Regensburg, Germany

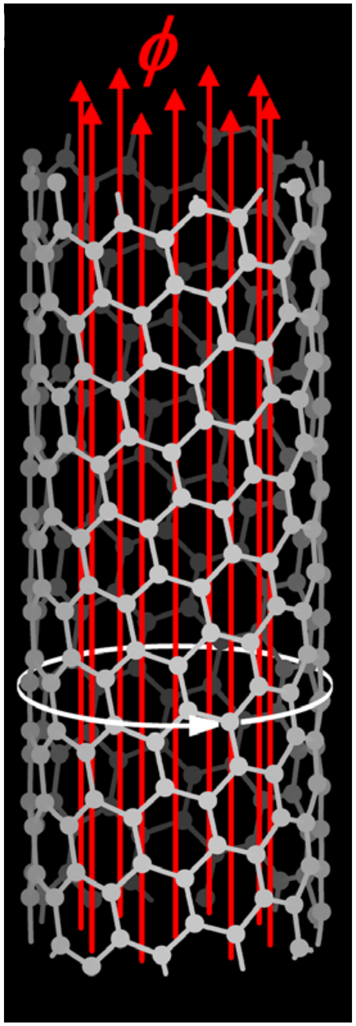
Thursday, September 30, 2005

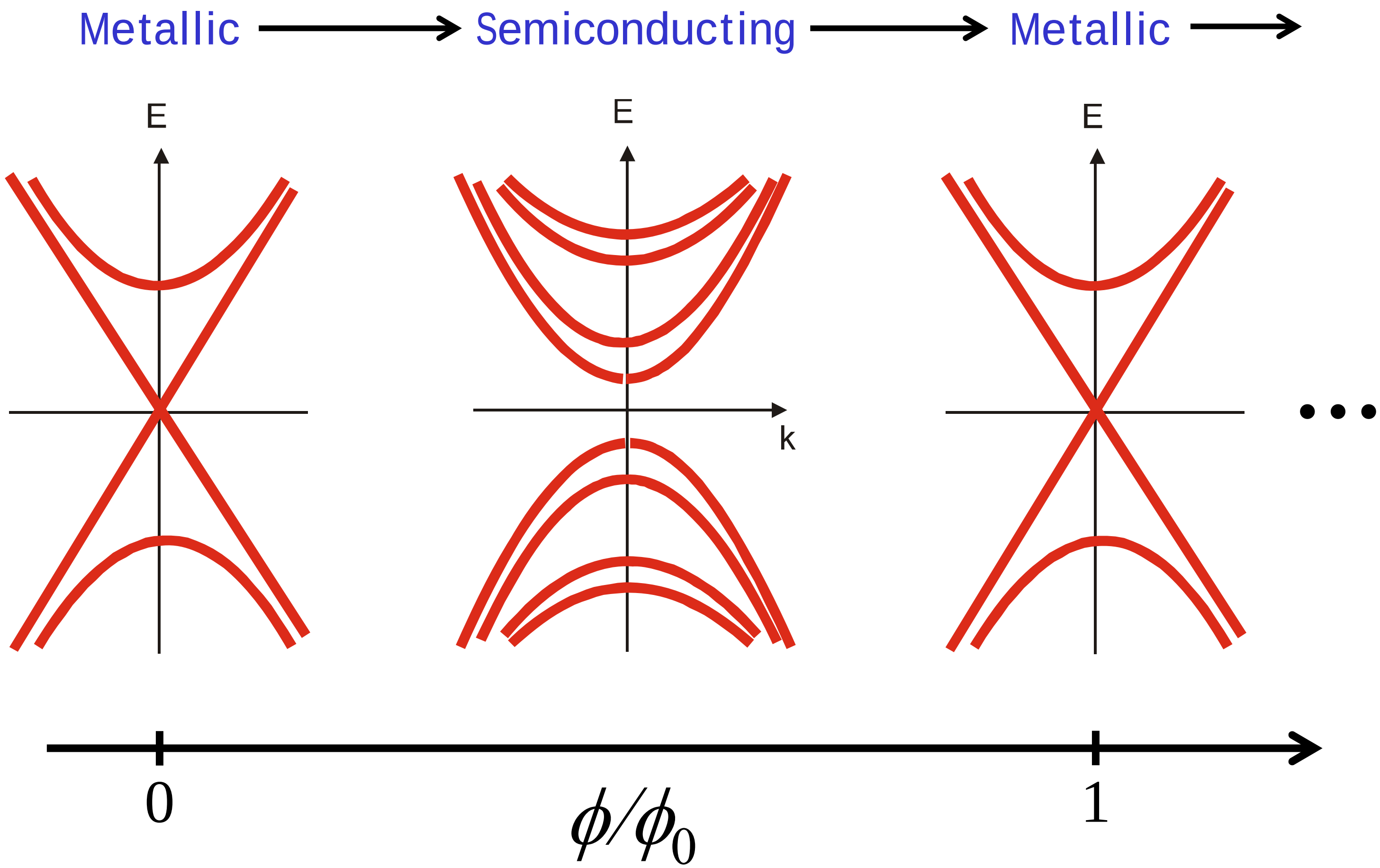
Spectroscopy of Carbon Nanotubes in Ultrahigh Magnetic Fields

Junichiro Kono

Department of Electrical & Computer Engineering, Rice University, Houston, Texas

ϕ_0-Periodic Band Structure





$\phi_0 = h/e = 4.14 \times 10^{15}$ Wb

Ajiki and Ando, J. Phys. Soc. Jpn. **62**, 1255 (1993)

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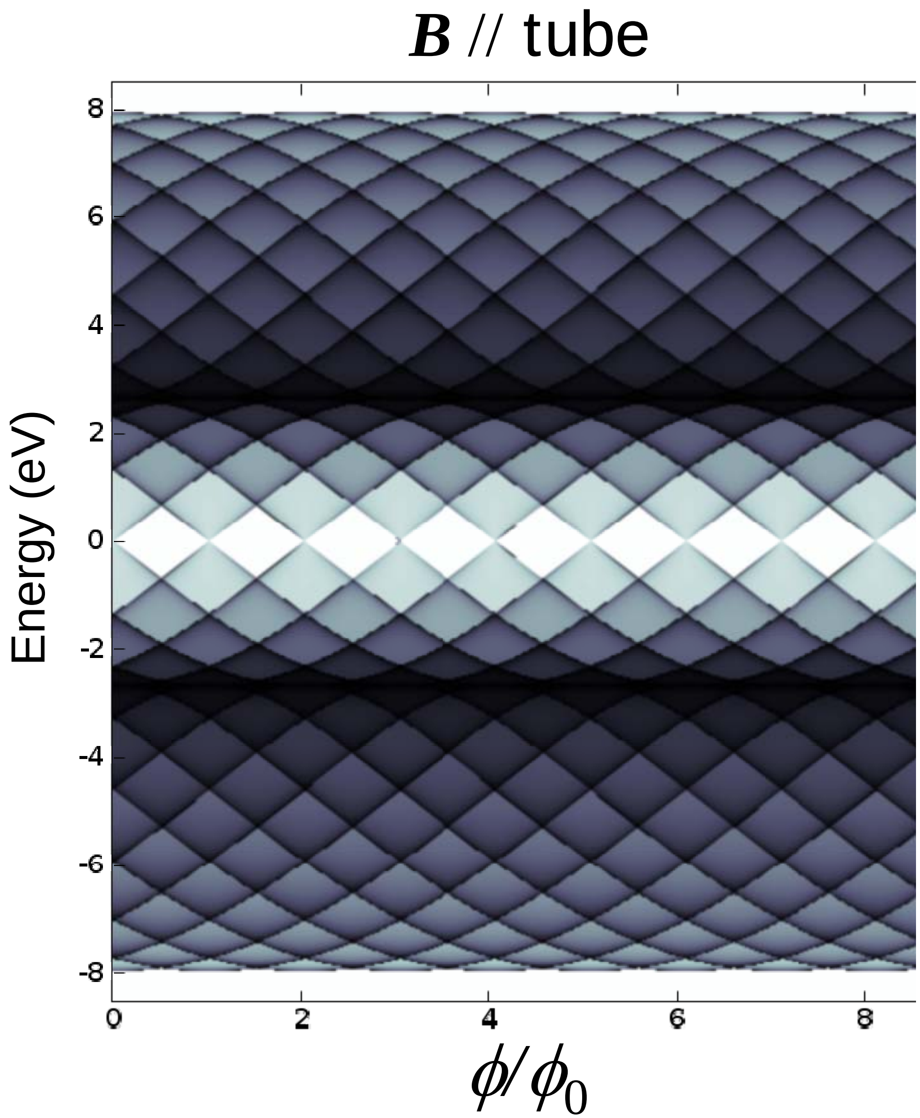
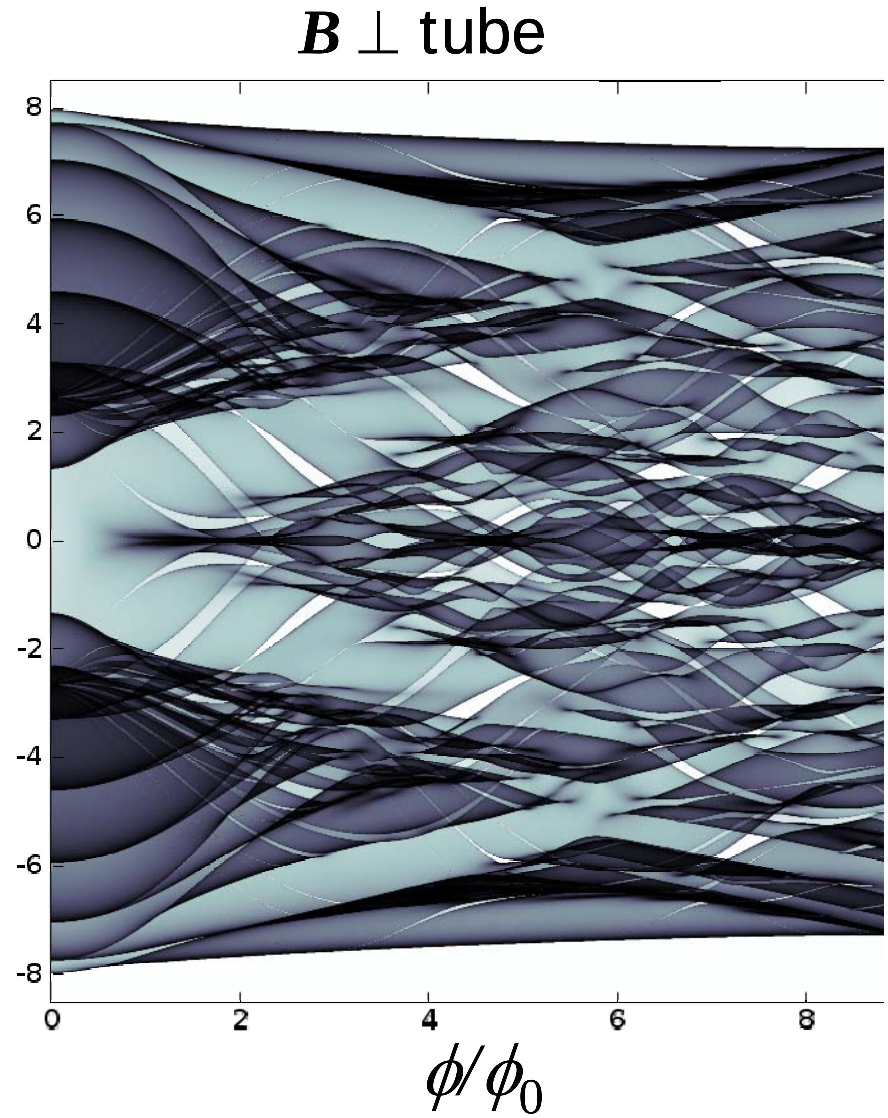
‘Regensburg Butterfly’ in a SWNT





Calculated by Norbert Nemec and Giovanni Cuniberti

ITP, University of Regensburg, D-93040 Regensburg, Germany

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Magneto-Transport in Carbon Nanotubes

Disentangling Aharonov-Bohm Phenomena in Multiwall Carbon Nanotubes

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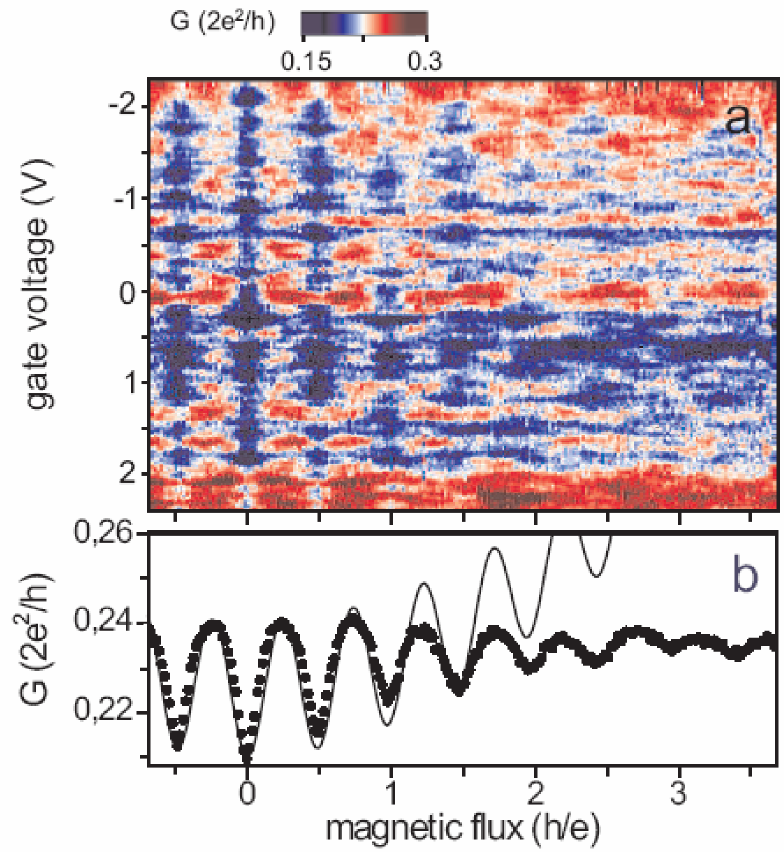
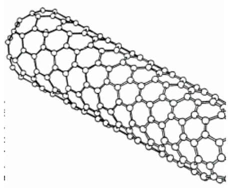
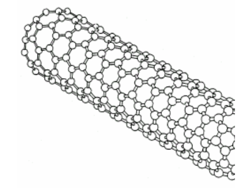
Institute of Experimental and Applied Physics, University of Regensburg, 93040 Regensburg, Germany
†*Commissariat à l'Énergie Atomique, DRFMC/SPSMS, 17 avenue des Martyrs 38054, Grenoble, France*
‡*Institute of Physics of Complex Matter, FBS Swiss Federal Institute of Technology (EPFL), CH-1015 Lausanne, Switzerland*
(Dated: May 13, 2005)

- **Conductance modulations** in multi-walled carbon nanotubes
- Relative contributions between the usual **quantum interference** and the predicted **band gap oscillations**





Outline



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   - **Aharonov-Bohm-phase**-dependent band structure
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   - Magneto-**PL**

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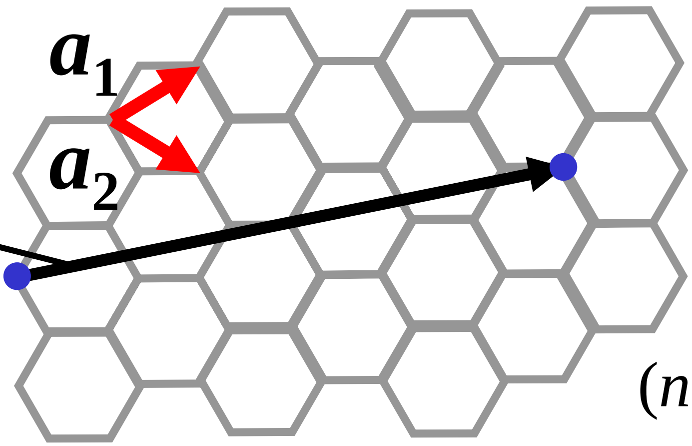
SWNT: Chirality-Dependent Metallicity

Chiral vector:

$$C_h = n\boldsymbol{a}_1 + m\boldsymbol{a}_2$$

$$\boxed{n - m = 3M + \nu}$$

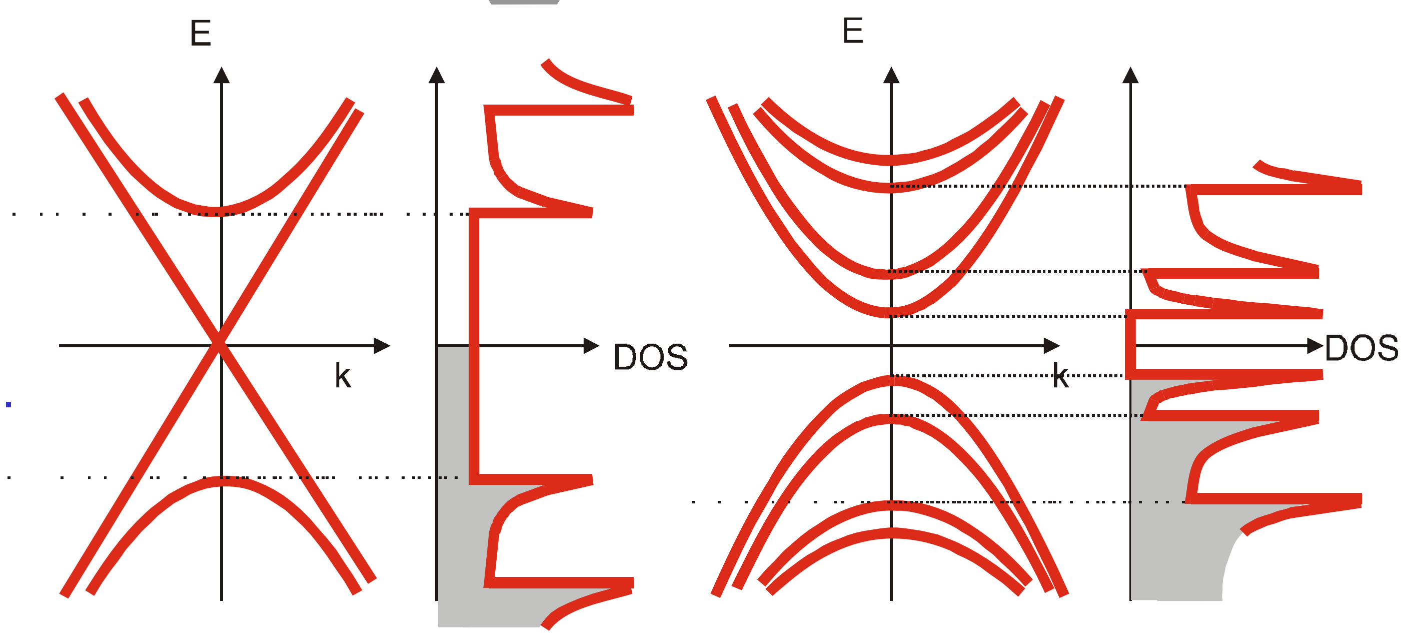


$(n,m) = (4,2)$

1) $M = \nu = 0$
Metal

2) $M \neq 0,\ \nu = 0$
Narrow Gap Semicond.

