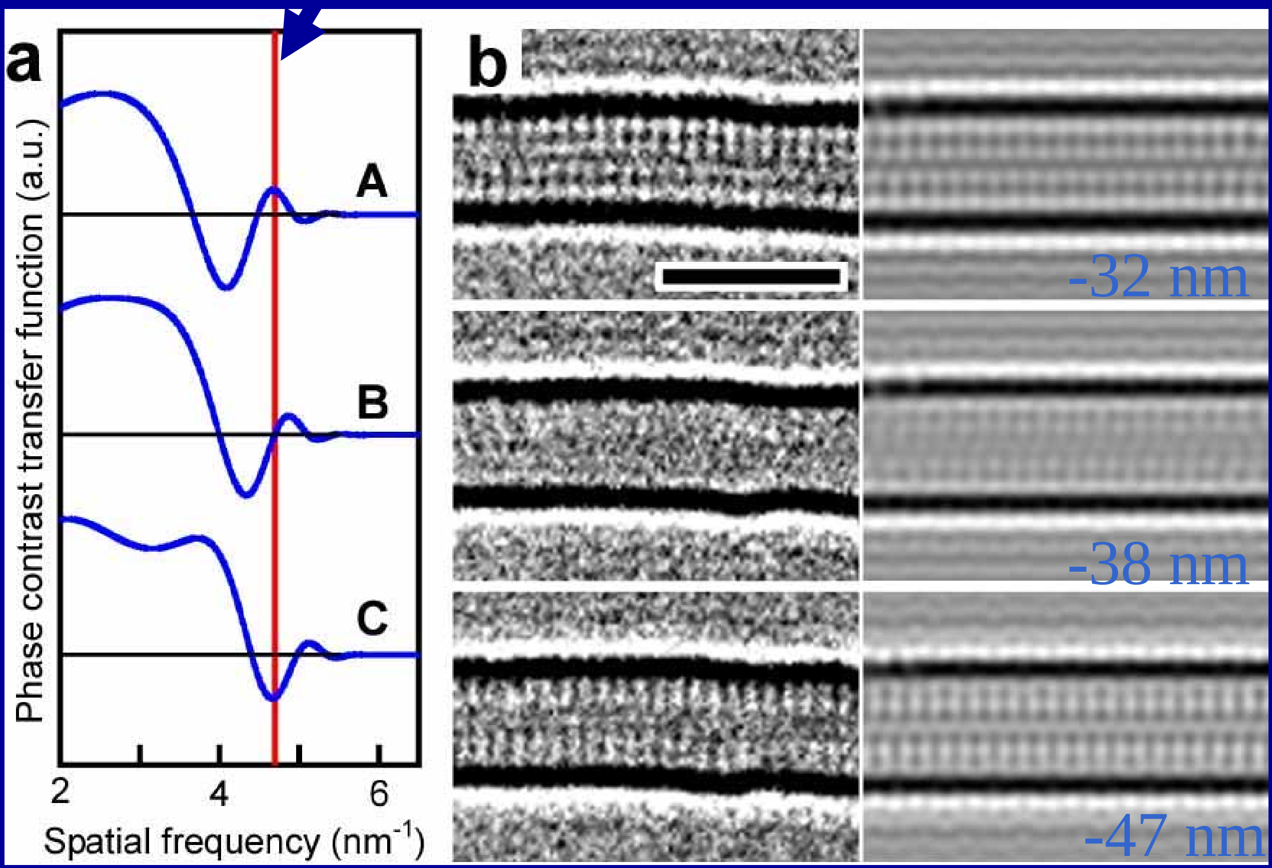
AIST

NEDO

The minimum of HR-TEM theory (an advantage of Cs-uncorrected TEM)

0.21nm

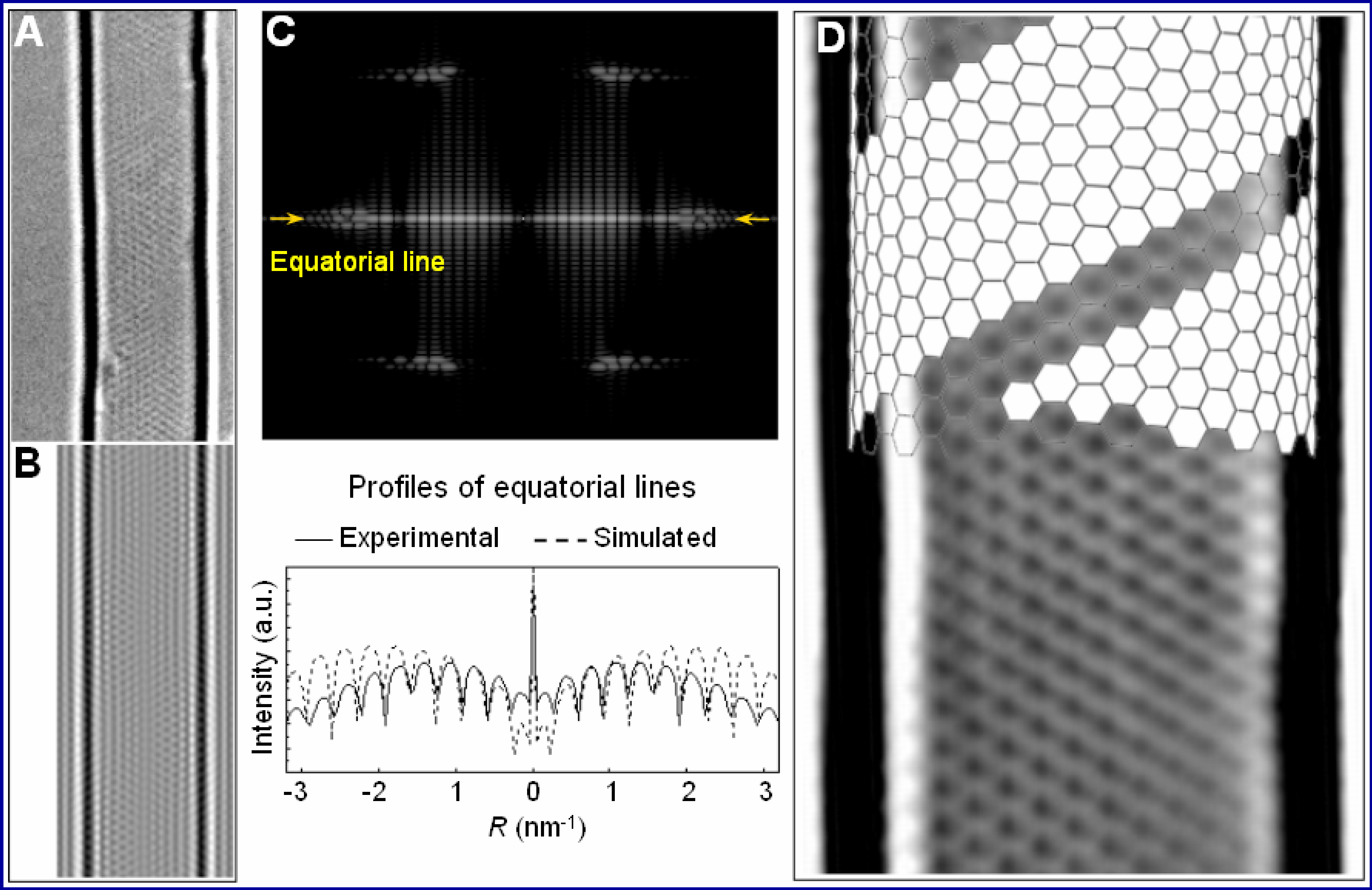




At 120 kV
Cs=0.45 mm

Y. Sato

Direct observation of graphen network in the case of SWNT

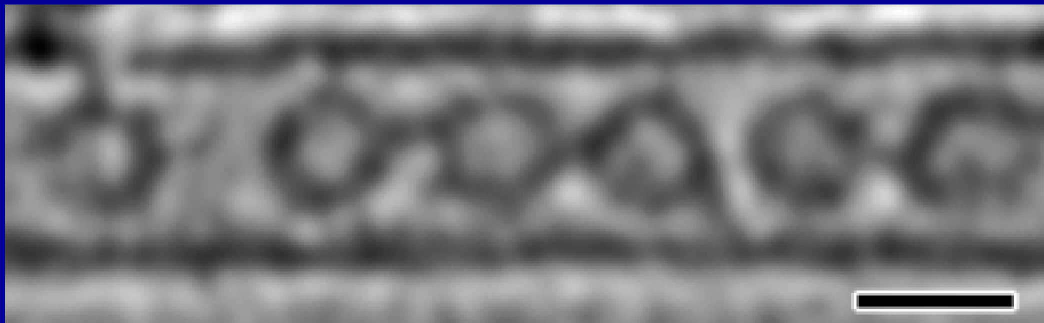


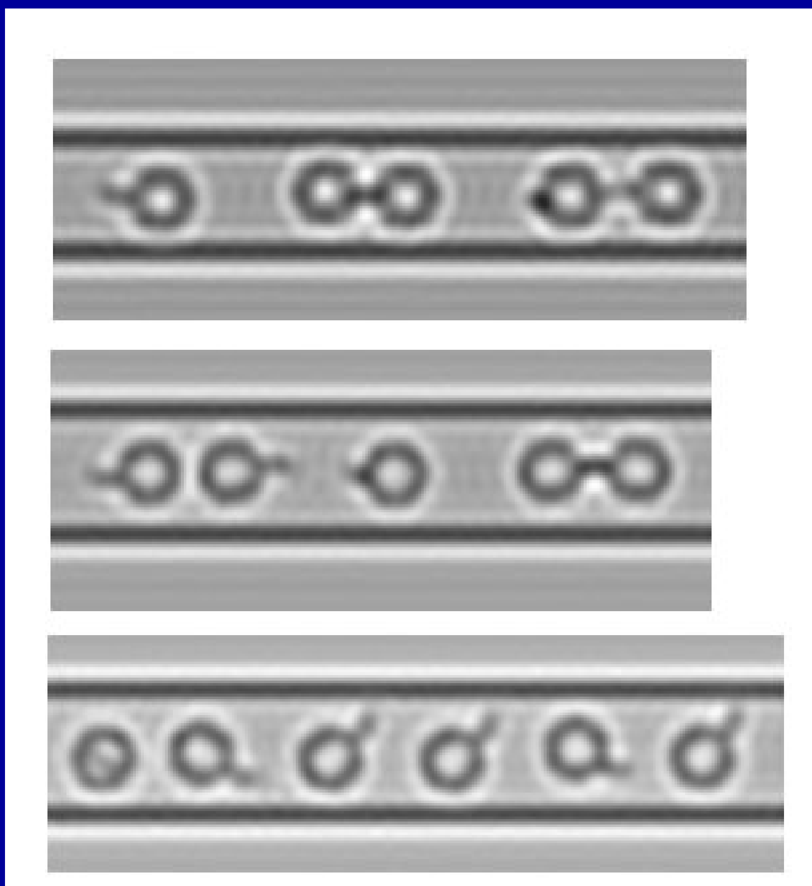
TEM imaging of individual functional groups of fullerene derivatives