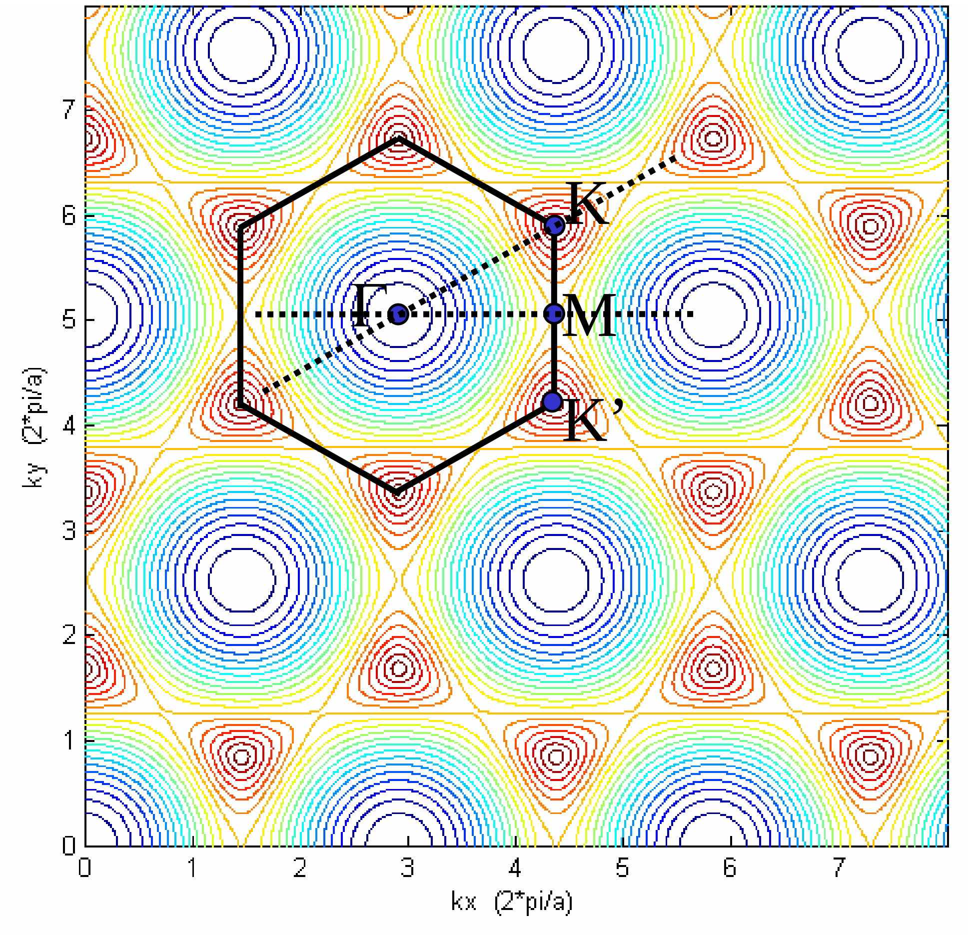
3) $M \neq 0,\ \nu = \pm 1$
Wide Gap Semicond.

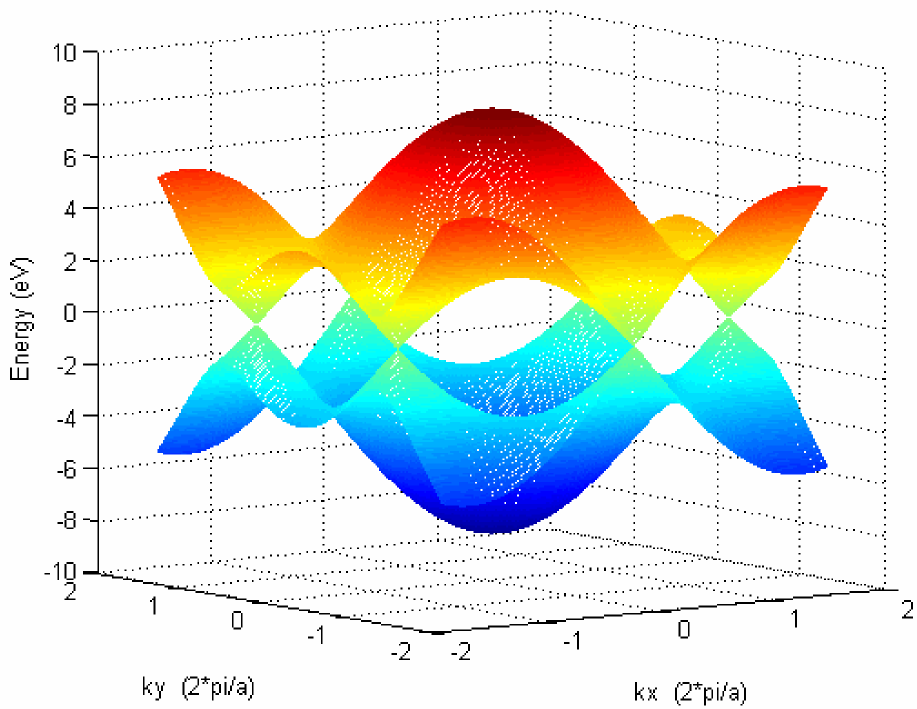


Metallic

Semiconducting

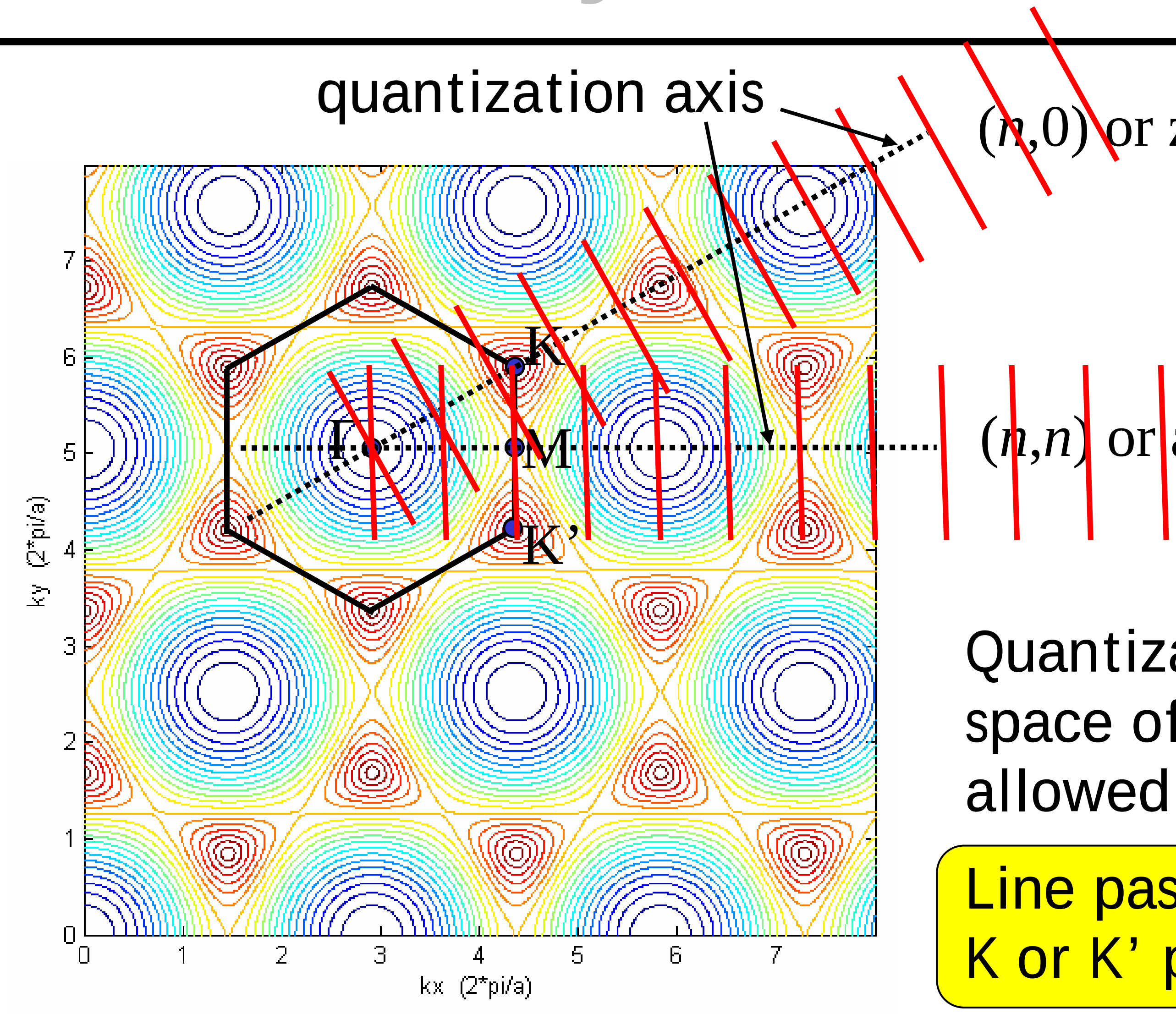
Band Structure of Graphene





2D Graphite: **zero-gap** semiconductor
(E_g = 0 at K and K' points)

Metallicity Criterion for SWNT

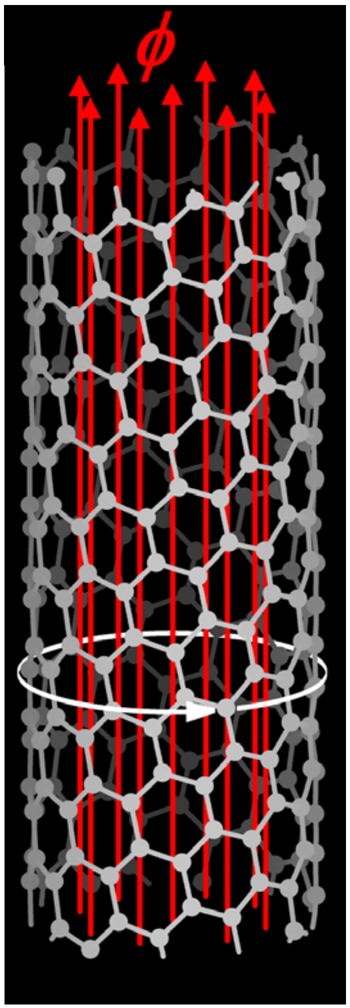


Quantization → **slice up** *k* space of 2D graphite into allowed *k* line segments

Line passing through the K or K' point → metallic

Carbon Nanotubes in Parallel *B*-field: The Aharonov-Bohm Phase

Magnetic Flux ϕ



Bloch theorem: $$\psi_{n\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi_{n\vec{k}}(\vec{r})$$

Periodic boundary cond., *B* = 0

$$\psi_{n\vec{k}}(\vec{r}+\vec{C}_h) = \psi_{n\vec{k}}(\vec{r}),$$
$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$$

$$\vec{k}\cdot\vec{C}_h = 2\pi j,$$
$$j = \text{integer}$$

Quantization condition

When *B* ≠ 0,

$$\psi_{n\vec{k}}(\vec{r}+\vec{C}_h) = \psi_{n\vec{k}}(\vec{r})e^{2\pi i(\phi/\phi_0)},$$
$$\phi = B\pi(d/2)^2,\ \phi_0 = h/e$$

$$\vec{k}\cdot\vec{C}_h = 2\pi\left(j+\frac{\phi}{\phi_0}\right),$$
$$j = \text{integer}$$

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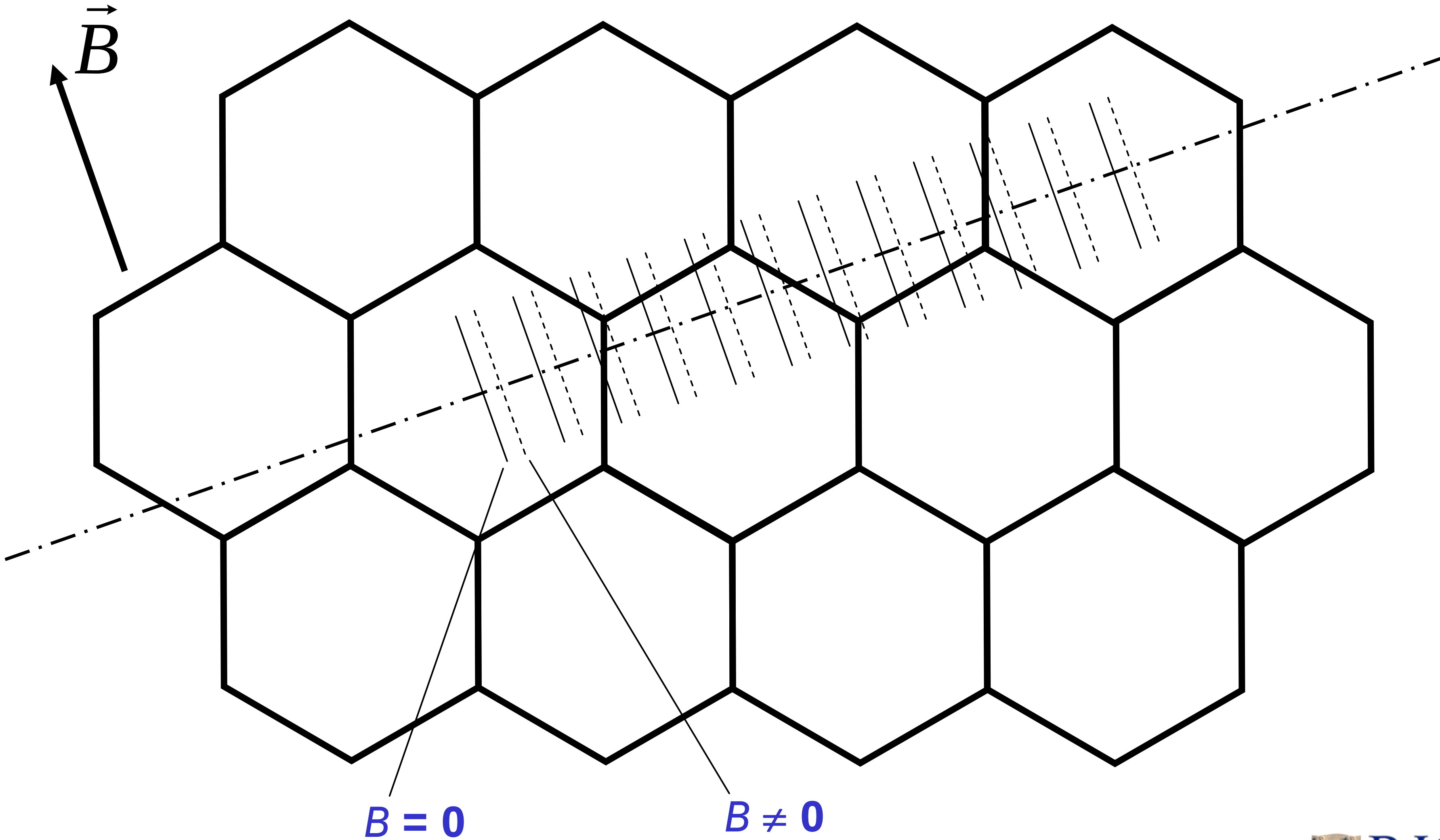
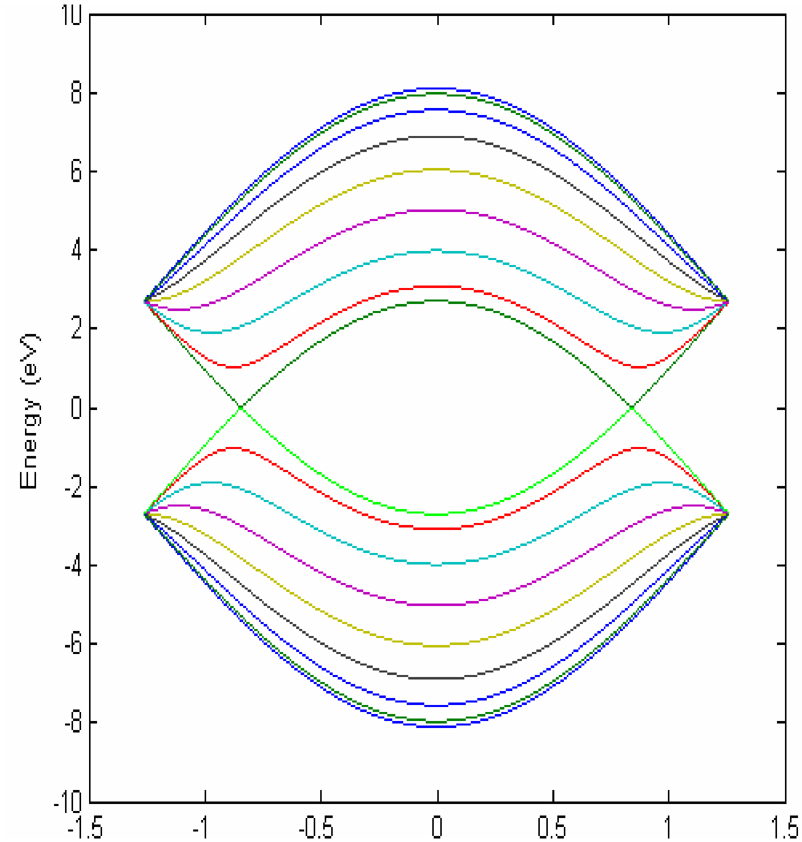
Allowed *k* States



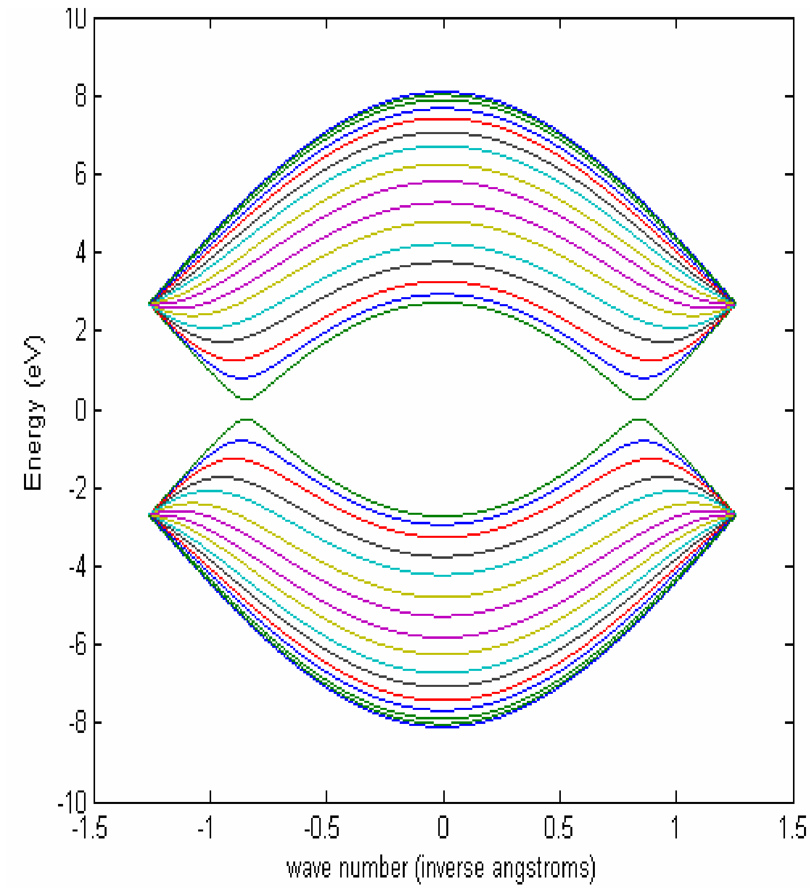
Band Structure of an (8,8) Tube

0 T



Metal

1000 T



Semiconductor
(E_g ~ 0.8 eV)

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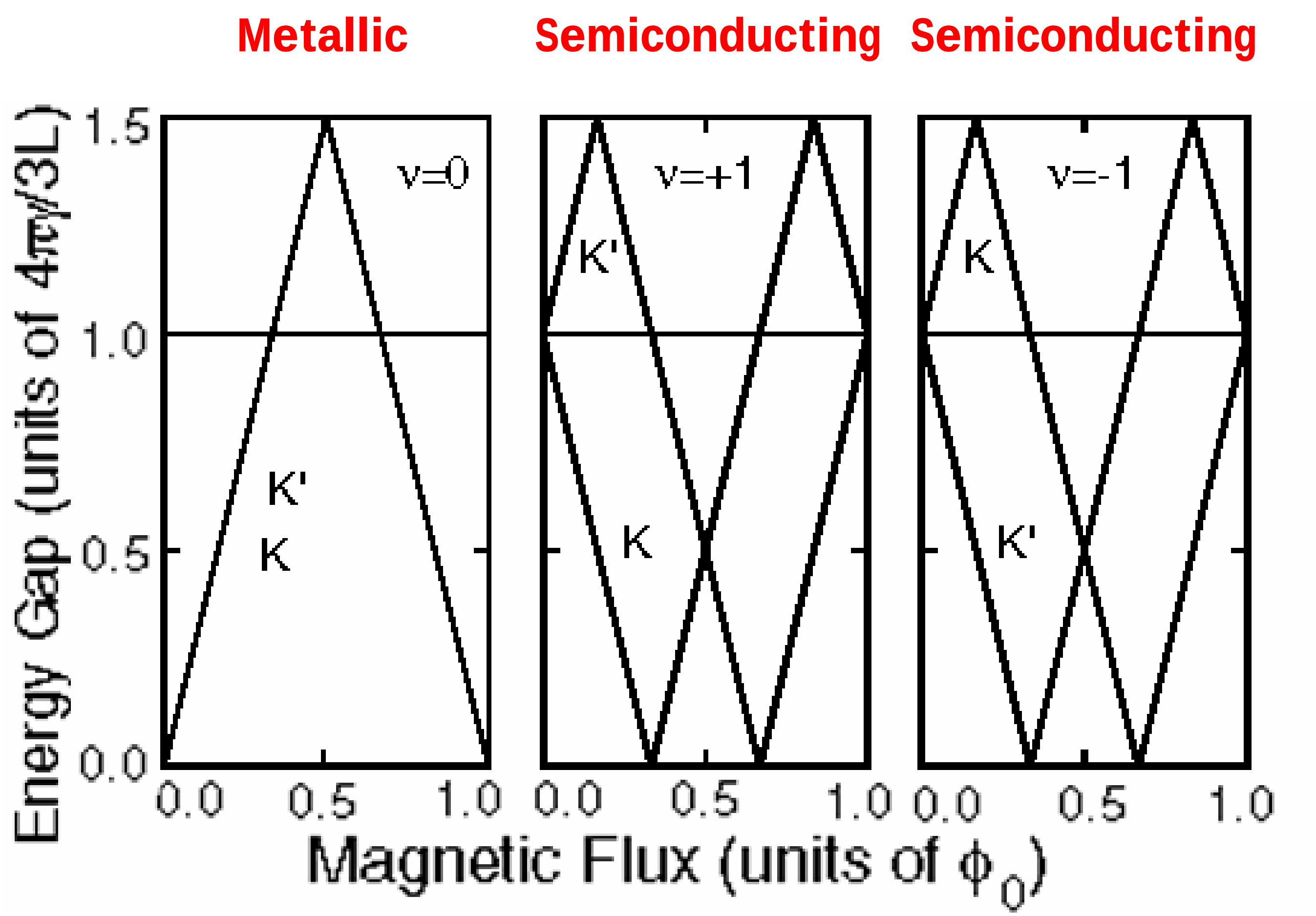
Predicted Aharonov-Bohm Oscillations of Band Gap in SWNT



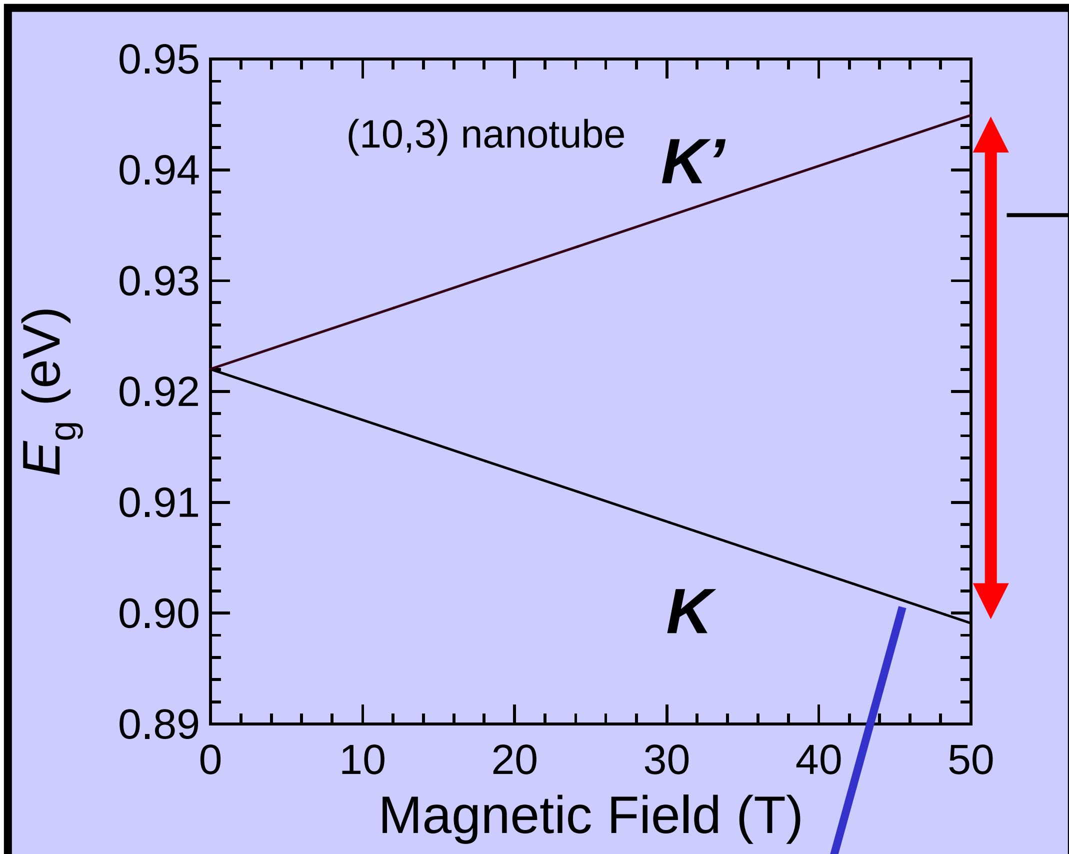
Oscillation period = ϕ_0 = h/e

Consider a tube with d = 1 nm

ϕ/ϕ_0 = 1 requires B ~ 6000 T !!!

H. Ajiki and T. Ando, J. Phys. Soc. Jpn. **62**, 1255 (1993)

Band Gap Shrinkage and the K-K' Splitting



~ 1 meV / T

K-K' splitting:

- Lifted time-reversal symmetry due to *B*
- Onset of the AB band gap oscillations

$$\varepsilon_g(\phi) = \varepsilon_g(0)\left(1 - \frac{3\phi}{\phi_0}\right)$$

: band gap shrinkage

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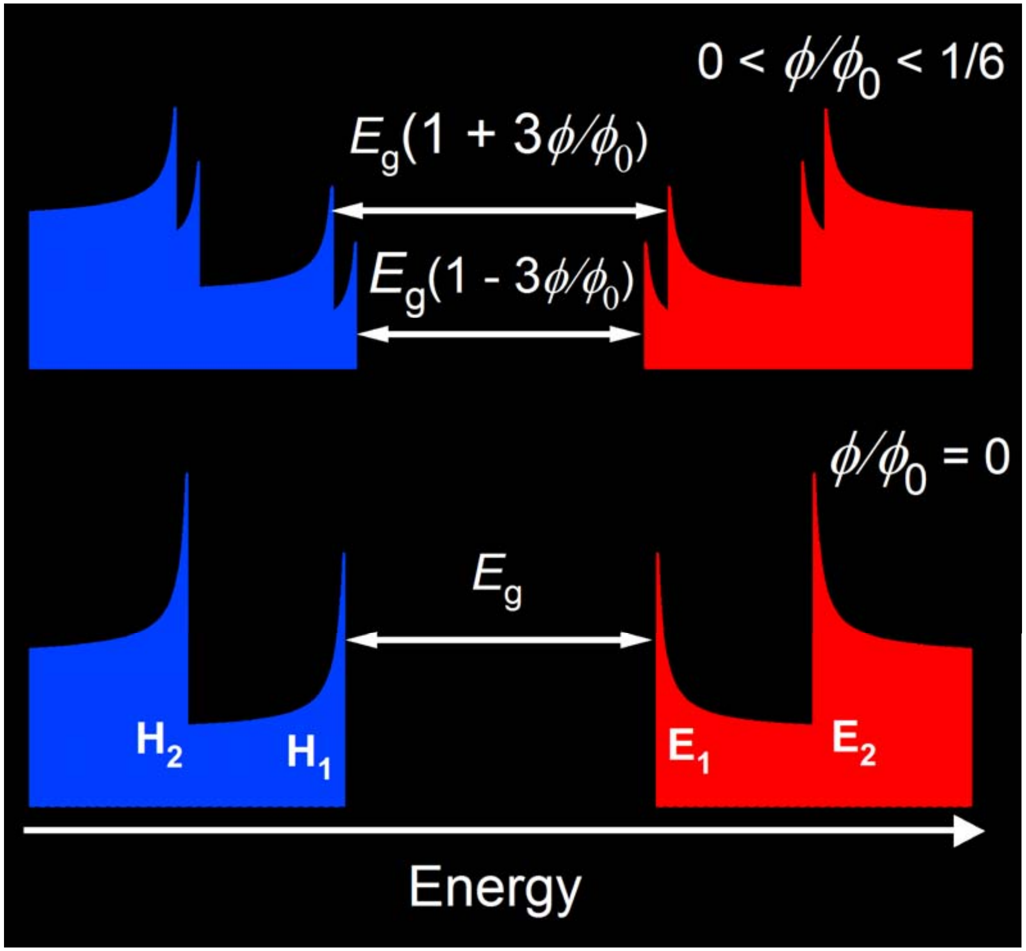
Relevant Energy Scales