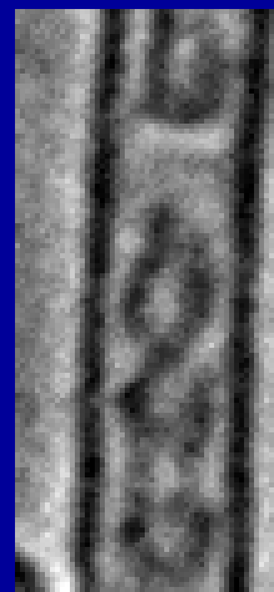
Liu, Koshino et al.,

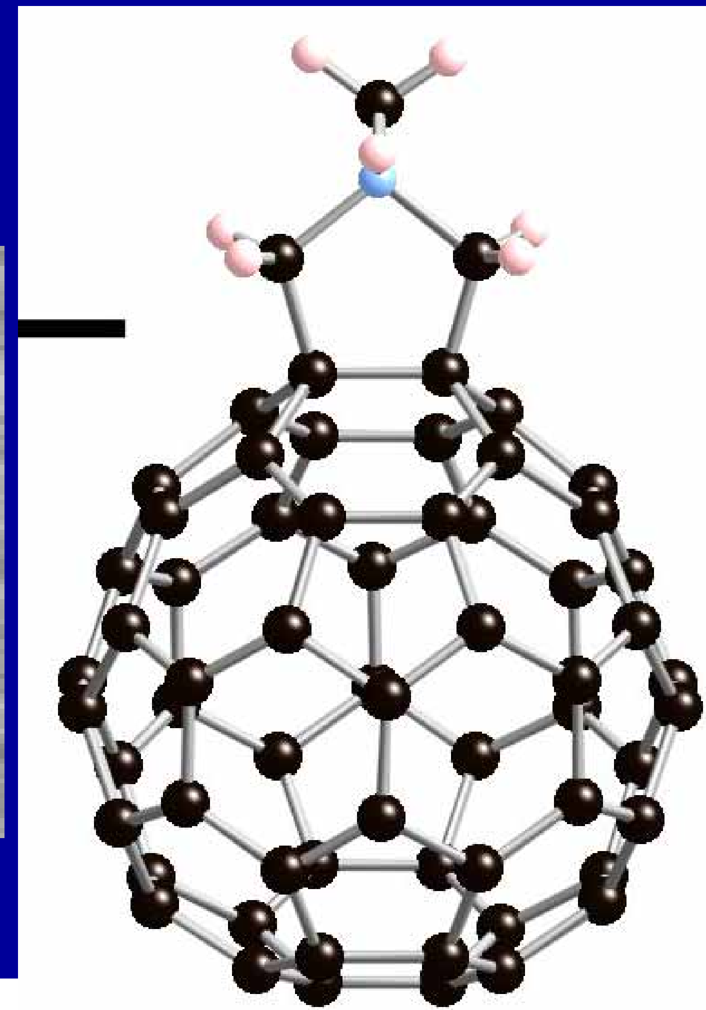
PRL 96 (2006) 088304

Fullerene derivatives
C_{60}-C_3NH_7

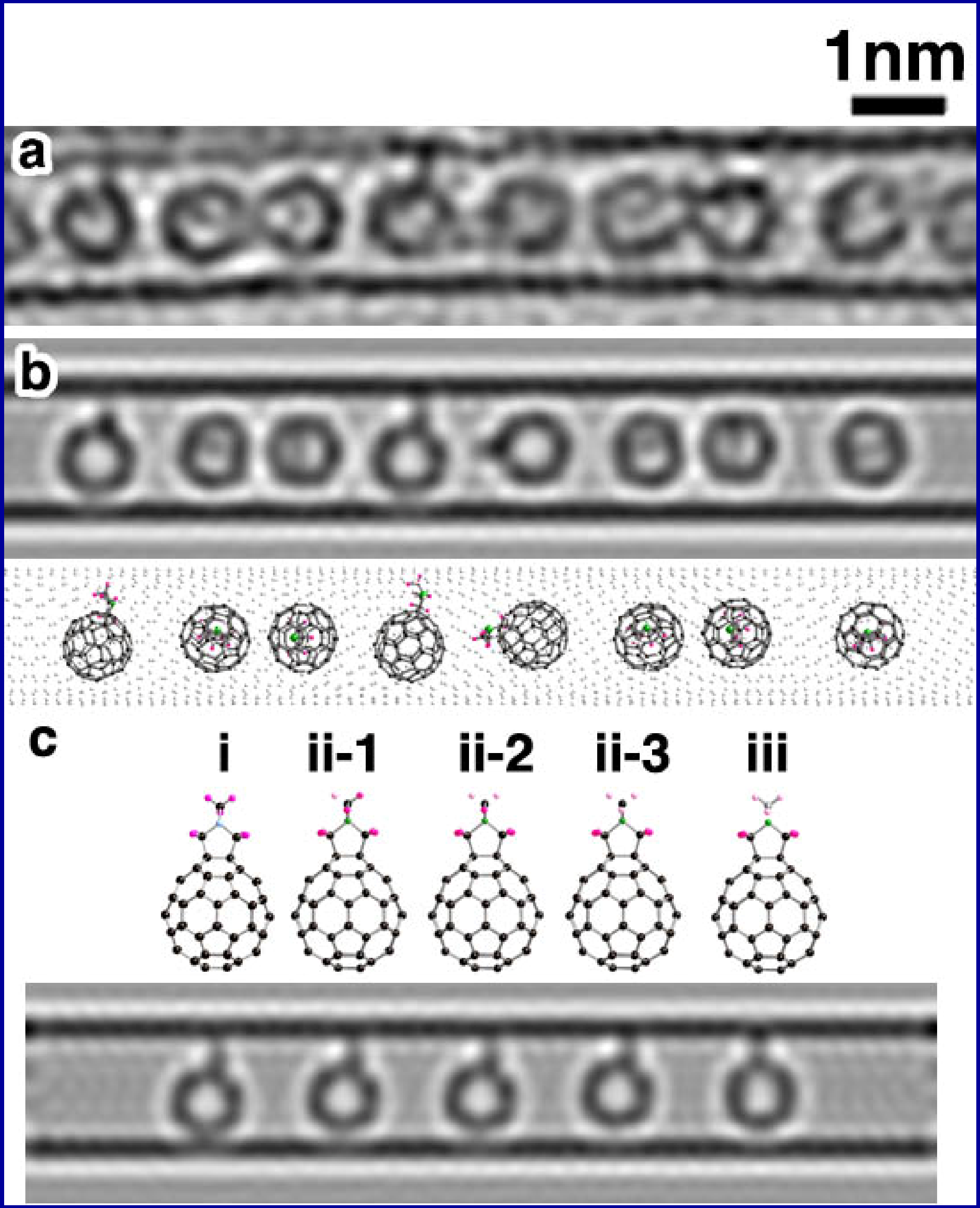




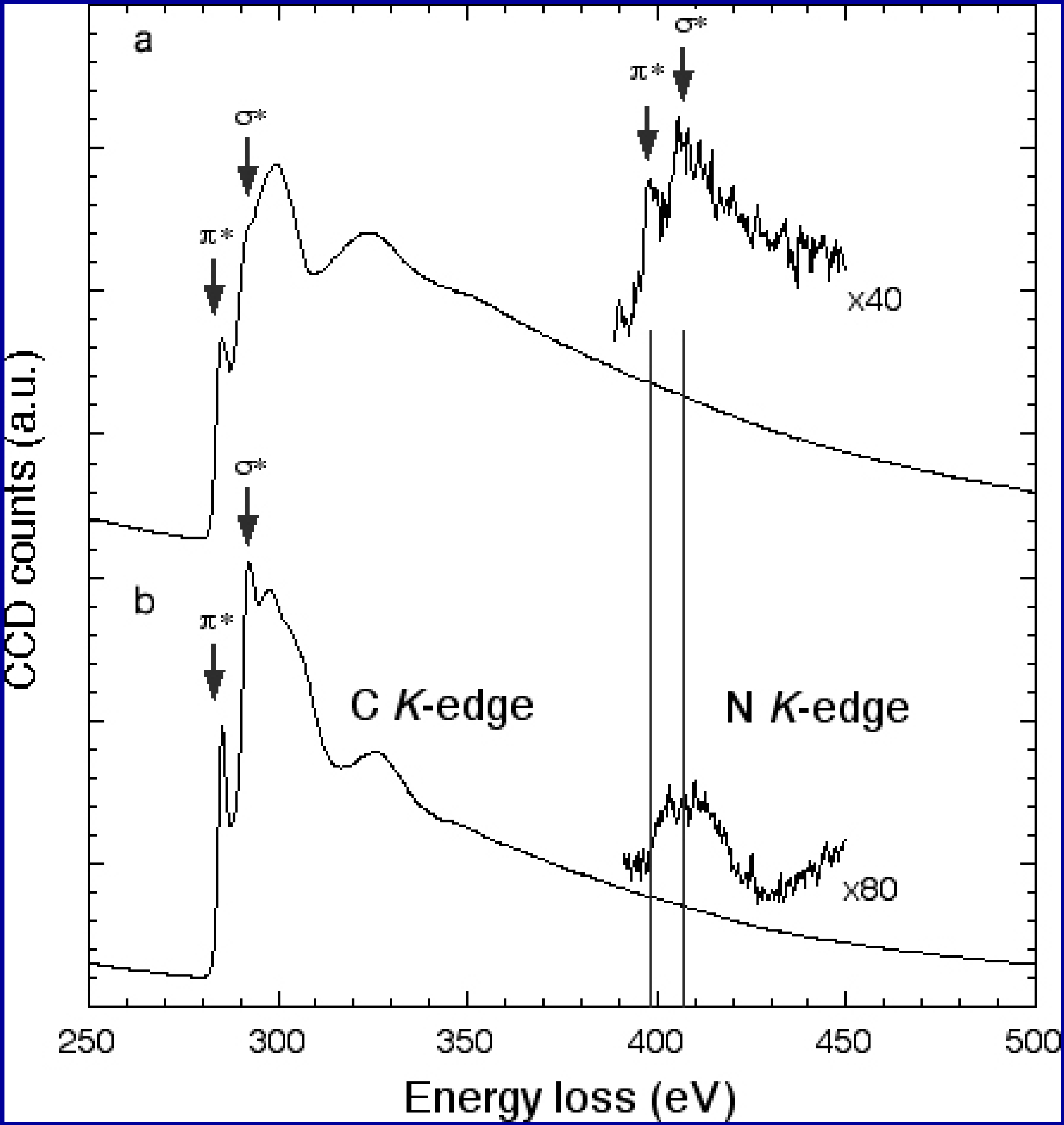




Liu et al.,
Specimen: Kataura and Mrzel



Detachment of H atoms or a methyl group due to the incident electron beam



A core-level shift of N K-edge.

Intact C_{60}-C_3NH_7

C_{60}-C_3NH_7 peapods

Visualization of ions trapped inside carbon nanospaces (K, Cs, Iodine and $FeCl_3$)

Guan et al., PRL (2005)

Sato et al., (unpublished)

Guan et al., (unpublished)