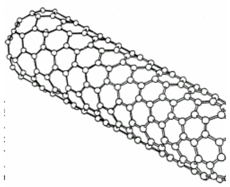
$E_g(0)$ ~ **1 eV**

$\Delta E_{K\text{-}K'}$ ~ **100 meV** at 100 T

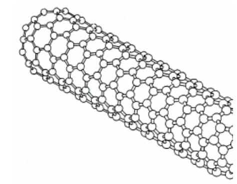
Linewidth ~ **20 meV**

Zeeman splitting ~ **10 meV** at 100 T

$\phi/\phi_0 \sim 10^{-2}$ at 100 T for d = 1 nm



Outline



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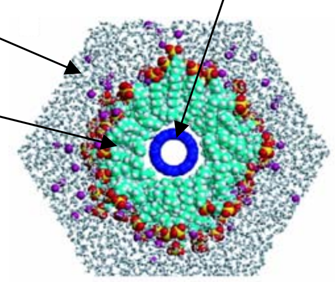
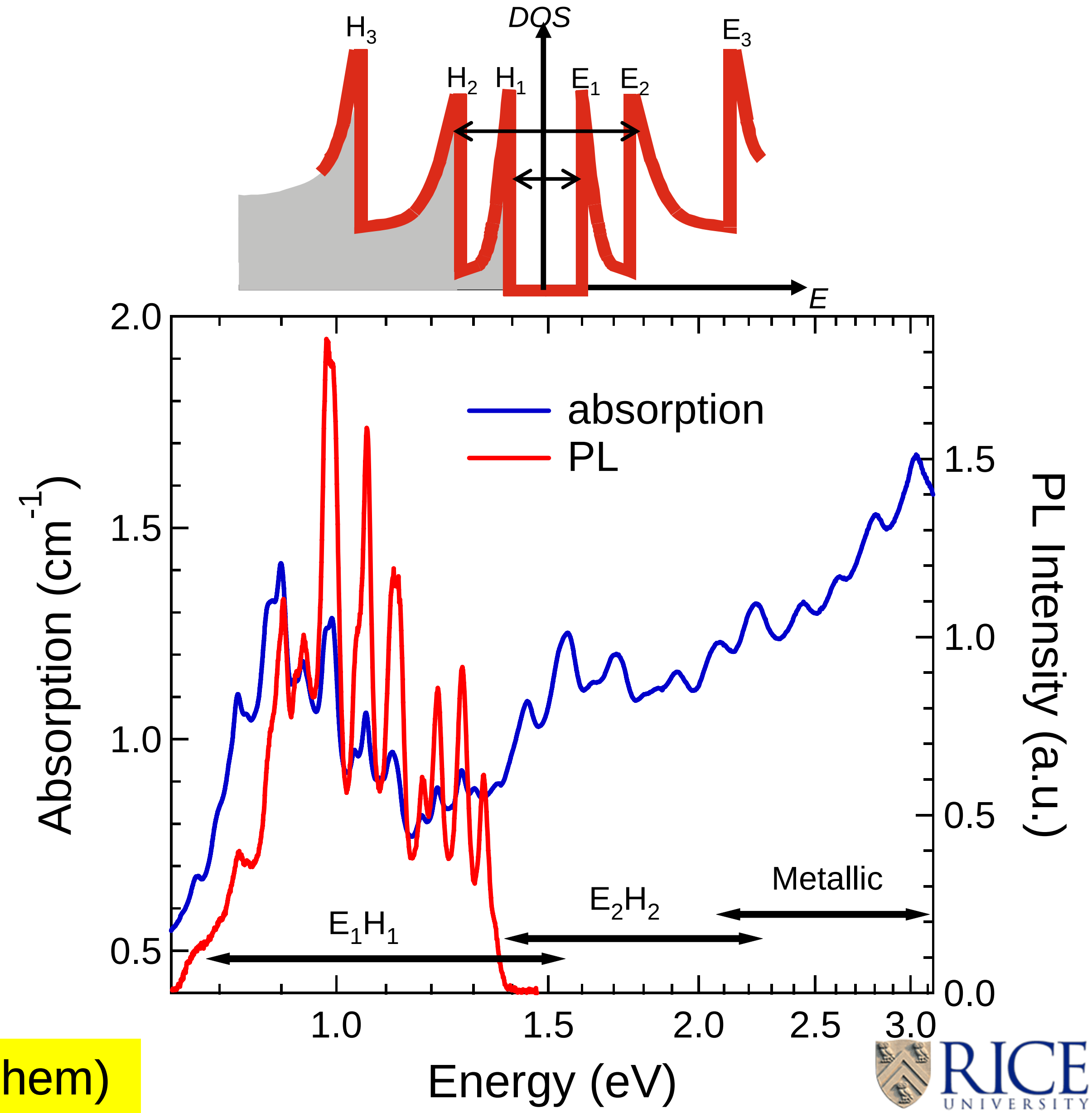
Individually-Suspended SWNTs



O'Connell *et al*., Science **297**, 26 (2002)

Produced by HiPco →
Dispersed in 1% D_2O solution of Sodium Dodecyl Sulfate (SDS) →
Sonicated →
Centrifuged



R.E. Smalley's group (Rice, Chem)

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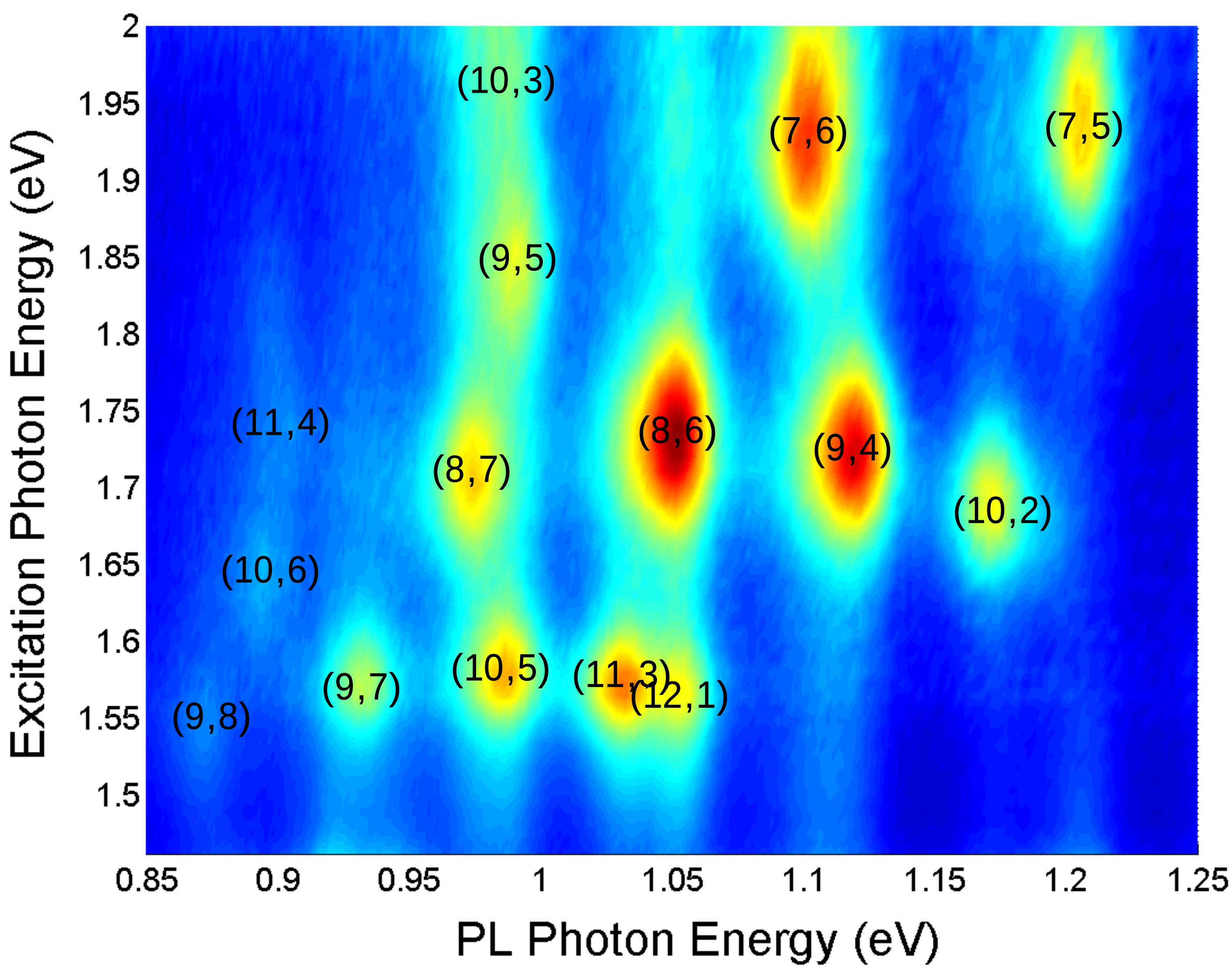
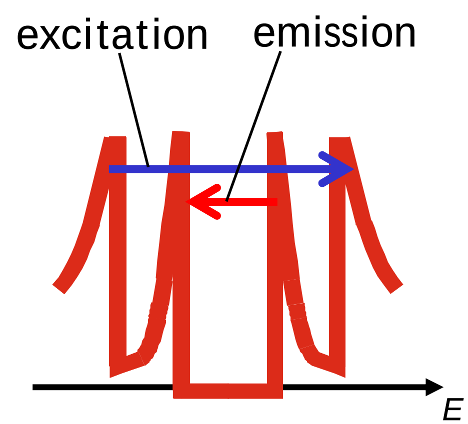
PL Excitation (PLE) Spectroscopy

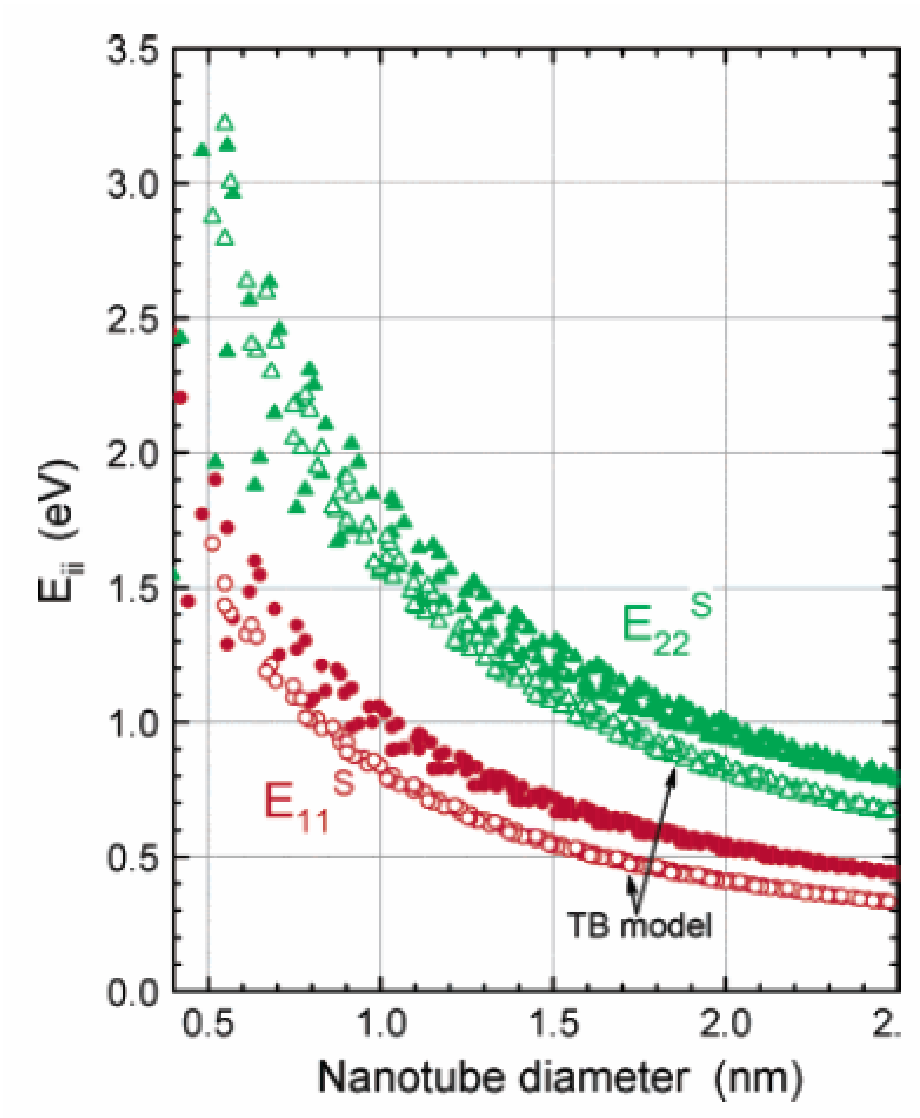


Each **peak** corresponds to particular ***(n,m)***



Excitation Energy vs. Diameter

S. M. Bachilo *et al*., Science **298**, 2361 (2002)



$$\bar{\nu}_{11} = \frac{1 \times 10^7 \text{ cm}^{-1}}{157.5 + 1066.9\, d_t} + \frac{A_1 \cos(3\alpha)}{d_t^2}$$

$$\bar{\nu}_{22} = \frac{1 \times 10^7 \text{ cm}^{-1}}{145.6 + 575.7\, d_t} + \frac{A_1 \cos(3\alpha)}{d_t^2}$$

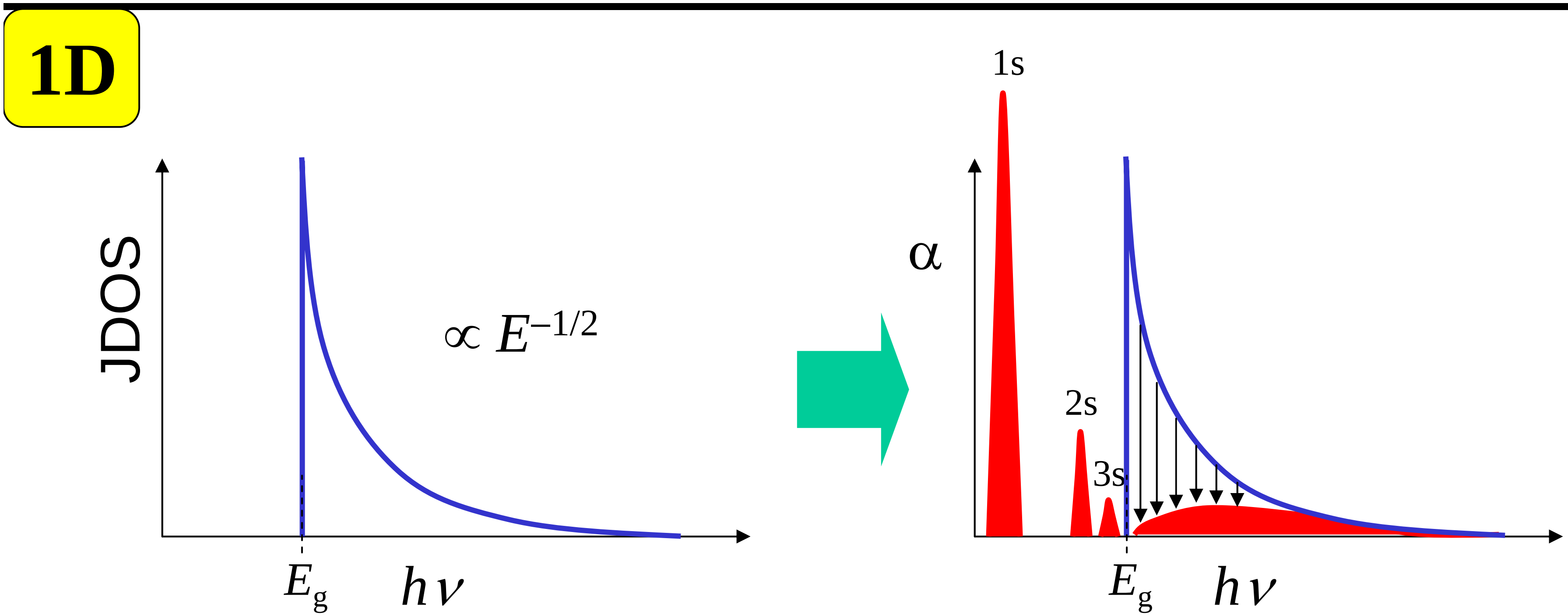
Experimental band gaps

$\vee$

Tight binding band gaps

???

Excitons



- Huge binding energy → extremely stable
- Lineshape: 1-D VHS (asymmetric) → 1-D excitons (symmetric)
- Sommerfeld factor < 1 (*collapse* of 1-D VHS)