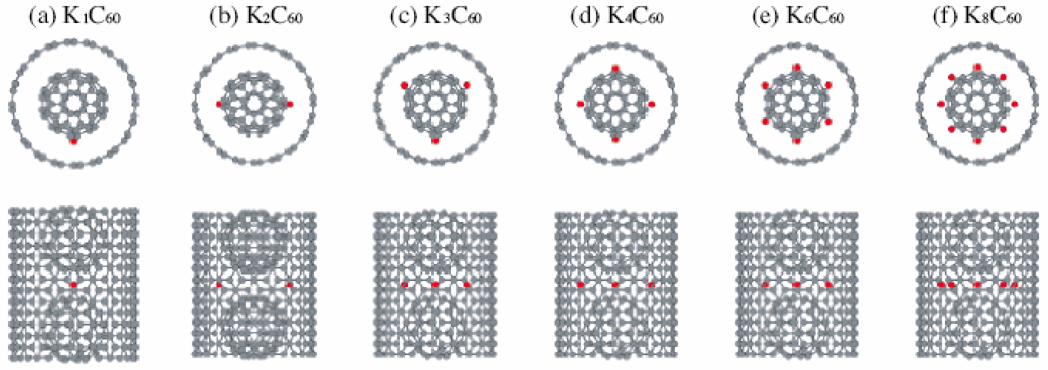
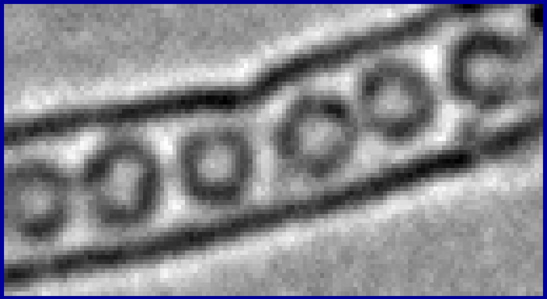
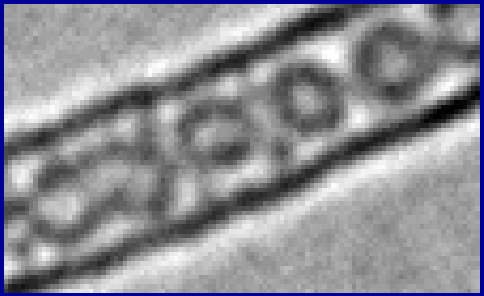


FIG. 1: Top and side views of geometric structures of potassium intercalated C_{60}-peapods, (a) K_1C_{60}, (b) K_2C_{60}, (c) K_3C_{60}, (d) K_4C_{60}, (e) K_6C_{60}, and (f) K_8C_{60}. Gray and red circles denote carbon and potassium atoms, respectively.



S. Okada PRB(2005)



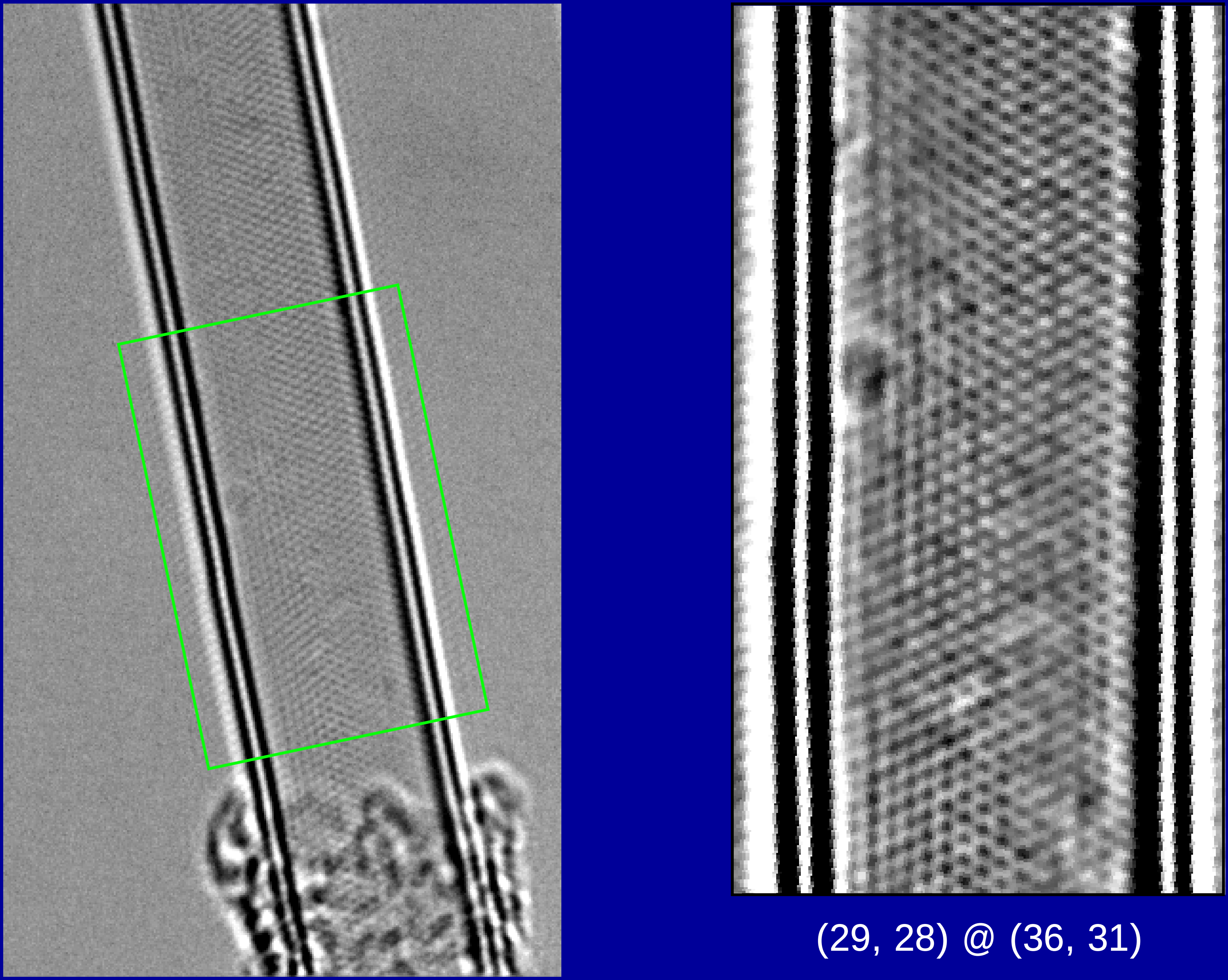
- Typical doping level : x = 1 ~2
  - (in K_xC_{60}@SWNT)
- Pichler et al. reported the C_{60}^{6-} in heavily doped peapods
- **“Intra- and inter-peapod doping sites”**

Determination of handedness of chiral DWNTs

Liu et al., PRL 95 (2005) 187406

Hashimoto at al., PRL 94 (2005) 045504

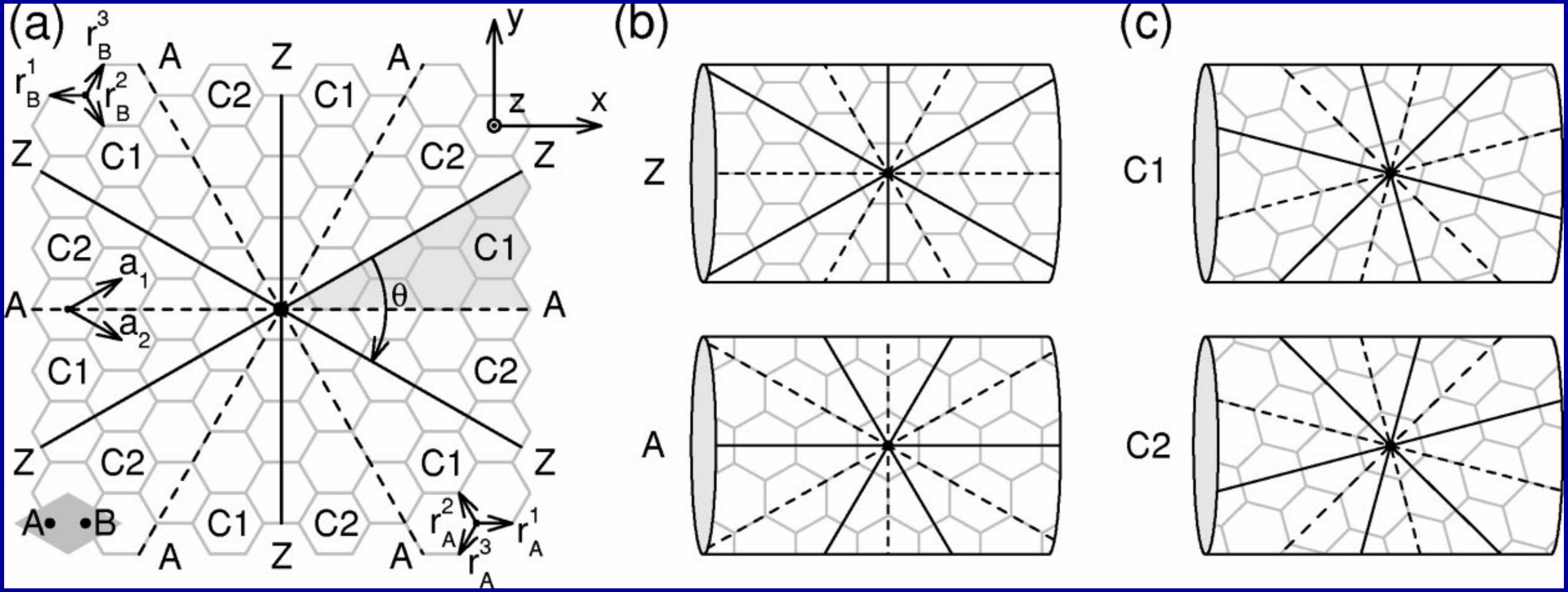
Zhu et al., CPL 412 (2005) 116



(29, 28) @ (36, 31)

Interband optical transitions in left- and right-handed single-wall carbon nanotubes

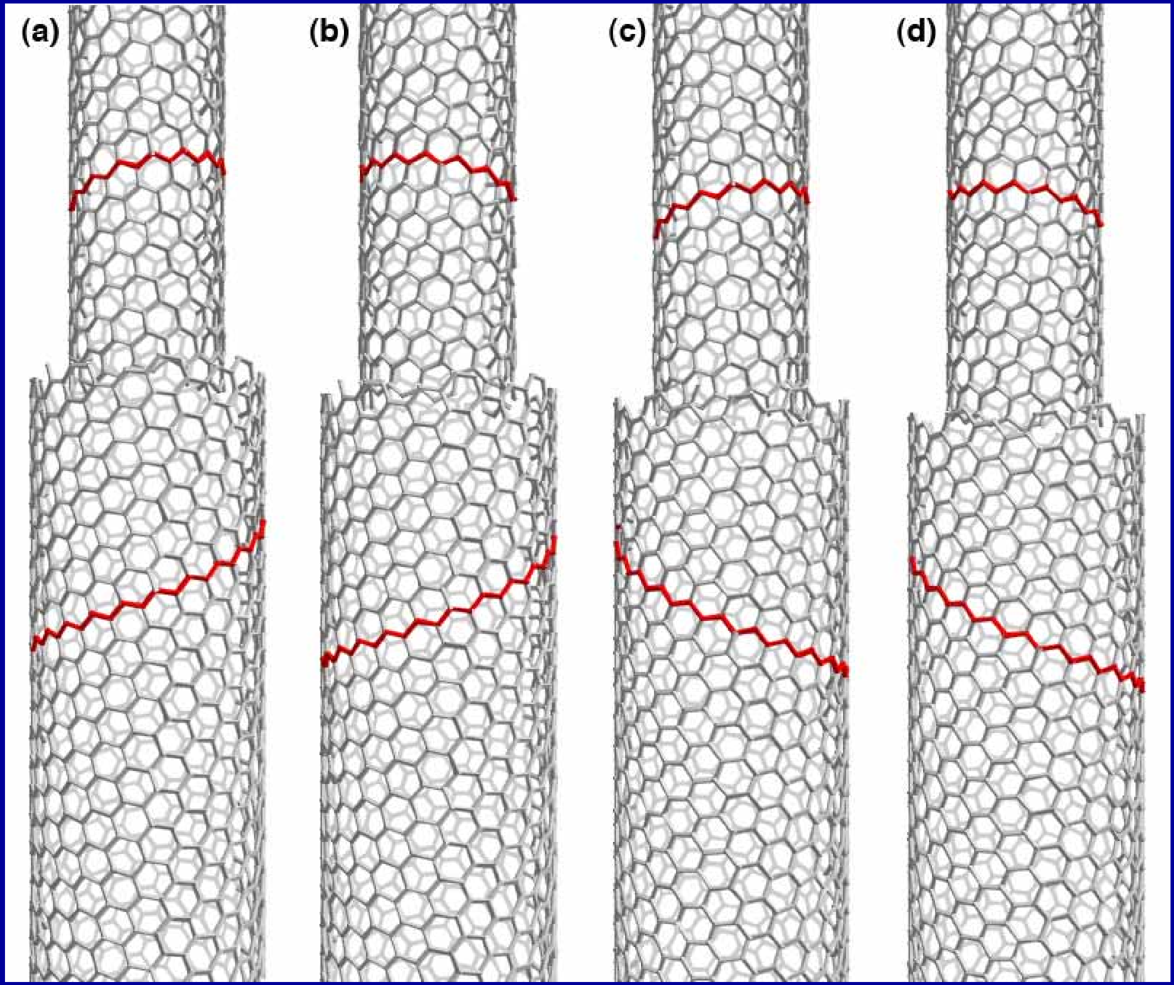
Ge. G. Samsonidze et al., Phys. Rev. B69 205402(2004)



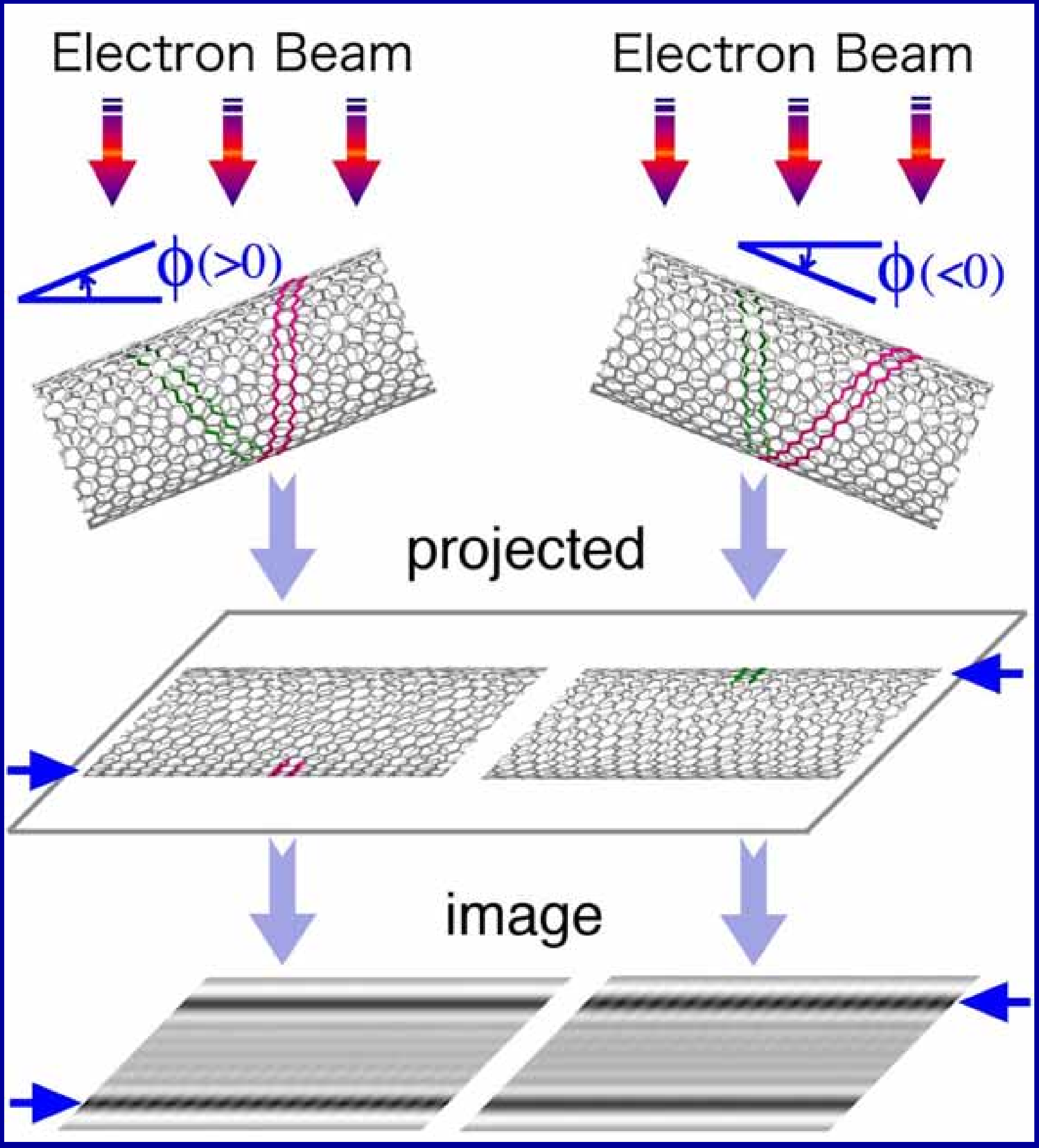
The (n, m) nanotube has a mirror image of (m, n).
Let's define the right handed nanotube when n>m.