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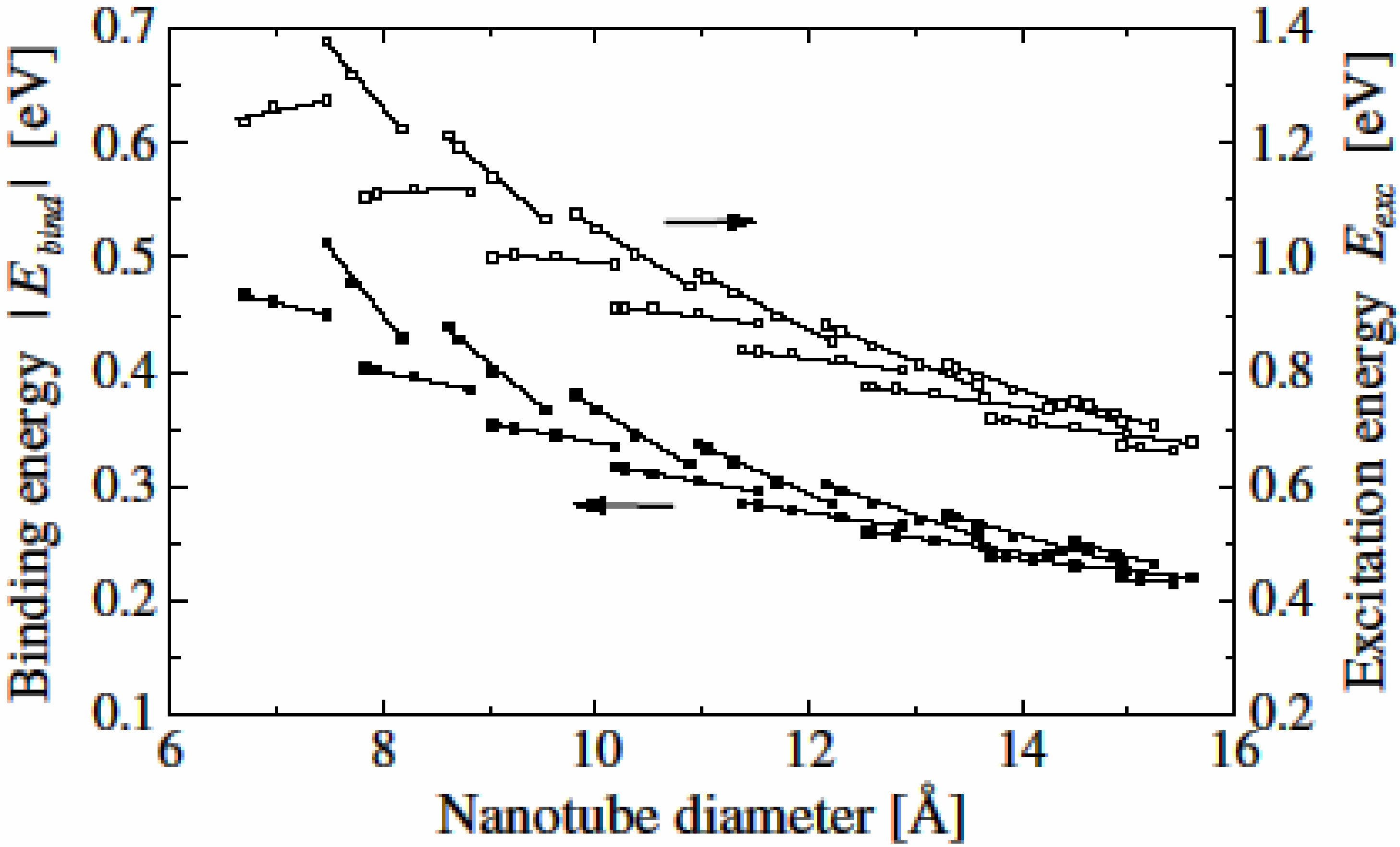
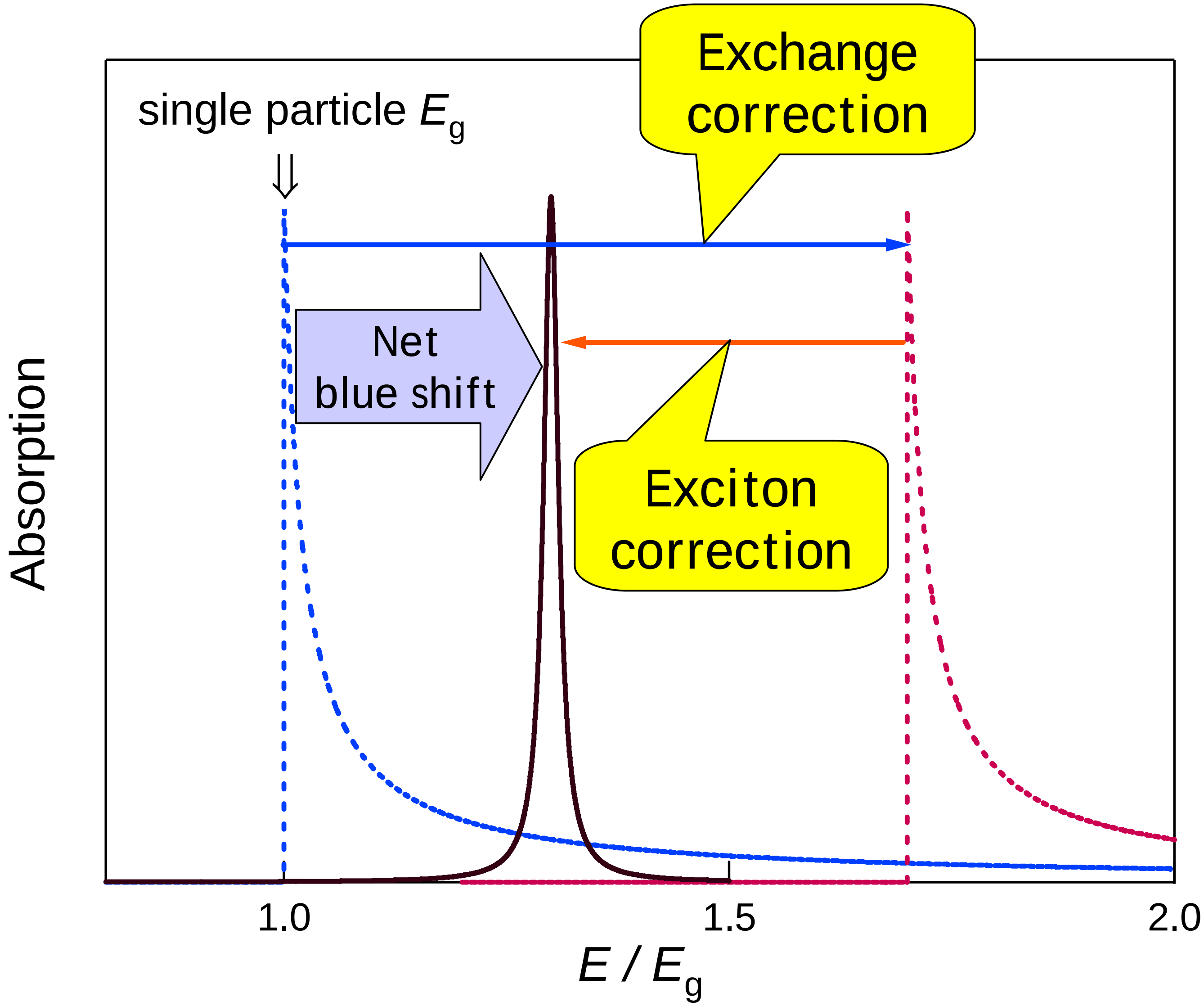
Exciton Binding Energies



T. G. Pedersen, Carbon **42**, 1007 (2004).

Many-Particle Effects



T. Ando, J. Phys. Soc. Jpn. **66**, 1066 (1997); C. Spataru et al., PRL **92**, 077402 (2004)

Excitons in Carbon Nanotubes

Recent theory papers:

- T. G. Pedersen, Phys. Rev. B **67**, 073401 (2003)
- C. L. Kane and E. J. Mele, Phys. Rev. Lett. **90**, 207401 (2003)
- C. D. Spataru, S. Ismail-Beigi, L. X. Benedict, and S. G. Louie, Phys. Rev. Lett. **92**, 077402 (2004)
- E. Chang, G. Bussi, A. Ruini, and E. Molinari, Phys. Rev. Lett. **92**, 196401 (2004)
- T. G. Pederson, Carbon **42**, 1007 (2004)
- V. Perebeinos, J. Tersoff, and P. Avouris, Phys. Rev. Lett. **92**, 257402 (2004)
- H. Zhao and S. Mazumdar, Phys. Rev. Lett. **93**, 157402 (2004)
- C. L. Kane and E. J. Mele, Phys. Rev. Lett. **93**, 197402 (2004)
- T. Ando, J. Phys. Soc. Jpn. **73**, 3351 (2004)
- V. Perebeinos, J. Tersoff, and P. Avouris, cond-mat/0506775
- C. D. Spataru, S. Ismail-Beigi, R. B. Capaz, and S. G. Louie, cond-mat/0507067

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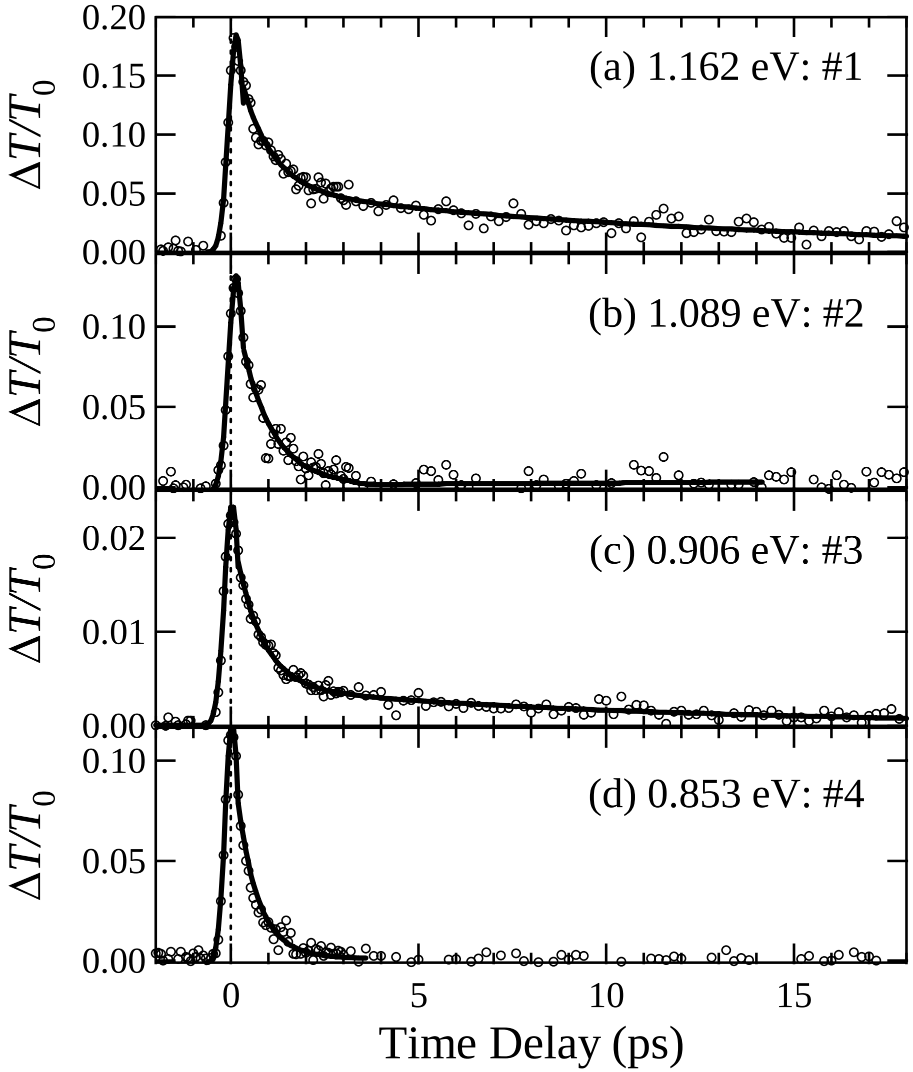
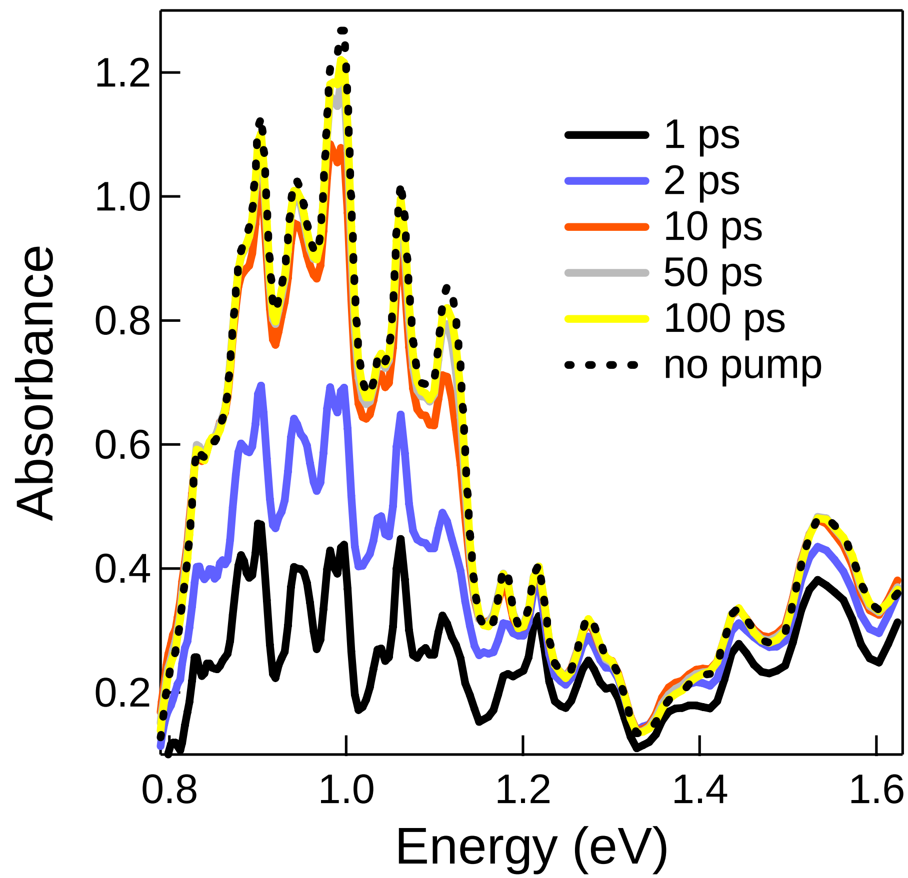
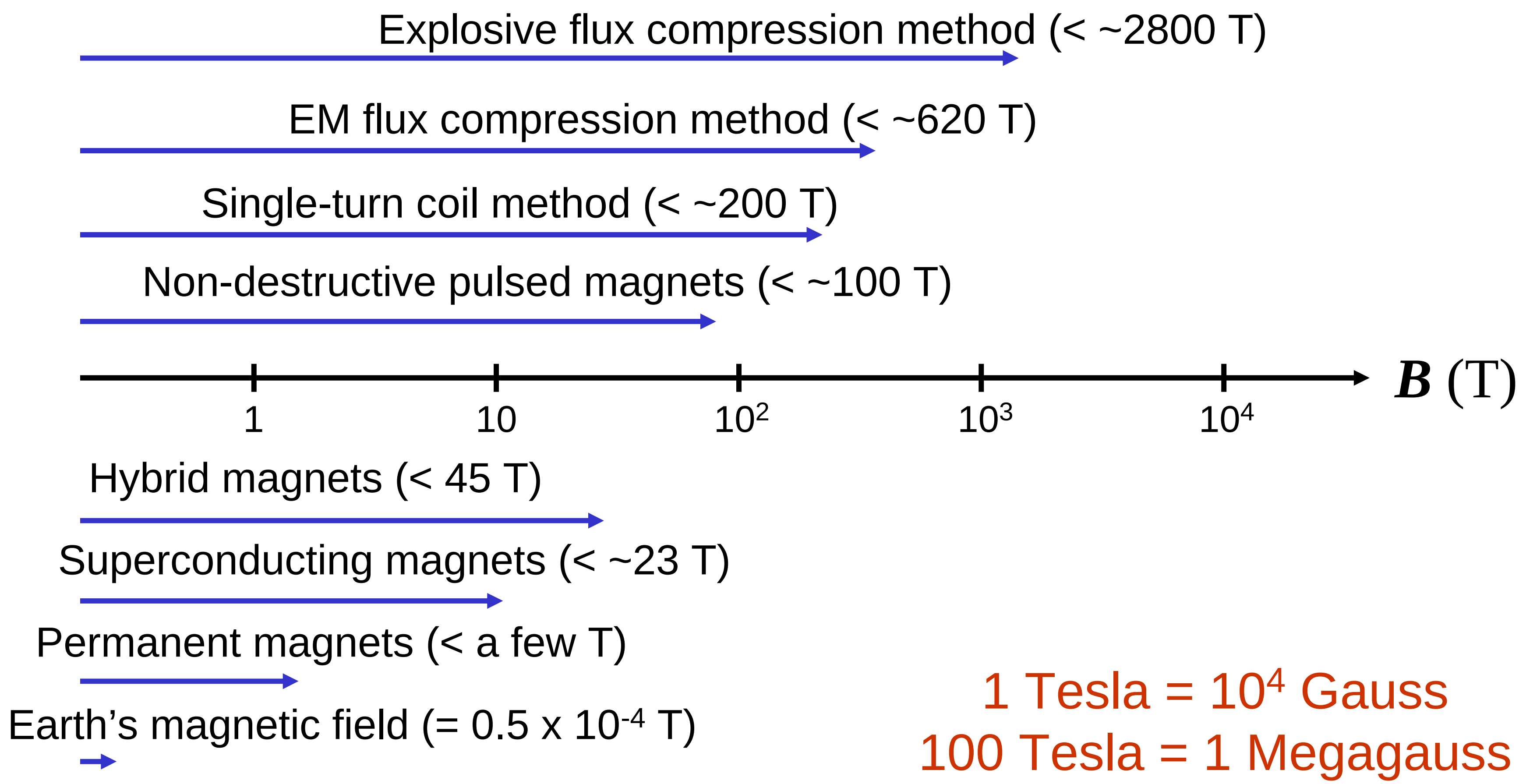
Ultrafast Optics in Carbon Nanotubes

G. N. Ostojic *et al*., Phys. Rev. Lett. **92**, 117402 (2004).
G. N. Ostojic *et al*., Phys. Rev. Lett. **94**, 097401 (2005).