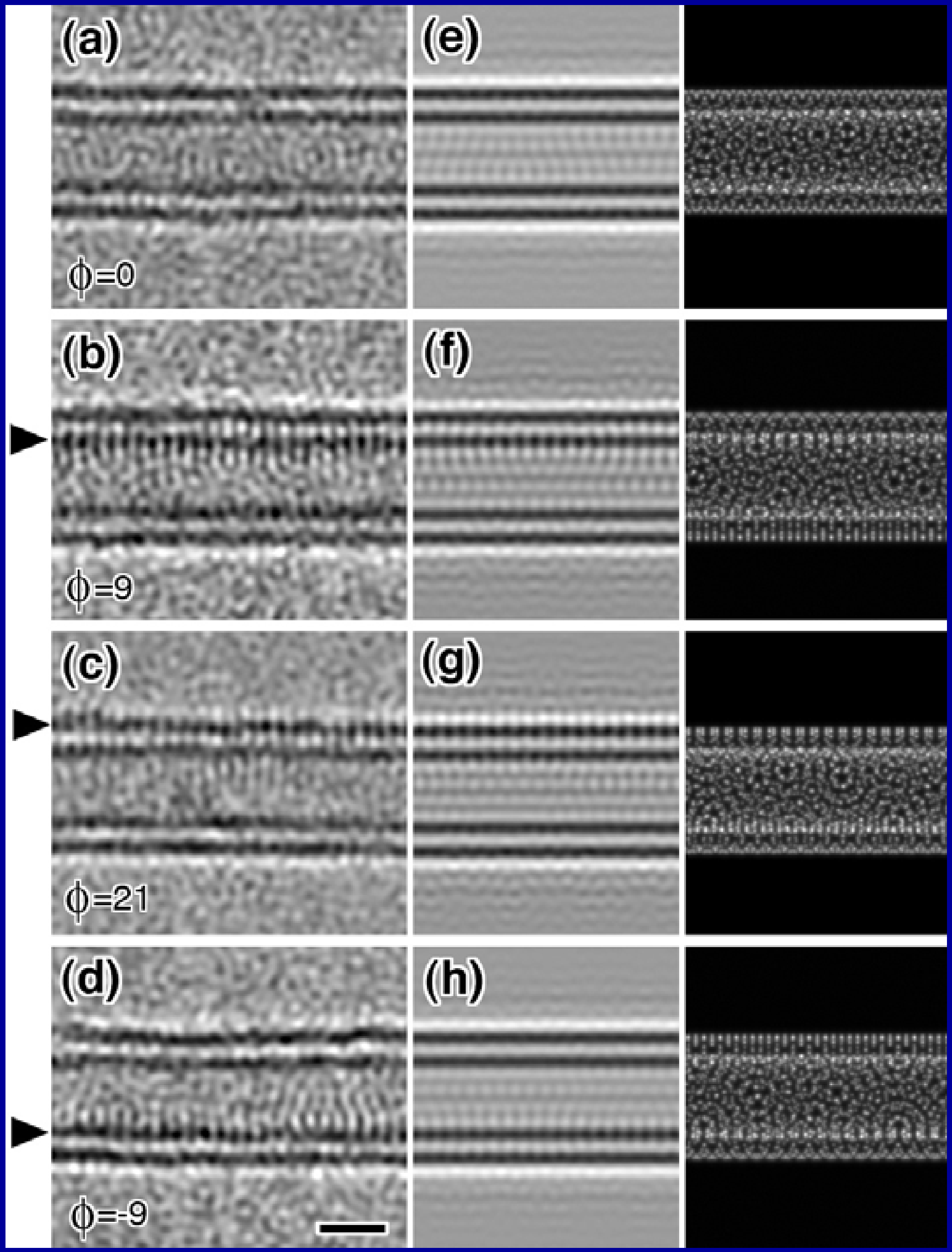
Cf. Wildoer et al., Nature (1998), Mayer et al., J. Micors. (2003),

Four combinations of different optical isomers in a chiral DWNT



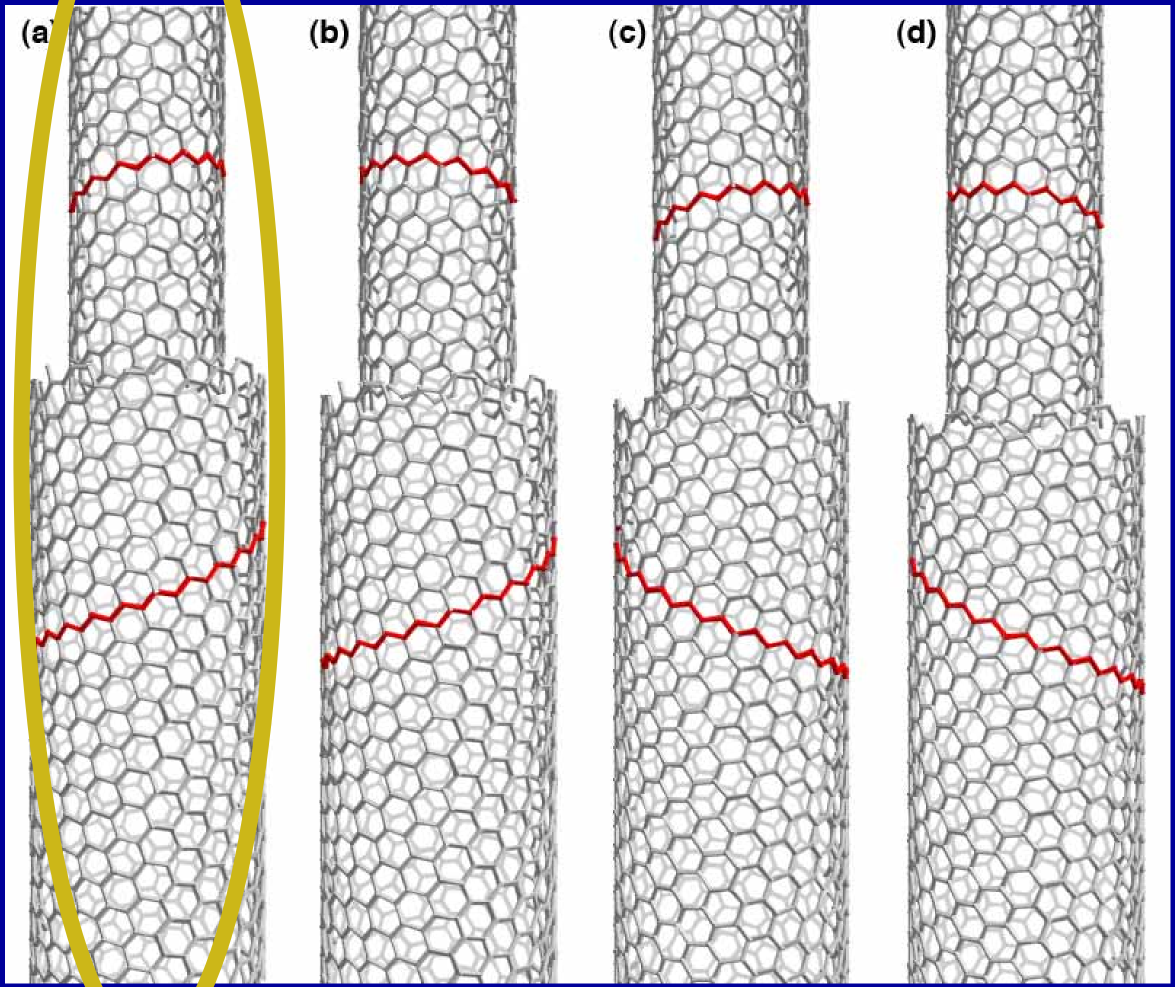
(a) (14, 3)@(17, 10)
(b) (3, 14)@(17, 10)
(c) (14, 3)@(10, 17)
(d) (3, 14)@(10, 17)


Electron Beam
Electron Beam
ϕ(>0)
ϕ(<0)
projected
image



(14,3)@(17,10)

Four combinations of different optical isomers in a chiral DWNT



(a) (14, 3)@(17, 10)
(b) (3, 14)@(17, 10)
(c) (14, 3)@(10, 17)
(d) (3, 14)@(10, 17)

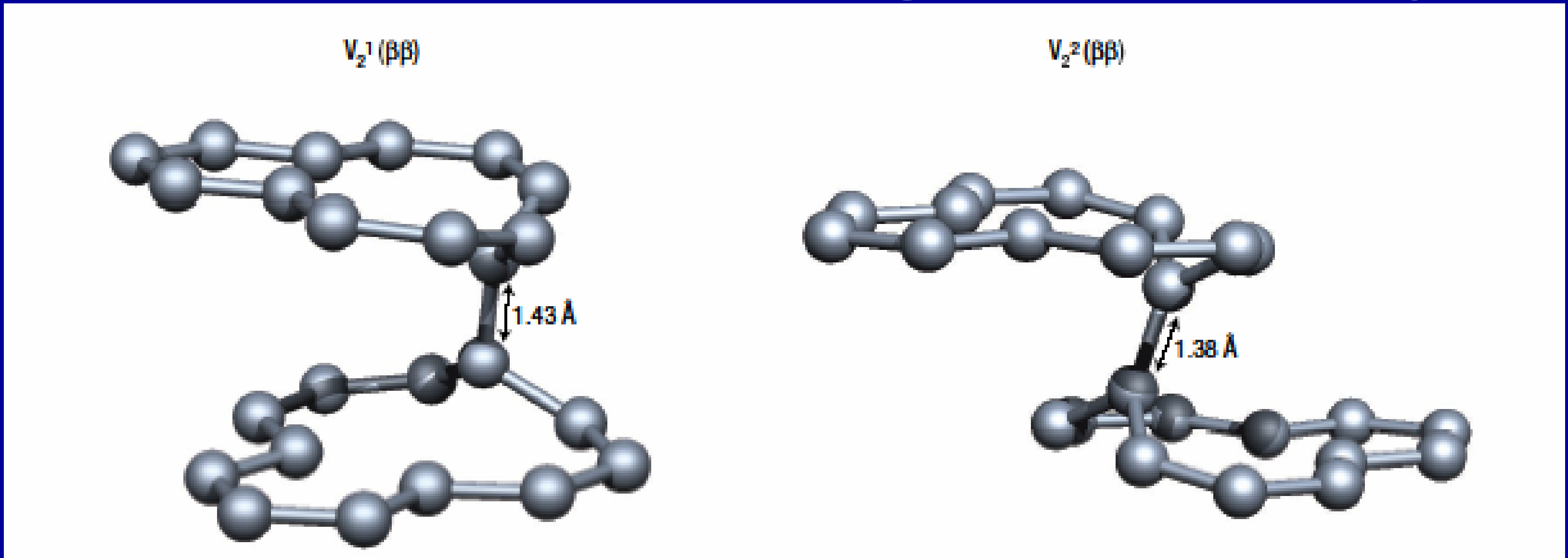
Handedness relationship in DWNT

DWNTs with the same handedness (R@R or L@L) are more likely to be found. Not randomly formed!?

Specimen	Inner nanotube	Outer nanotube
1	R	R
2	L	L
3	L	L
4	L	L
5	R	R
6	R	R
7	L	R
8	L	L
9	R	L
10	L	R
11	L	L
12	L	L
13	R	R
14	R	L
15	R	R
16	L	L
17	unidentified	R
18	unidentified	R

Hetero (R@L or L@R) /Homo (R@R or L@L) ~4/16

Atomic defects in graphene layers



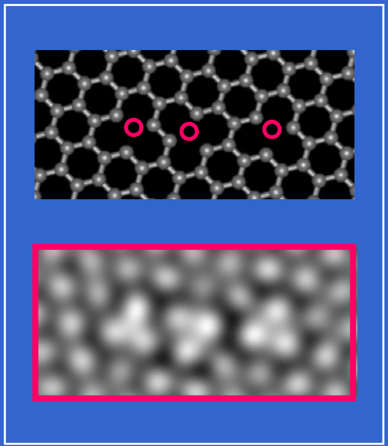
R. Telling et al., Nature Mat. (2003)

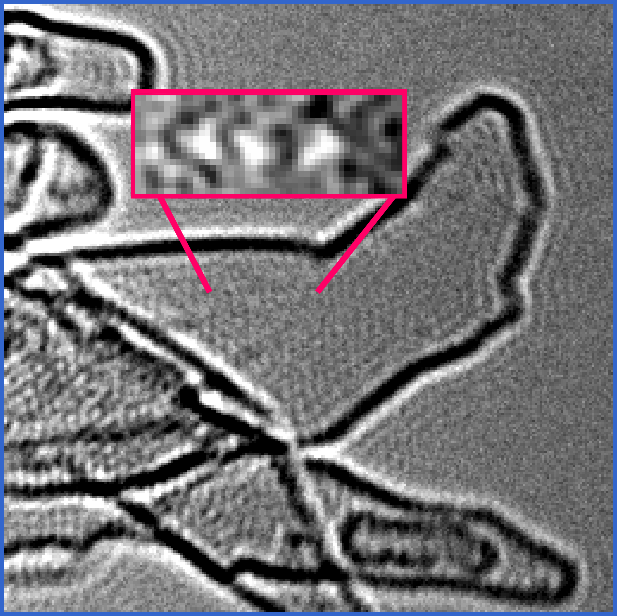
- Topological defect (5-7 pair through the Stone-Wales process)
- Atomic vacancy
- Adatom
- Inter-lay
- Combina

Knock-on displacement of carbon atoms
due to the energetic particles (electron beam)
At 120 kV electrons

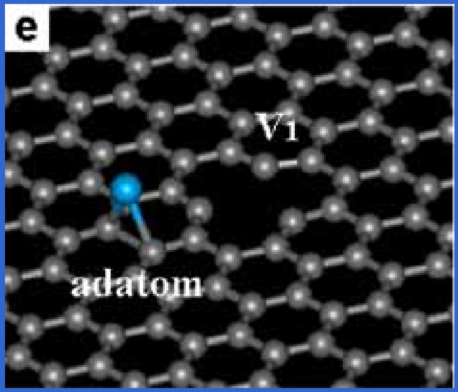
have been predicted by theory.

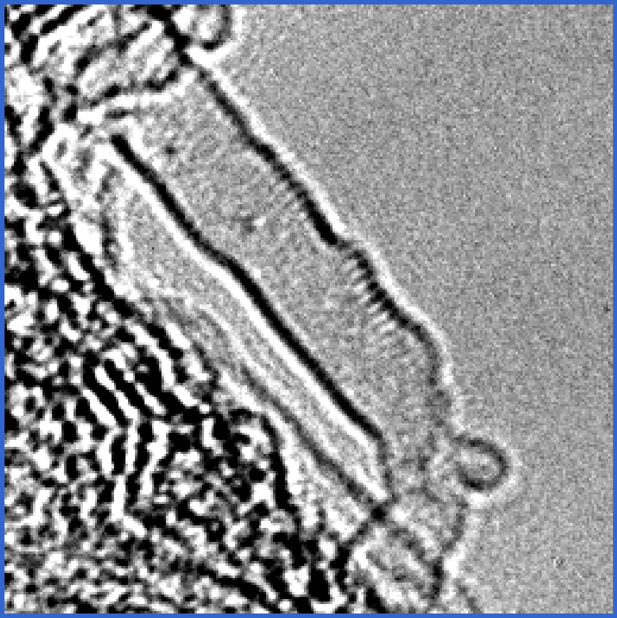
Mono-vacancy

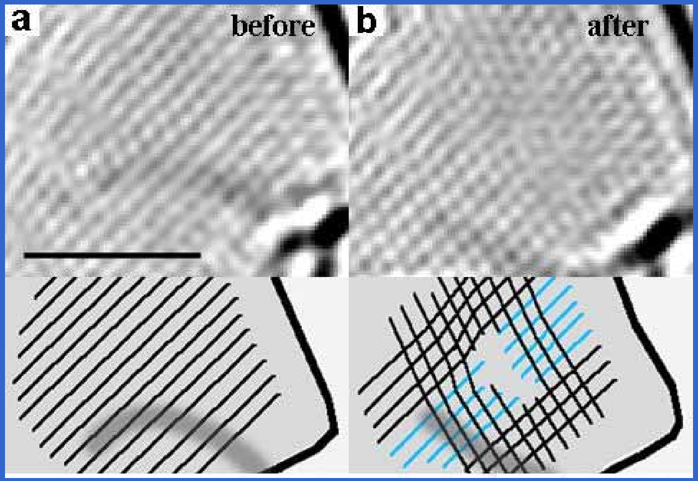


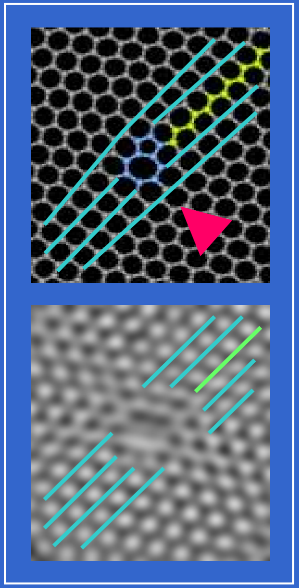


Vacancy-adatom pair







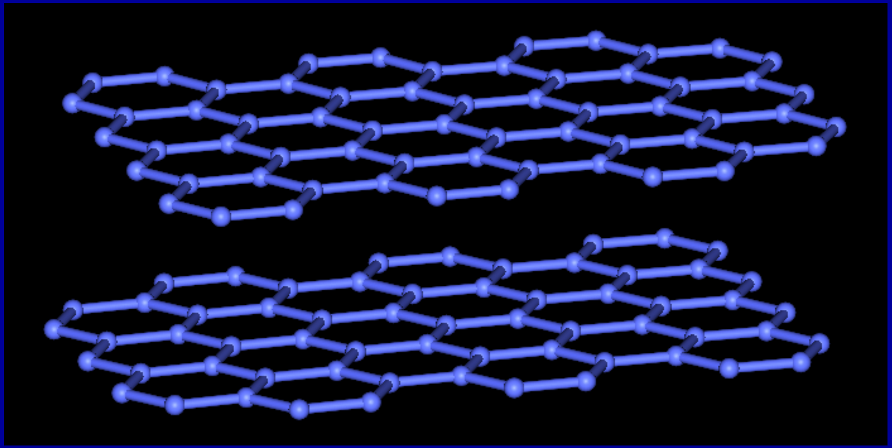


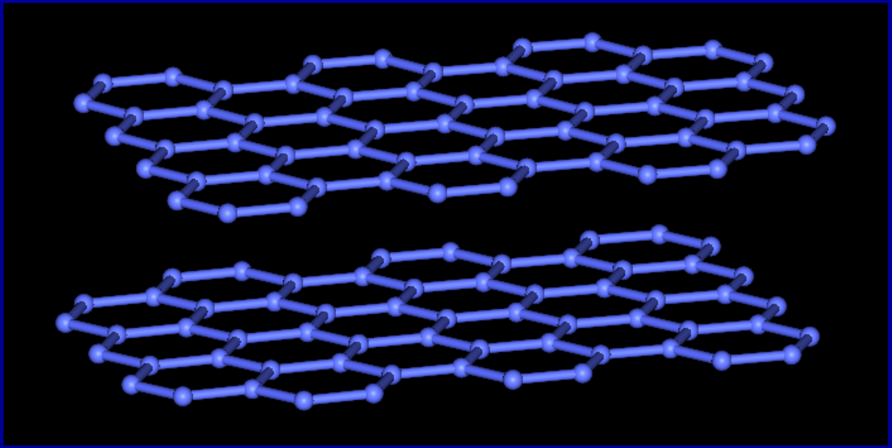
Topological defects

Nature 430(2004) 870

Formation and annihilation of inter-layer defects

A single interstitial and vacancy pair (I-V pair)





A couple of interstitial and vacancy pairs: a divacancy and a cluster of two interstitial atoms