Exploration of Ultrahigh Magnetic Fields



1 Tesla = 10^4 Gauss

100 Tesla = 1 Megagauss

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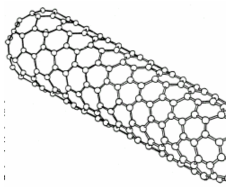
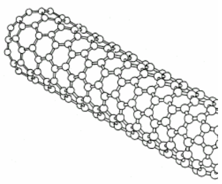
High-Field Magnets

- DC Magnetic Fields:
  - $B < 10$ T → Superconducting magnet (Rice)
  - $B < 33$ T → Resistive magnets (NHMFL, Tallahassee)
  - $B < 45$ T → Hybrid magnet (NHMFL, Tallahassee)
- Pulsed Magnetic Fields
  - $B < 75$ T (non-destructive, ms) Toulouse, France
  - $B < 75$ T (non-destructive, ms) NHMFL, Los Alamos
  - $B < 150$ T (destructive, μs) Humboldt Univ., Berlin



Outline



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Observation 1

Magnetic Alignment

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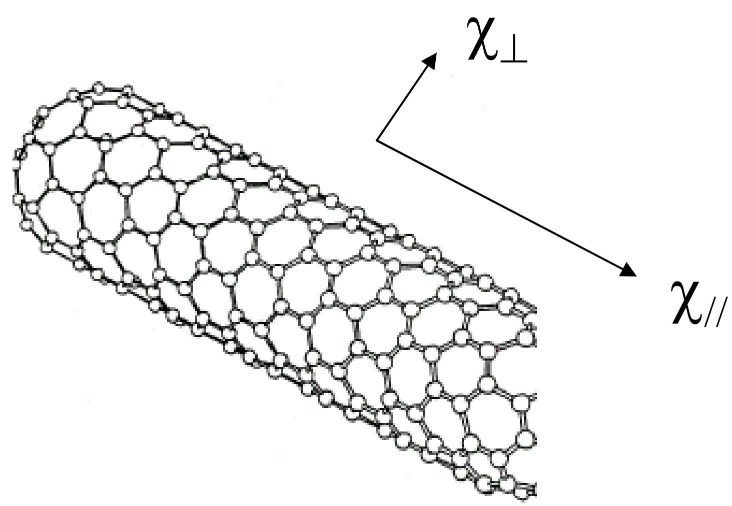
Magnetic Alignment



Metallic Tubes

$$\chi_{//} > 0,\ \chi_\perp < 0,\ |\chi_{//}| >> |\chi_\perp|$$

Semiconducting Tubes

$$\chi < 0,\ |\chi_{//}| << |\chi_\perp|$$

Ajiki & Ando (1993); Lu (1995)

Alignment Energy

$$\Delta U = U(90^\circ) - U(0^\circ) = B^2 N(\chi_{//} - \chi_\perp)$$

Measure of alignment: $$u = \sqrt{\frac{\Delta U}{k_B T}} \propto Bd \quad \text{for given } T$$

D. A. Walters *et al*., Chem. Phys. Lett. **338**, 14 (2001)

Magnetic Alignment of an Ensemble of SWNTs

Angular distribution function:

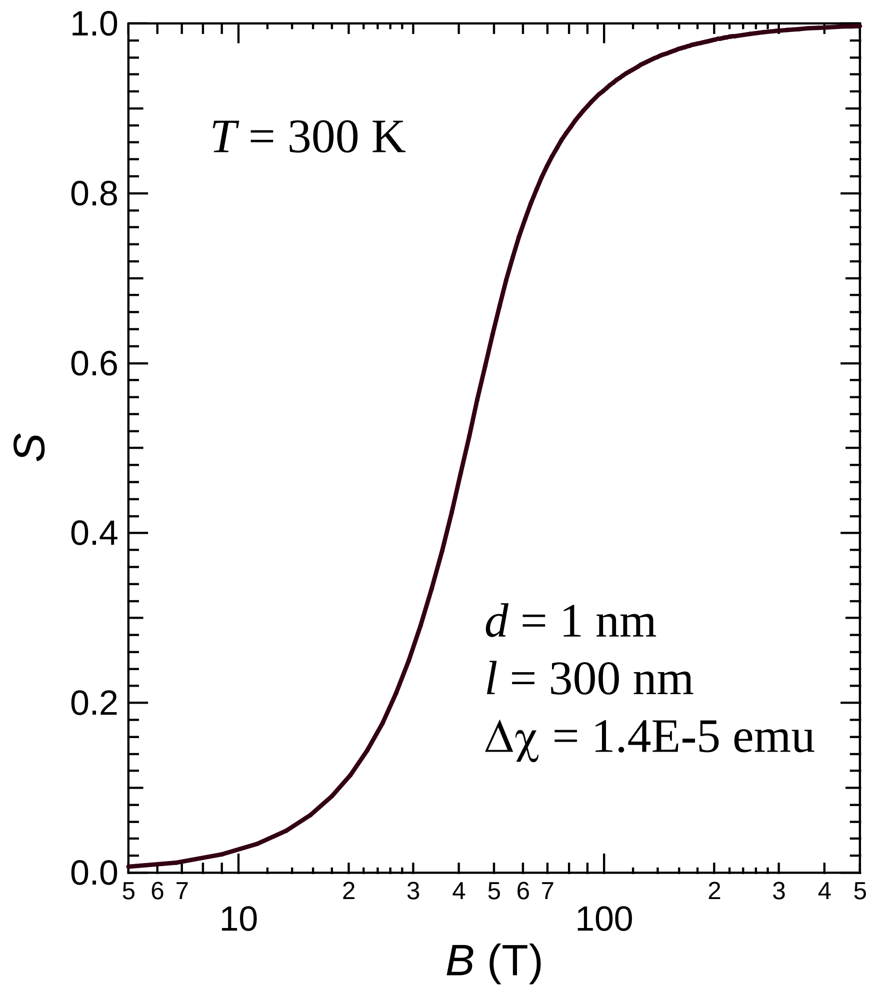
$$P(\theta) = \frac{\exp(-u^2 \sin^2 \theta) \sin\theta}{\int_0^{\pi/2} \exp(-u^2 \sin^2 \theta) \sin\theta d\theta}$$

$$u = \sqrt{\frac{B^2 N(\chi_{//} - \chi_{\perp})}{k_B T}}$$

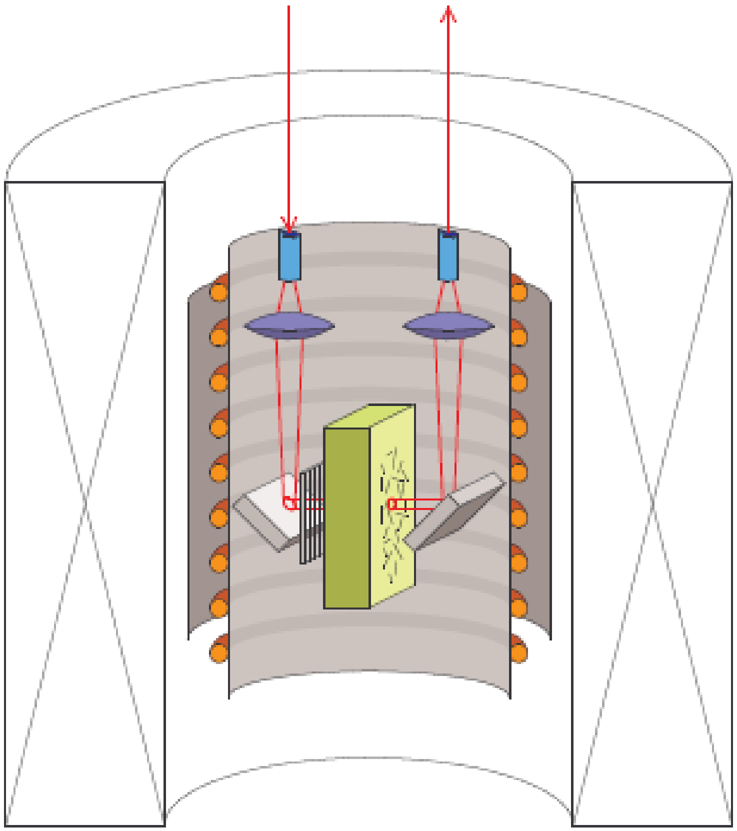
$$\longrightarrow \quad < f(\theta) >= \int_0^{\pi/2} f(\theta) P(\theta) d\theta$$

Nematic order parameter:

$$S = (3 < \cos^2 \theta > -1)/2$$

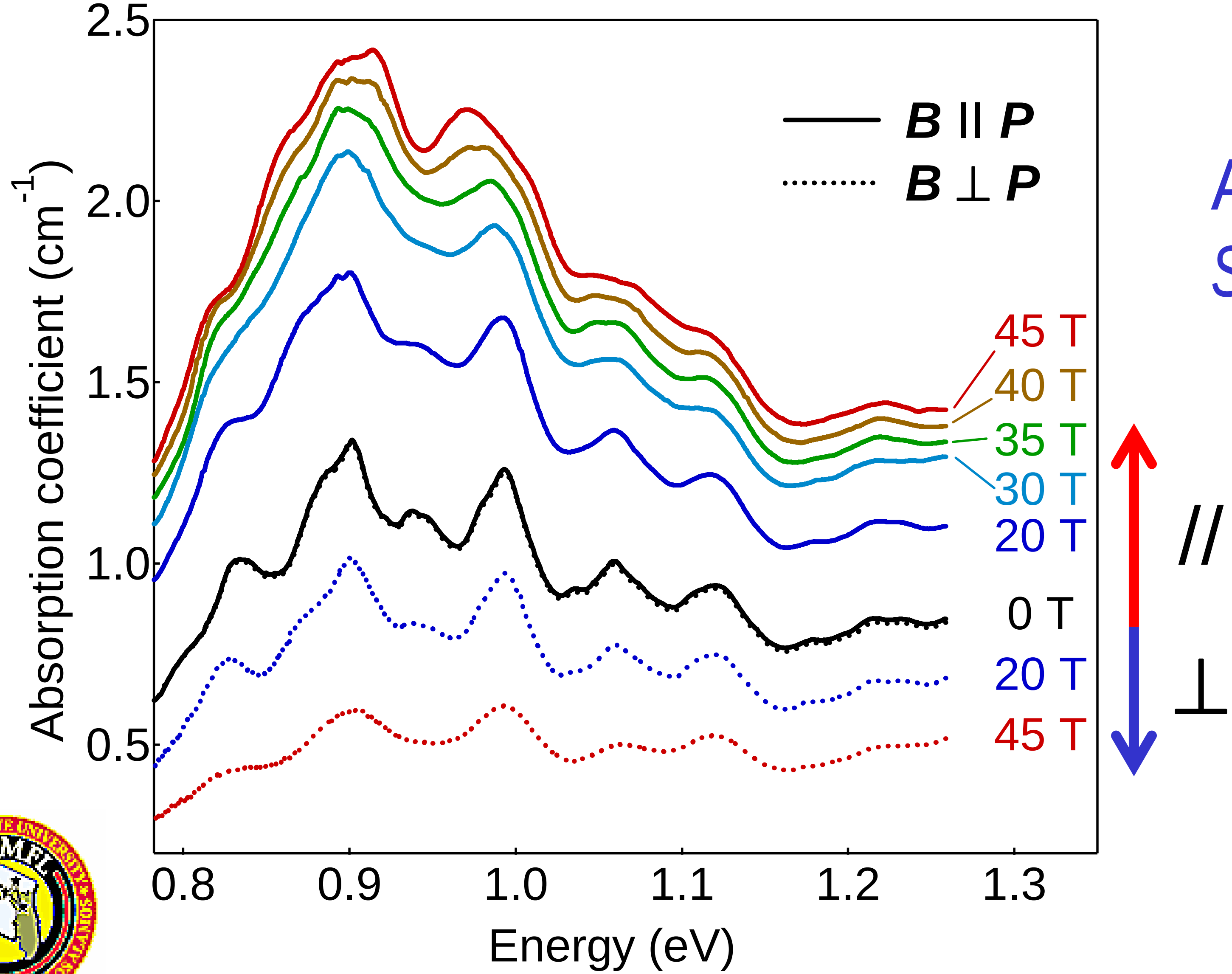


Polarization-Dependent Absorption in the Voigt Geometry



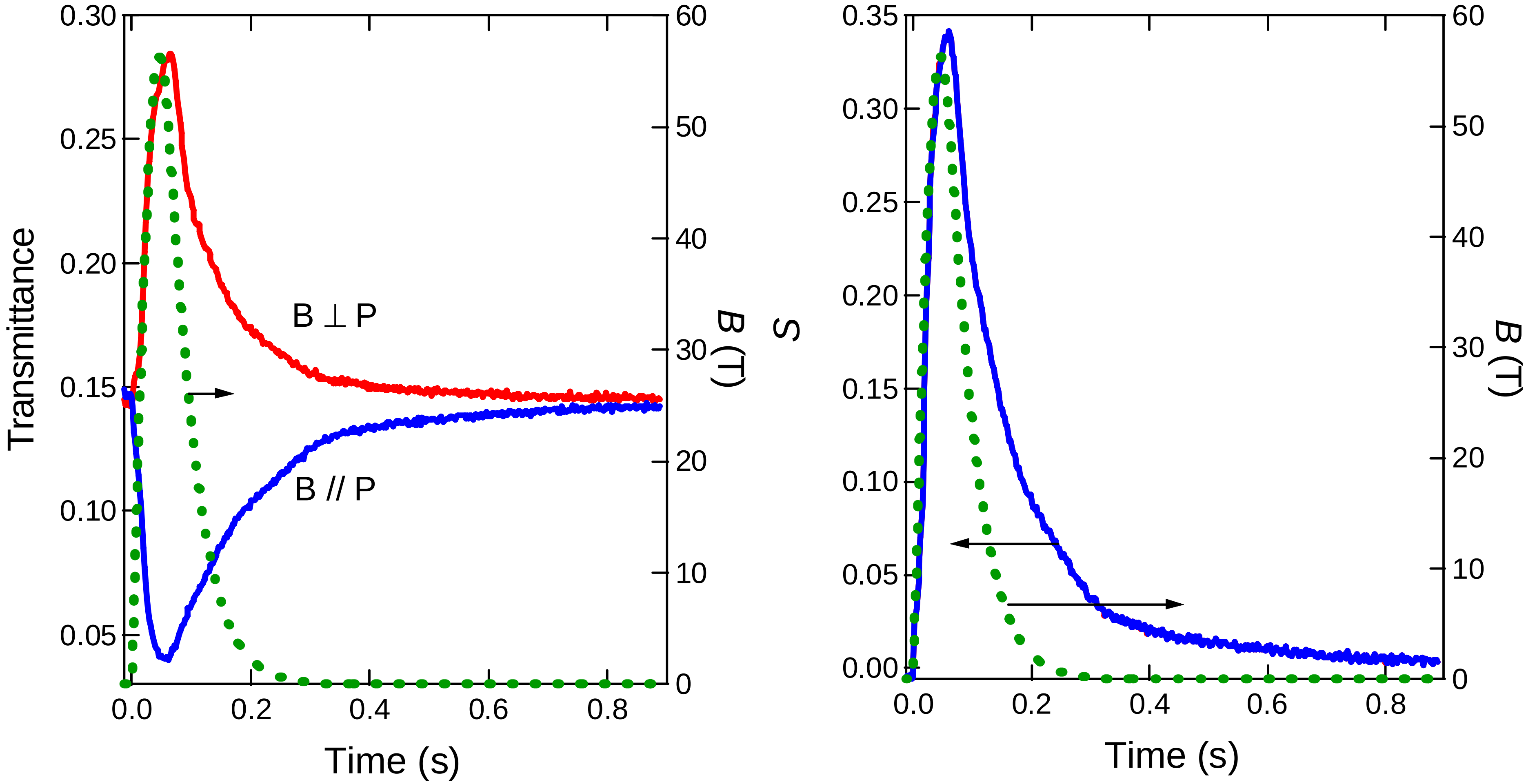
- The *Voigt* geometry: $k \perp B$
- Two polarization configurations:
  $B \parallel P$ or $B \perp P$
- *B*-field *aligns* the tubes
  → *optical anisotropy*