Defect formation frequency during electron microscopic observation

Electrons accelerated at 120 kV

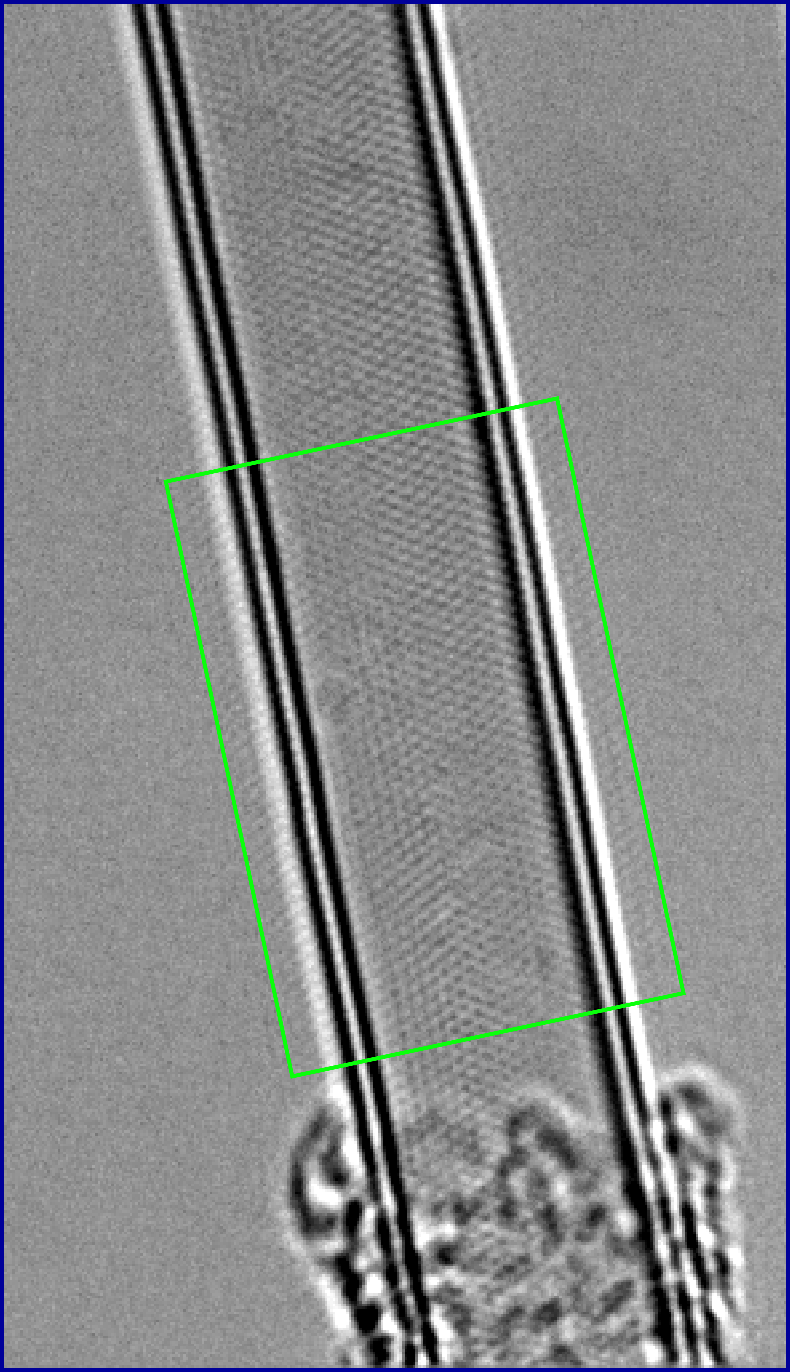
60,000 electrons / nm^2 in a second

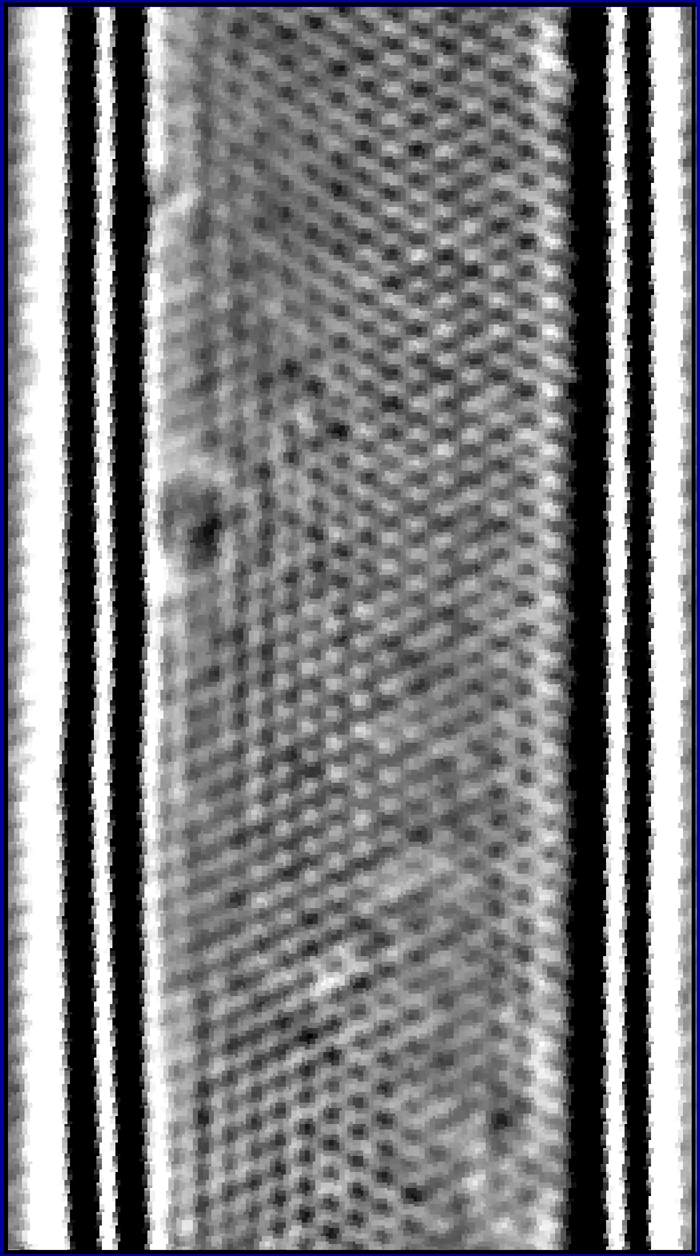
300 seconds dose

↓

0.3 defects per nm^2

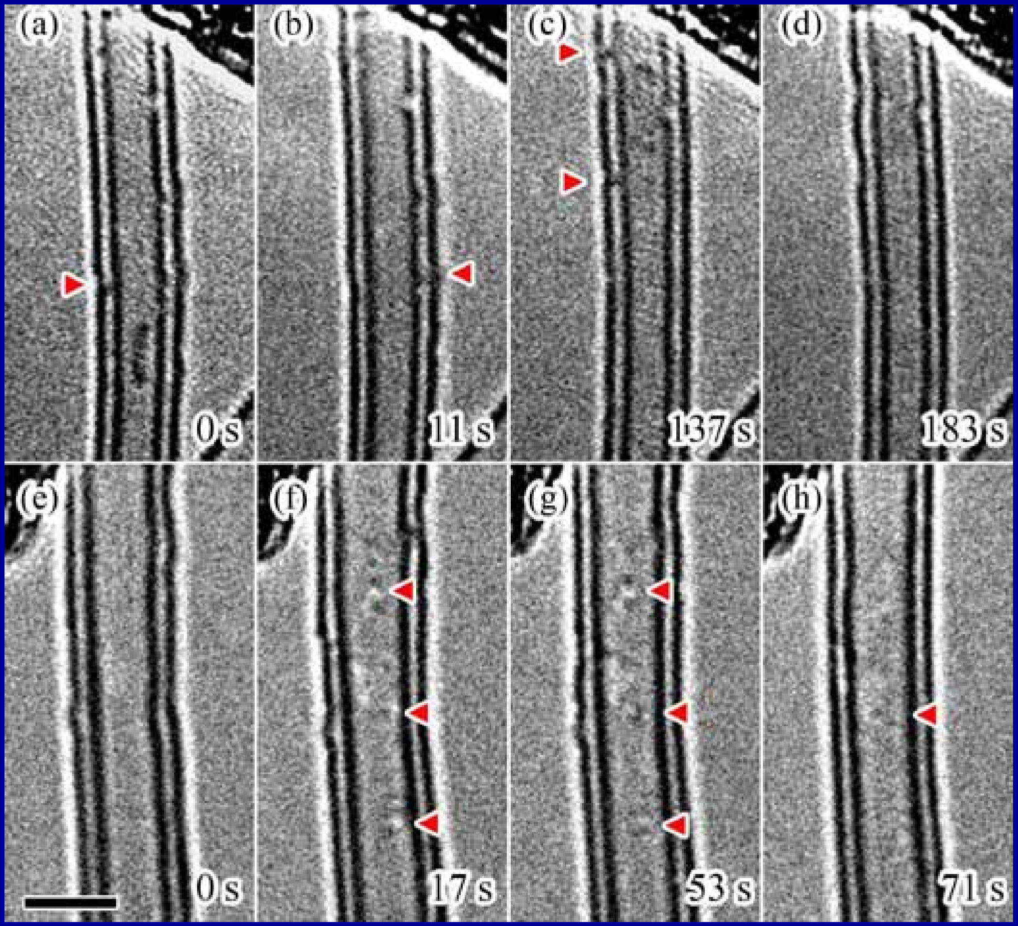
160 barns (estimated cross section for atomic displacement)
(180 barns predicted at 100kV)





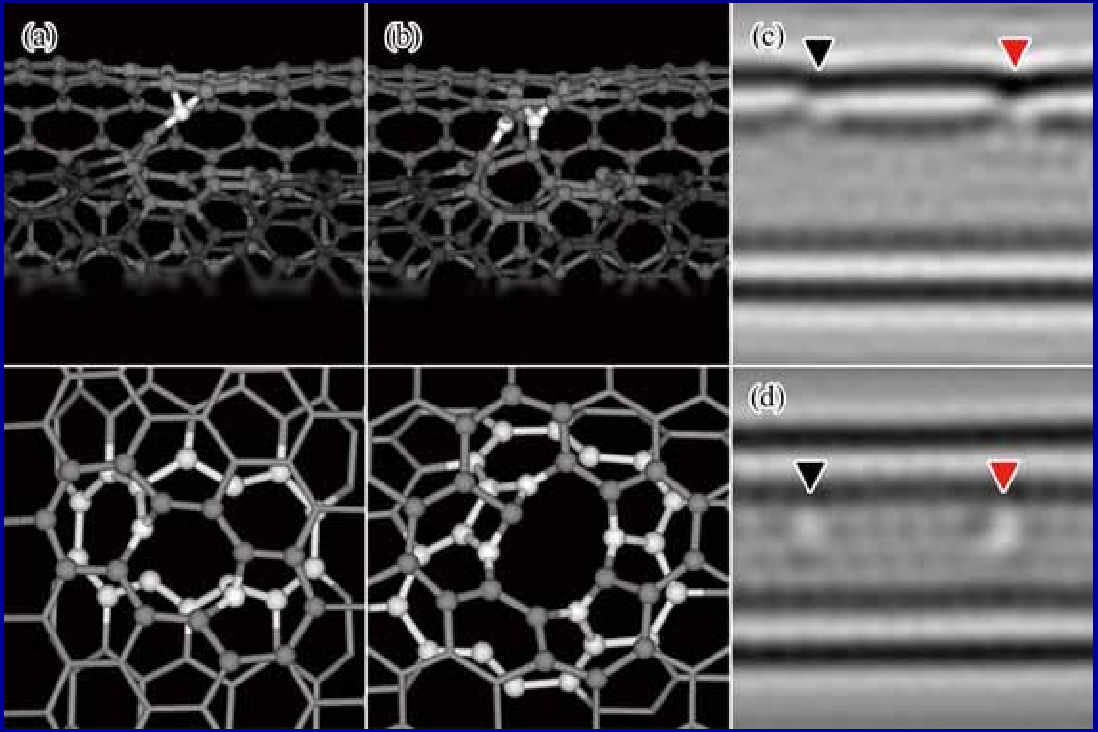
(29, 28) @ (36, 31)

Inter-layer defects in bi-layer graphen (DWNT)



523K

Structural models for the interstitial and vacancy pair defect

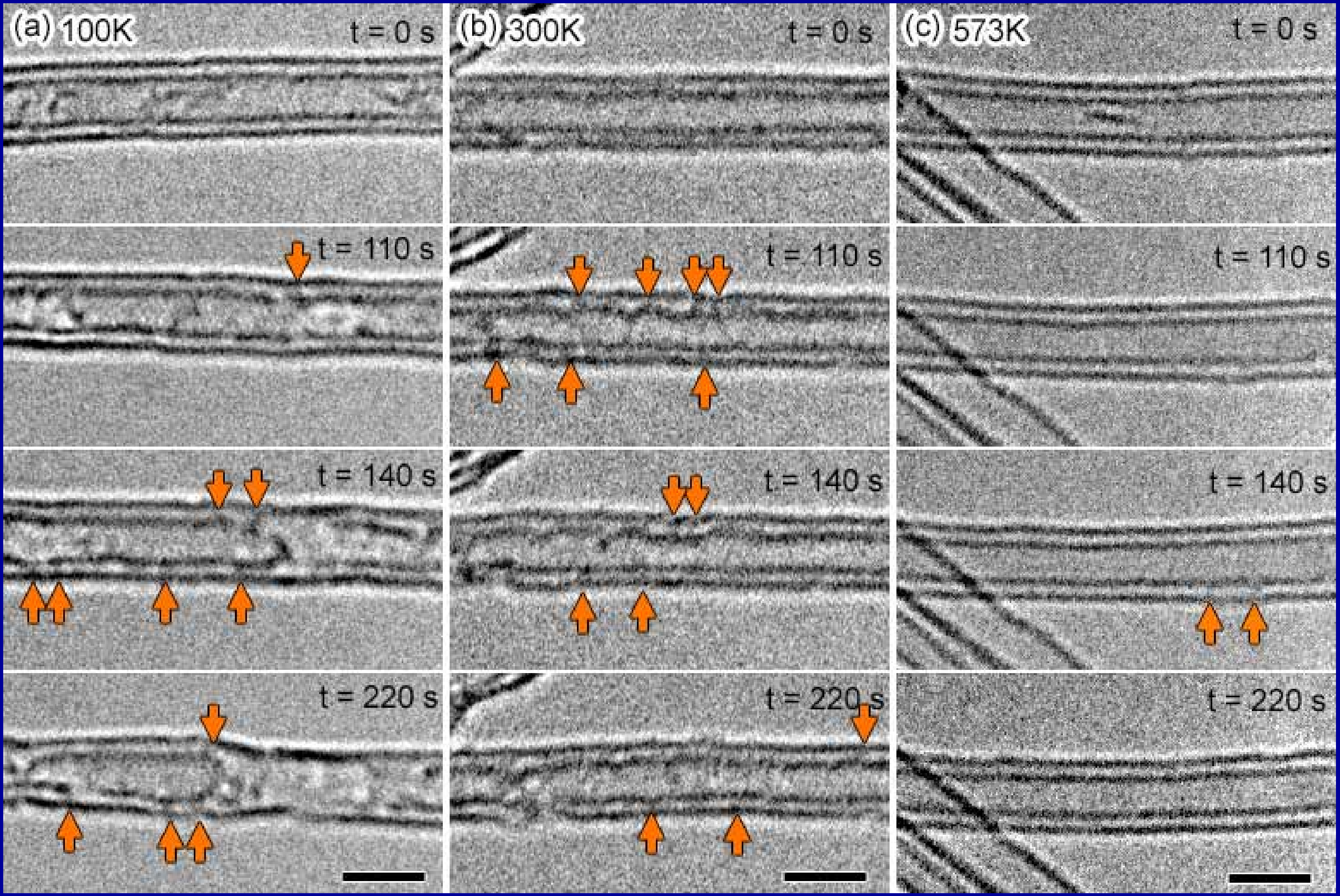


(a) A single I-V pair
(b) A couple of I-V pairs
(c) Simulation in side-view
(d) Simulation in top-view

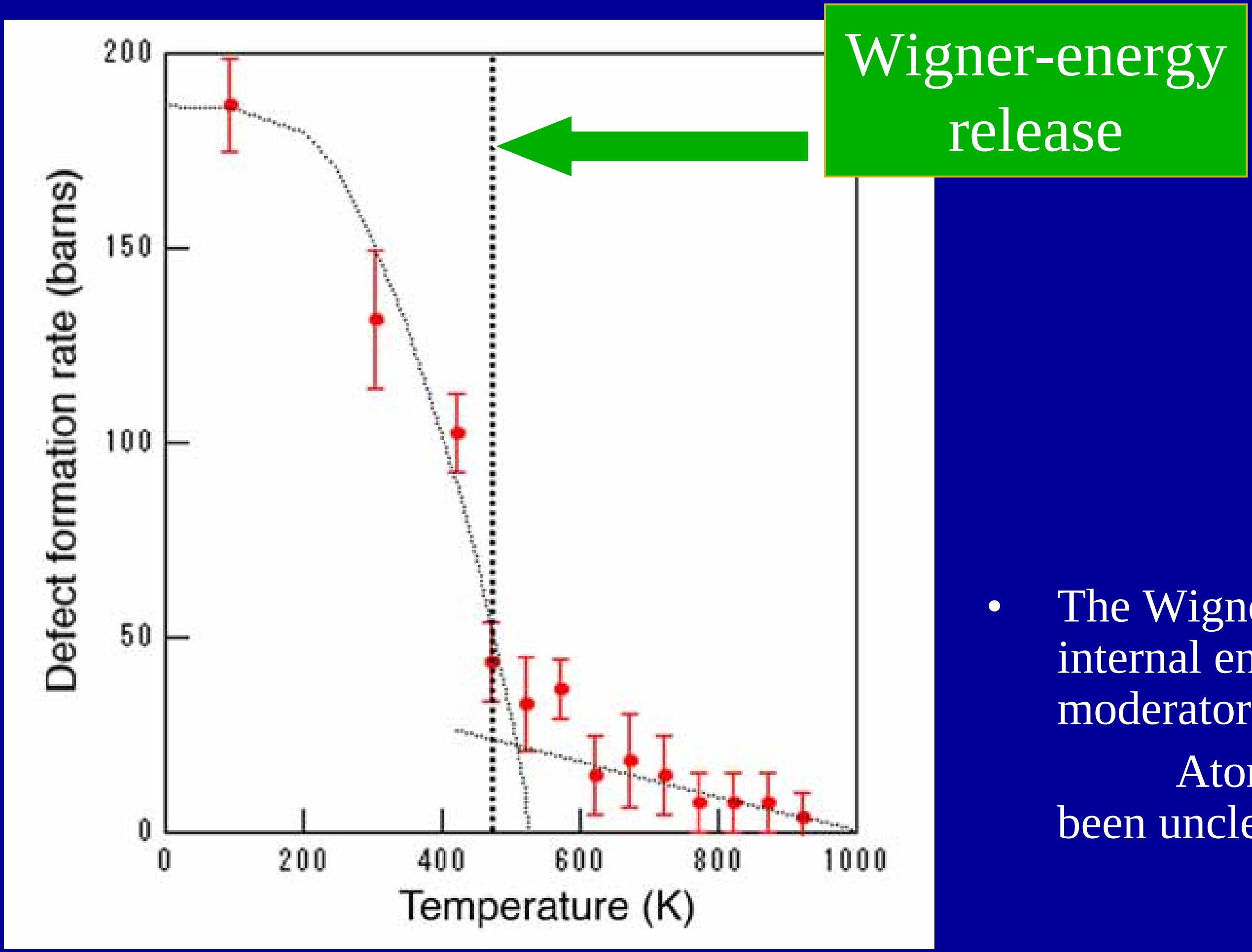
R. Telling et al., Nature Mat. (2003)

Both relaxed by a semi-empirical potential

Temperature dependence for the I-V defect formation



Recombination of I-V pair defects



- The Wigner-effect: an increase of internal energy of graphite moderator after irradiation.

  Atomistic mechanism has been unclear.

The unique structure of individual carbon nanotubes has been finally determined!

- Chirality relationship $(n_1, m_1)@(n_2, m_2)$

  PRL 05(Hashimoto), CPL 05 (Zhu)

- Handedness

  PRL 05(Liu)

- Defect types

  Nature 04(Hashimoto), PRL05(Urita)

- Atomic-level impurities and dopants

  Science 00(Suenaga), PNAS 04(Hashimoto), PRL 05(Guan)

Collaborators

AIST
S. Iijima
Z. Liu
Y. Sato
M. Koshino (JST)
L. Guan
A. Hashimoto
A. Gloter
K. Urita
H. Zhu
H. Wakabayashi
T. Yumura (JSPS)

AIST/NRI
H. Kataura

Nagoya Univ.
H. Shinohara
T. Okazaki
T. Sugai
and others…

Bejing Univ.
Z. Gu
Z. Shi

Tokyo Univ.
E. Nakamura
H. Isobe
H. Yorimitsu

JST/SORST
S. Bandow
K. Hirahara
M. Kociak
K. Ajima
M. Yudasaka