CW Absorption up to 45 T



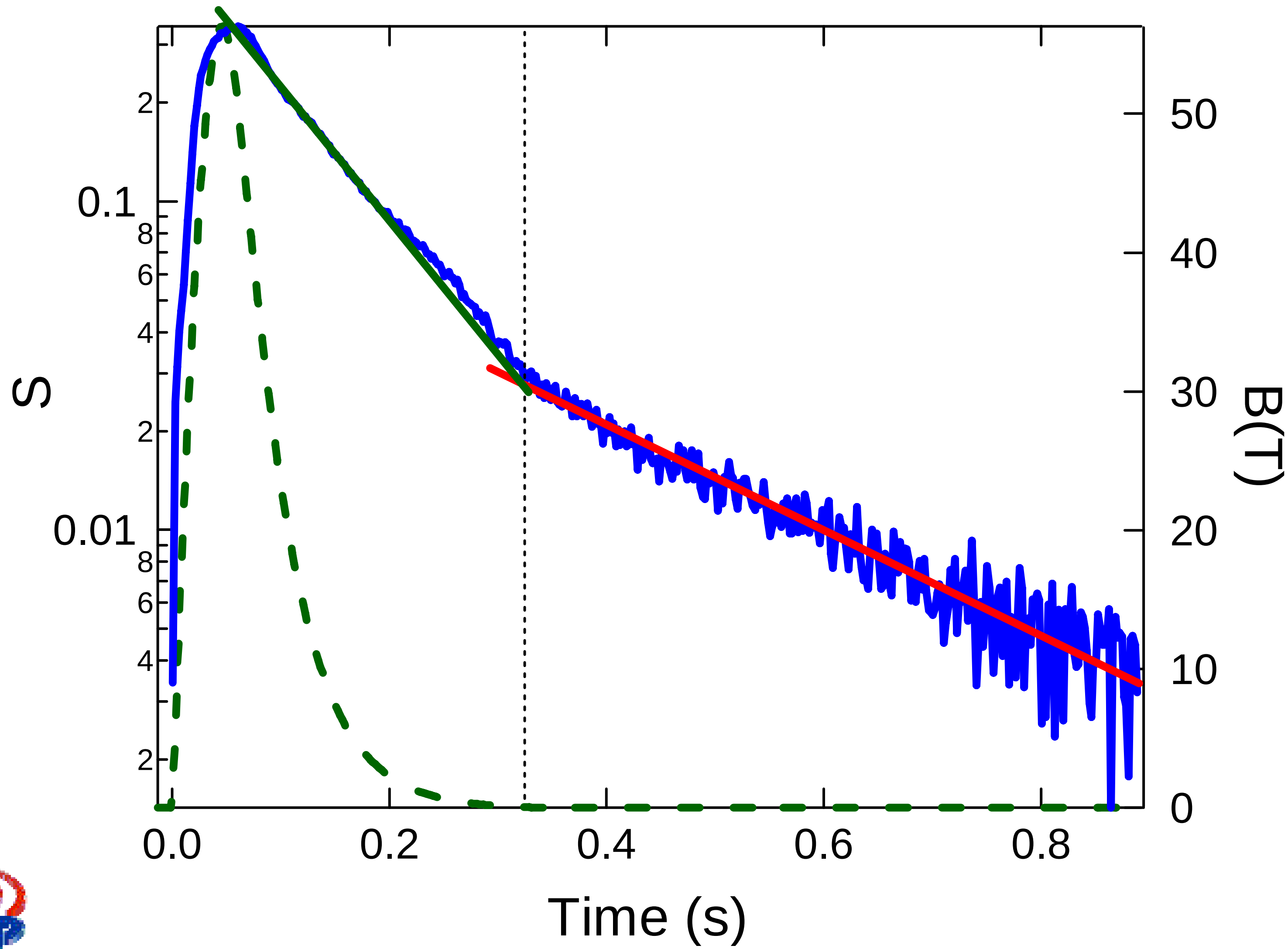
At 45 T:
$S \sim 0.5$

Dynamic Magnetic Alignment



Non-destructive, ~100 msec

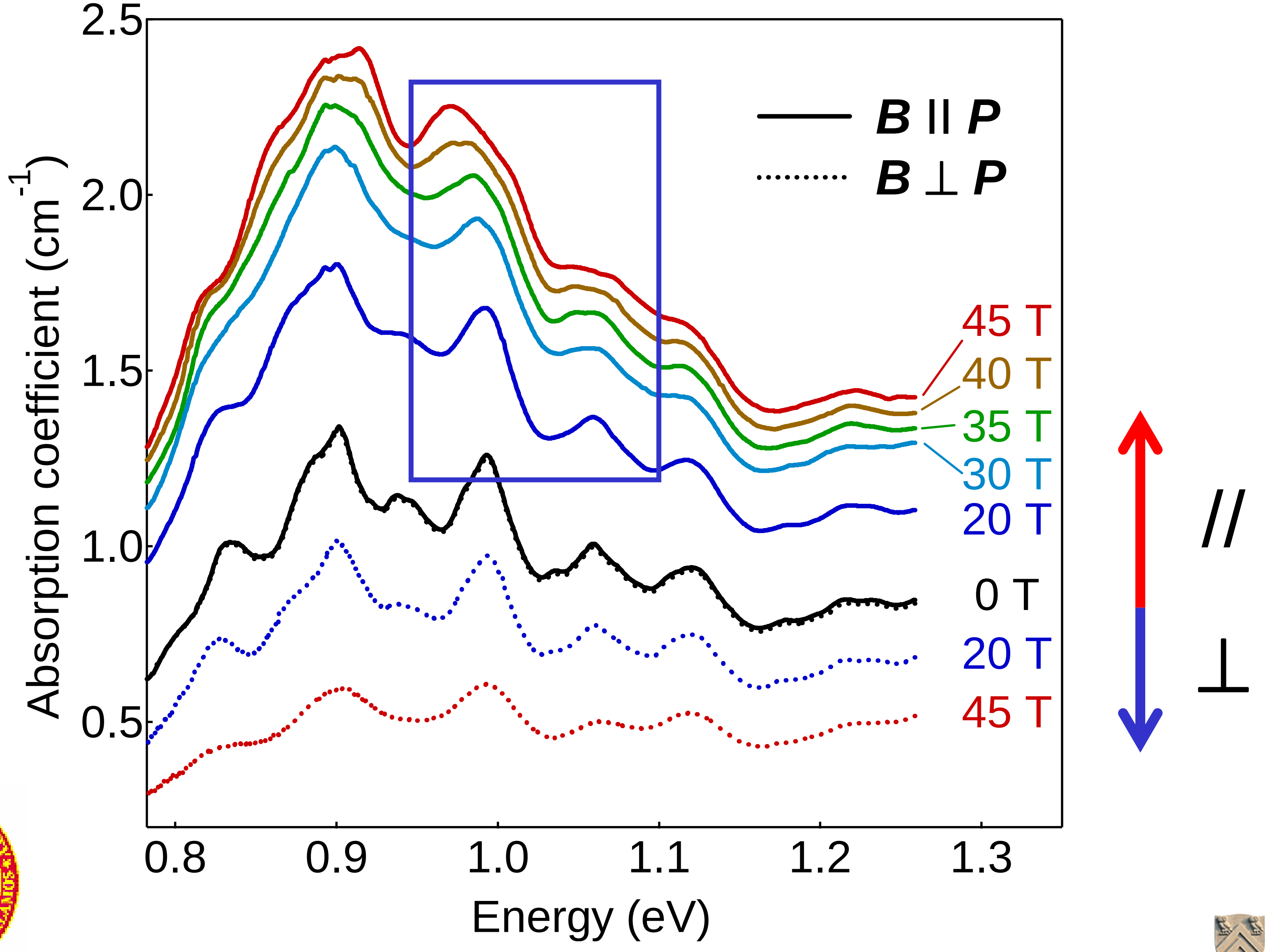
Probing Relaxation Time (55 T, 100 ms pulse)



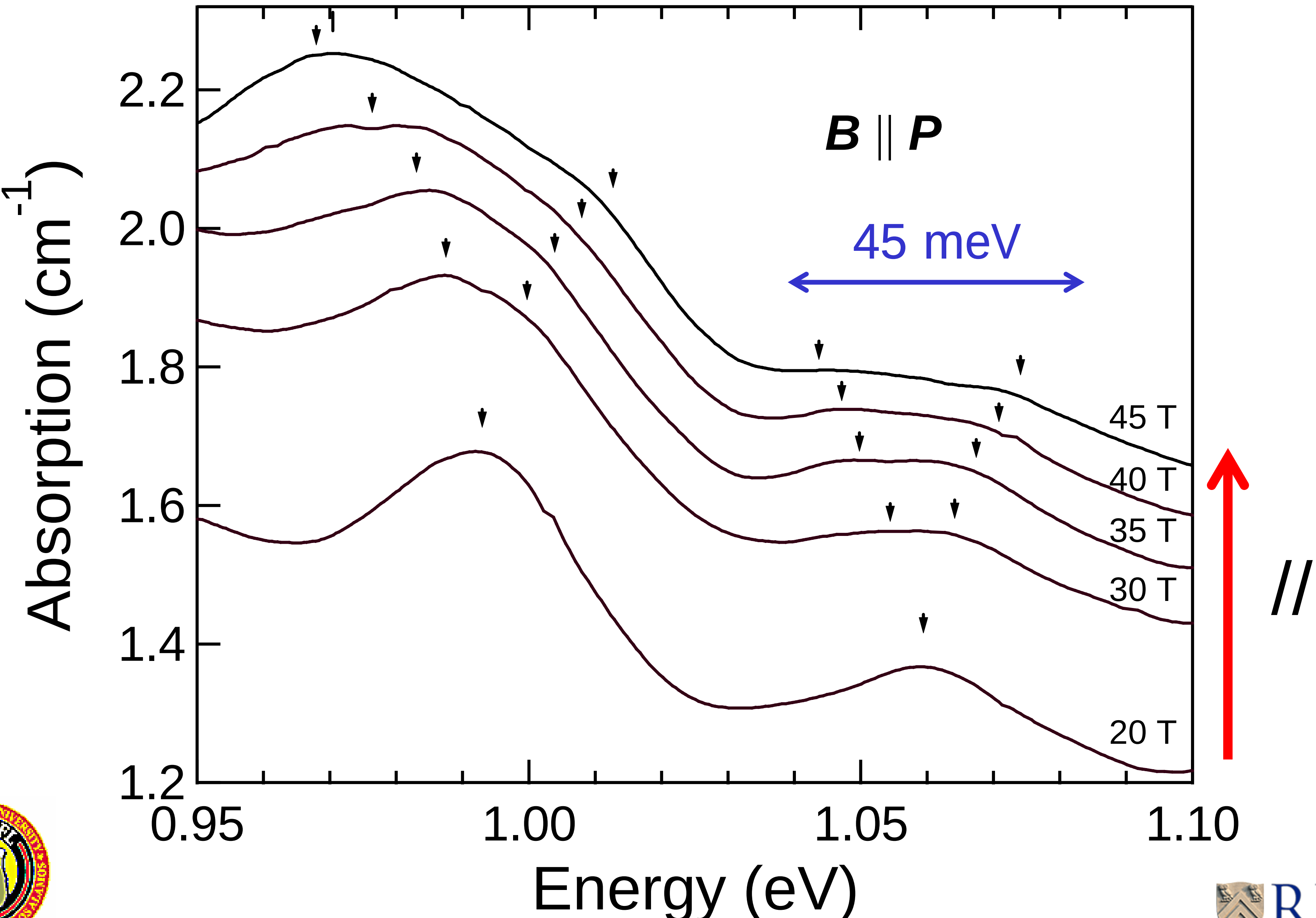
Observation 2

Splittings in Absorption

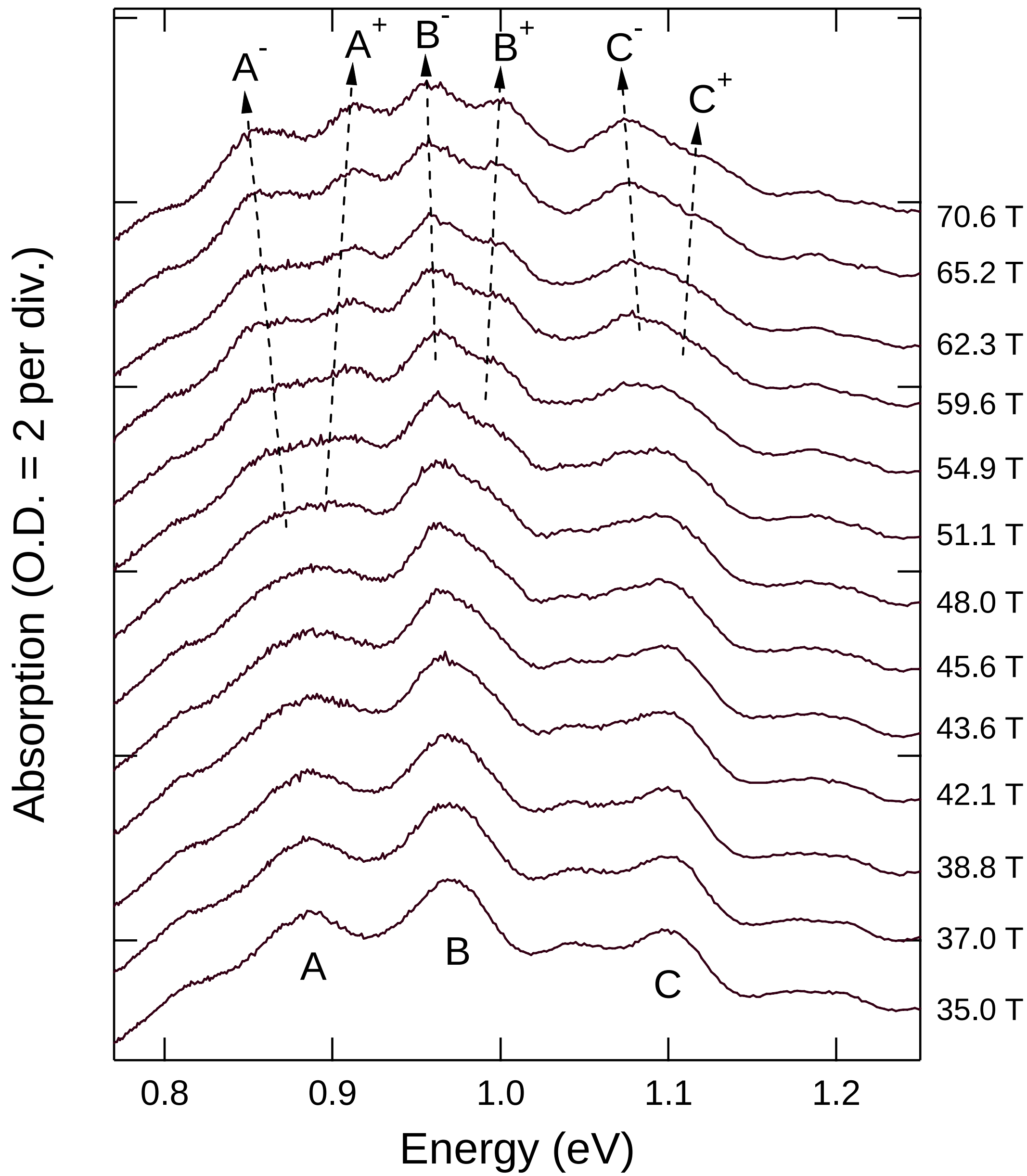
E_{11} Absorption up to 45 T



B-induced Peak Broadening (< 45 T)



B-induced Peak Splitting (> 55 T)



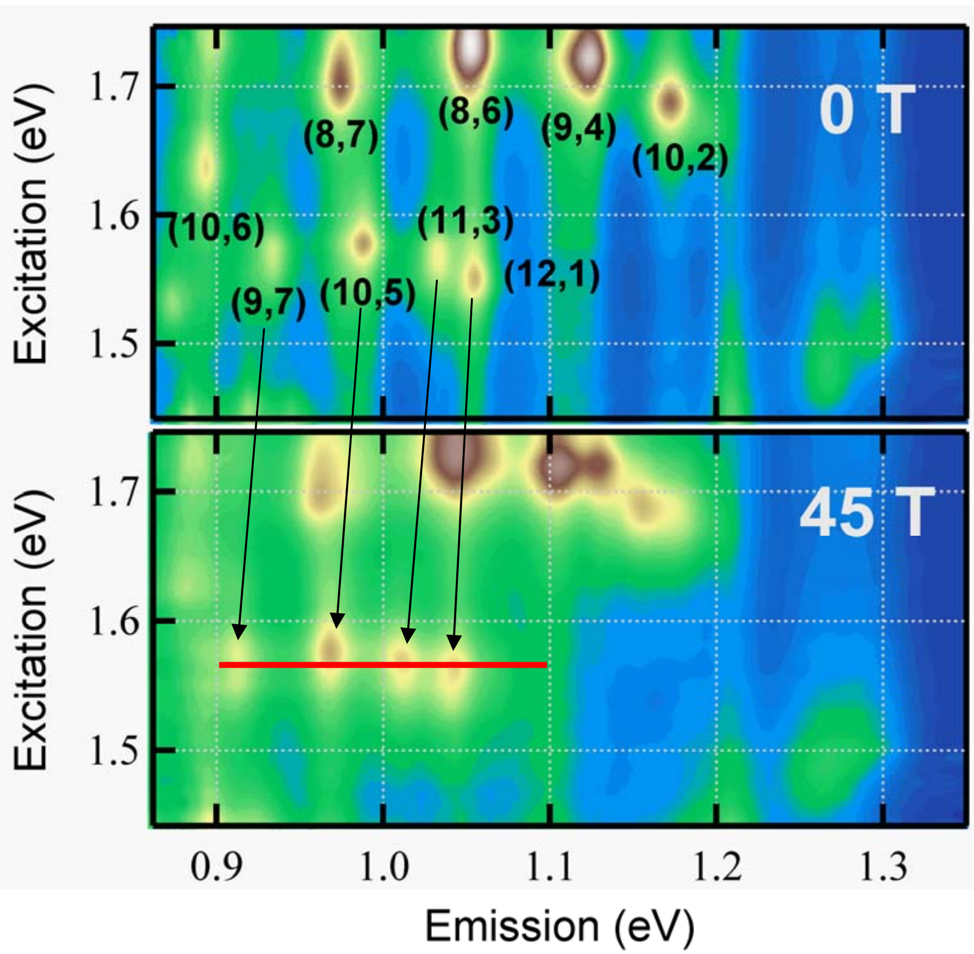
B* // *P

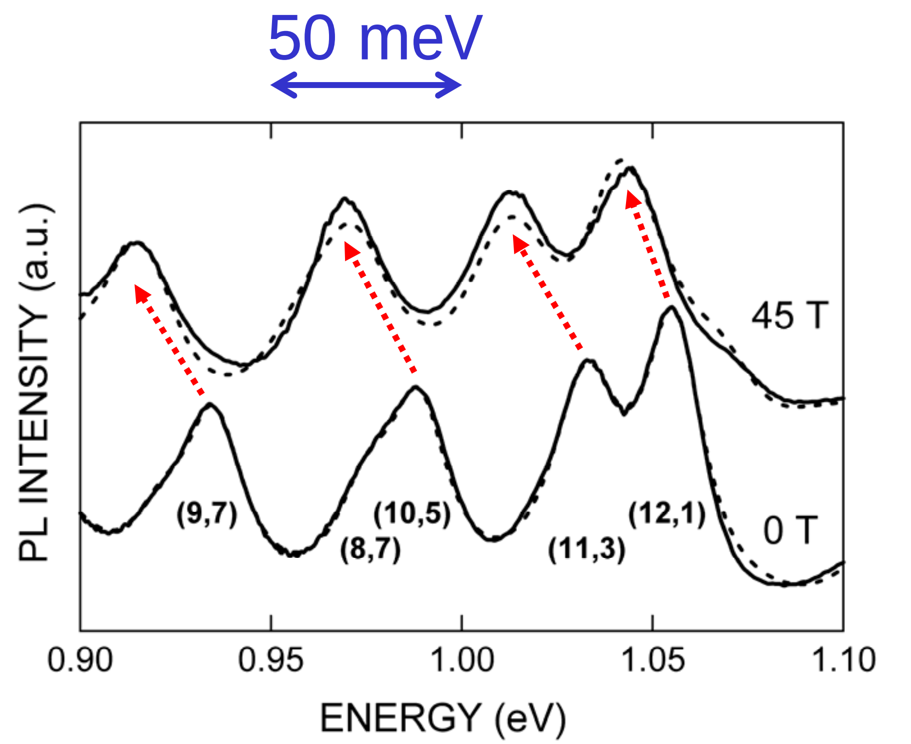
S. Zaric *et al*.,
cond-mat/0509429

Observation 3

Red-Shifts in Photoluminescence

B-induced Red Shifts of PL Peaks





All peaks red shift with increasing *B* !!!

S. Zaric *et al*., Science **304**, 1129 (2004); Nano Lett. **4**, 2219 (2004)

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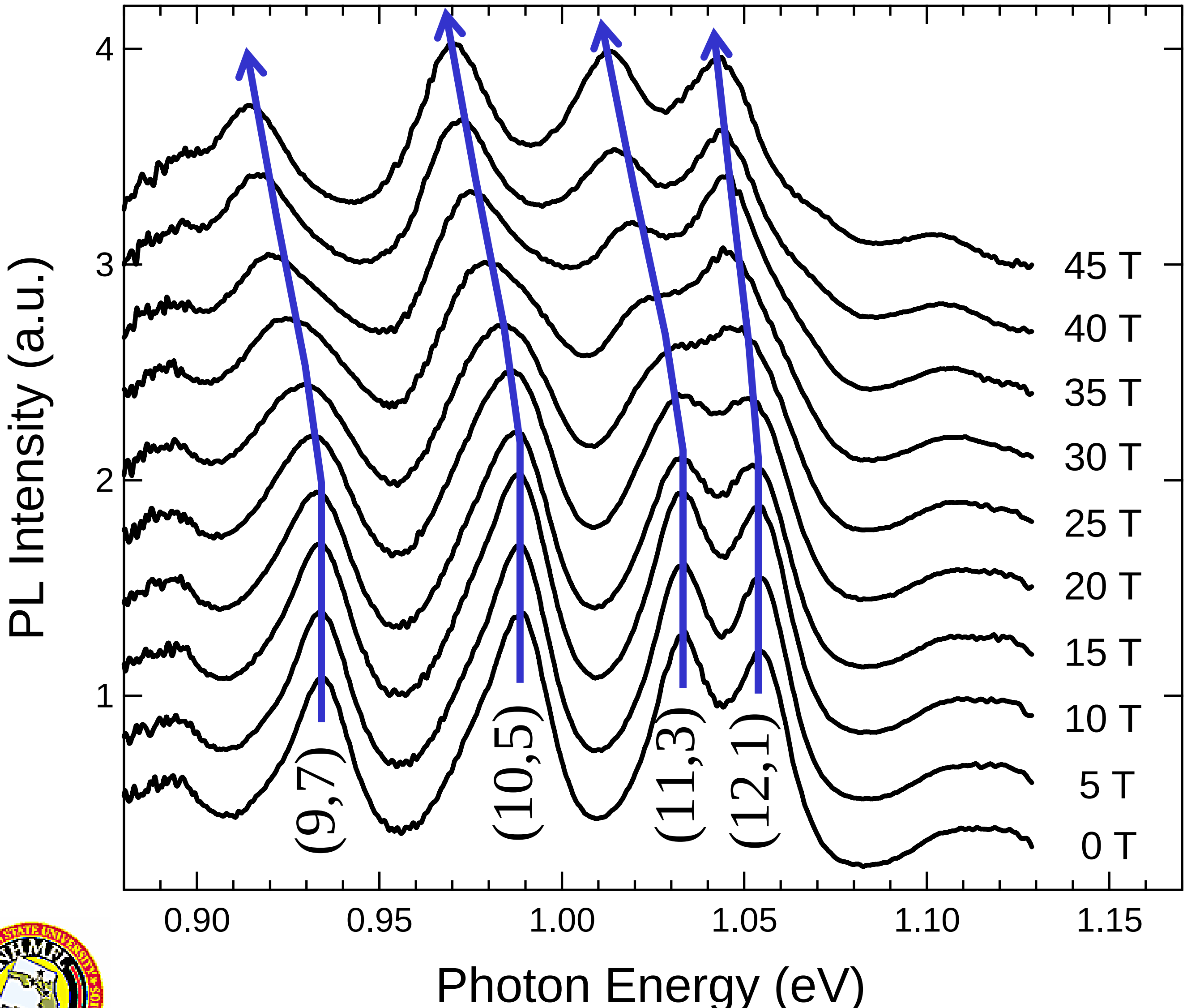
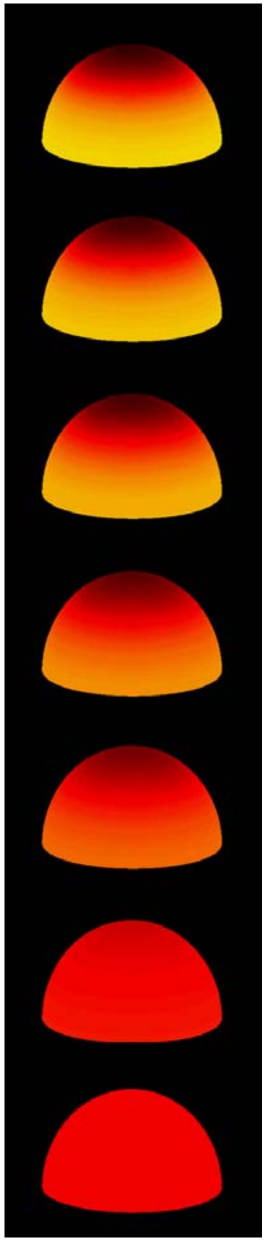
Nonlinear *B* Dependence



- 790 nm (1.57 eV) excitation, RT
- Peaks **broaden** and **red shift** with increasing *B*
- **Nothing happens until *B* reaches 20-25 T**

S. Zaric *et al*., Science **304**, 1129 (2004)

Magnetic Alignment of a SWNT *Ensemble*

$u \sim 2$		45 T
$u \sim 1.8$		40 T
$u \sim 1.6$		35 T
$u \sim 1.3$		30 T
$u \sim 1.1$		25 T
$u \sim 0.9$		20 T
$u = 0$		0 T

Measure of alignment:

$$u = \sqrt{\frac{B^2 N(\chi_{//} - \chi_{\perp})}{k_B T}} \propto B$$

Defines the angle distribution

Has to be > 1 for alignment to occur

$$dP(\theta) = \frac{\exp(-u^2 \sin^2\theta)\sin\theta d\theta}{\int_0^{\pi/2} \exp(-u^2 \sin^2\theta)\sin\theta d\theta}$$

Maxwell-Boltzmann

S. Zaric *et al*., Science **304**, 1129 (2004); Nano Lett. **4**, 2219 (2004)

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PL Simulations

- Peak positions calculated from **Ajiki-Ando theory**
- Multiple **Lorentzian** peaks
- **Zeeman splitting** with g = 2 included (→ 5.22 meV at 45 T)
- Carrier population taken into account according to $P_i \propto \exp(-E_i/kT)$ (**Boltzmann factor**)
- Incomplete magnetic alignment → **angular distribution** of nanotubes

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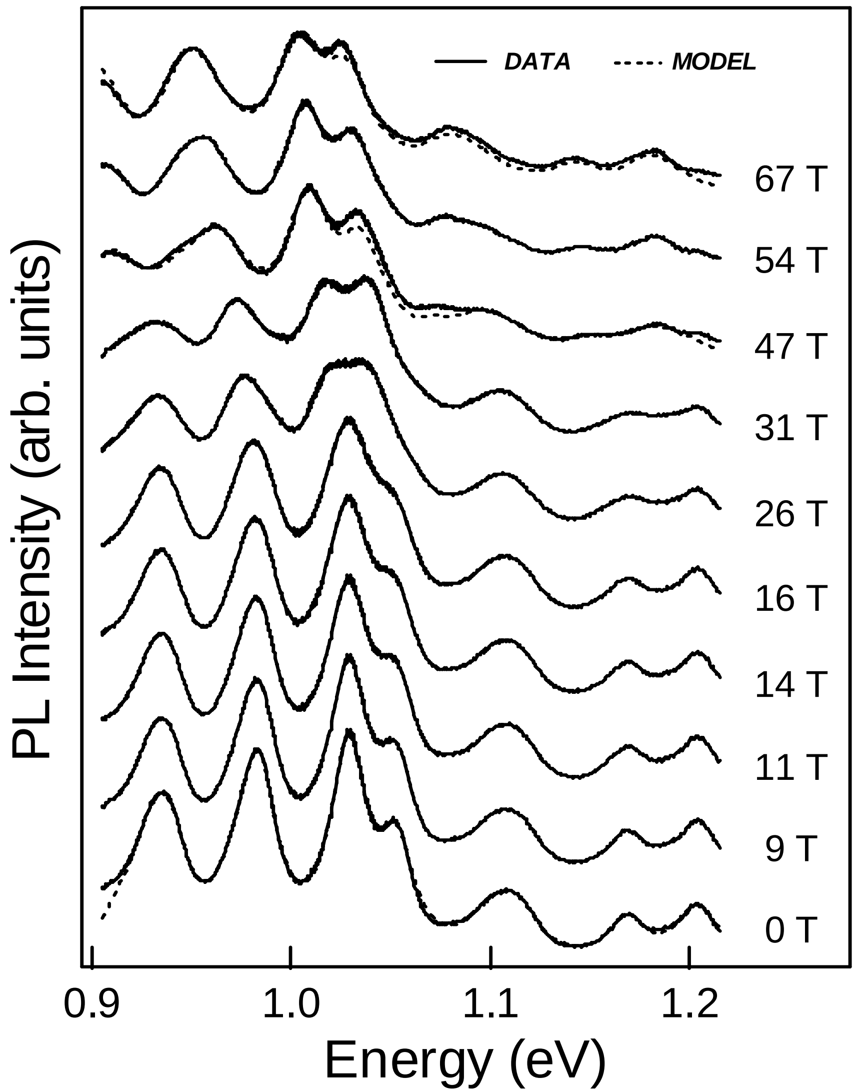
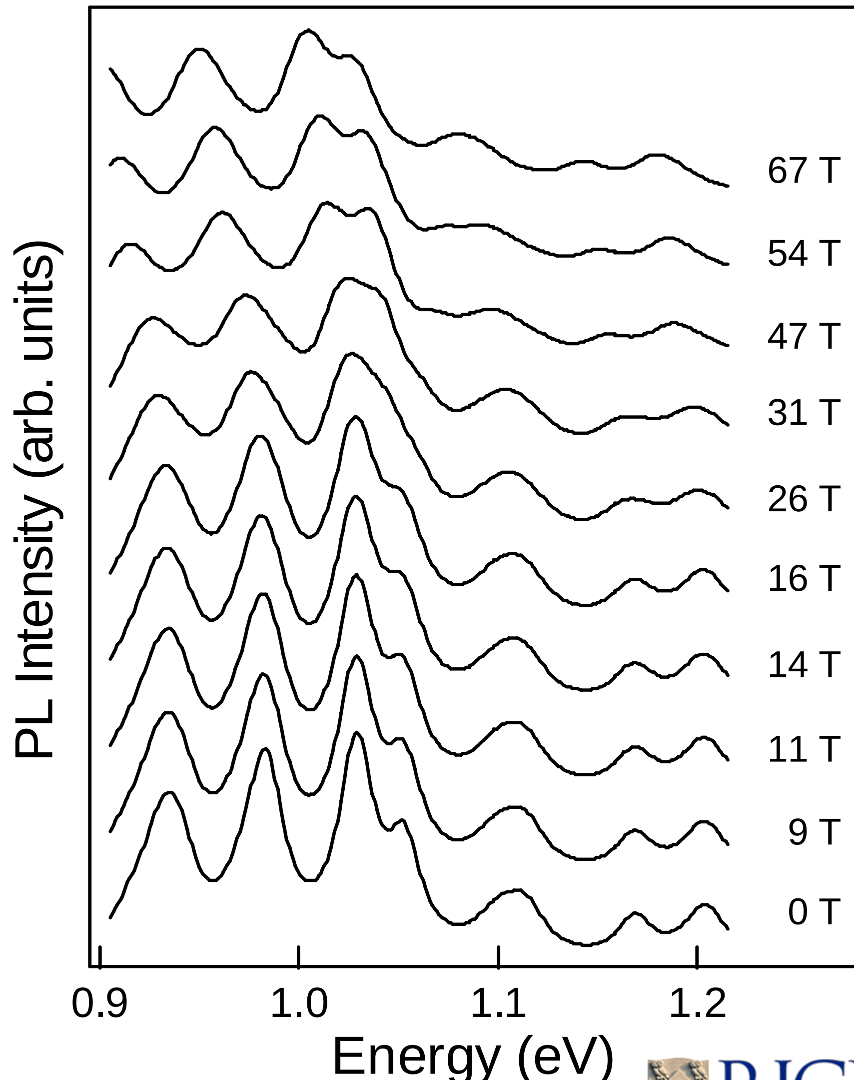
Nonlinear *B*-Dependence of PL

Experiment



Simulation



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Summary

High-Field Magneto-Optics in SWNTs

Accomplished:

- ✓ Magnetic alignment (induced large optical anisotropy)
- ✓ Absorption peaks show broadening and splitting
- ✓ PL peaks show significant red shifts with *B*
- ✓ Simulation taking into account carrier population and angular distribution shows agreement → **Evidence of AB phase $2\pi\phi/\phi_0$ in optical spectra of SWNTs**
- ✓ Estimated χ anisotropy: $\chi_{//} - \chi_{\perp} = 1.4 \times 10^{-5}$ emu/mole

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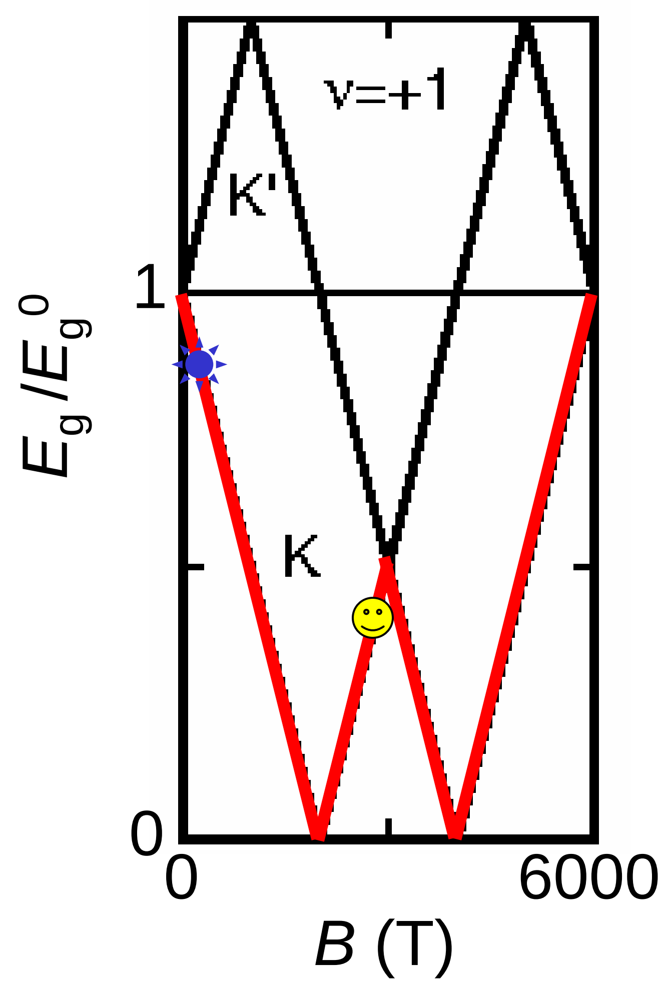
Current & Future Work

- Higher field necessary to see **band gap collapse** and **oscillations** → experiments with destructive pulsed magnets in progress (< **300 T**: ✹) and in preparation (< **2800 T**: ☺)
- Wider-diameter nanotubes preferred → **double-walled** nanotubes
- **Low temperature PL** on **films** → narrower line widths & no need to consider alignment dynamics
- Metallic nanotubes should show **band gap opening** with *B* → FIR/THz spectroscopy in *B*



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