Magneto-Optical Spectroscopy of 2D Materials

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MOMB

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Outline:

- Why combining optical spectroscopy with magnetic fields ?

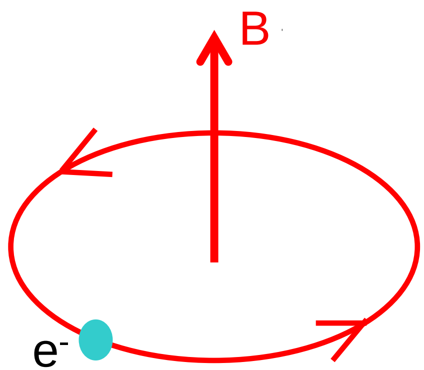
- Experimental techniques

- Dirac fermions in graphene:
  - Cyclotron motion/resonance & Landau levels
  - Magneto-Raman scattering
  - Interaction effects (electron-phonon and electron-electron)

- Semiconducting transition metal dichalcogenides
  - Excitonic properties
  - Zeeman spectroscopy
  - Magnetic brightening

- Summary

Two-dimensional electronic systems + magnetic fields =
a fruitful association



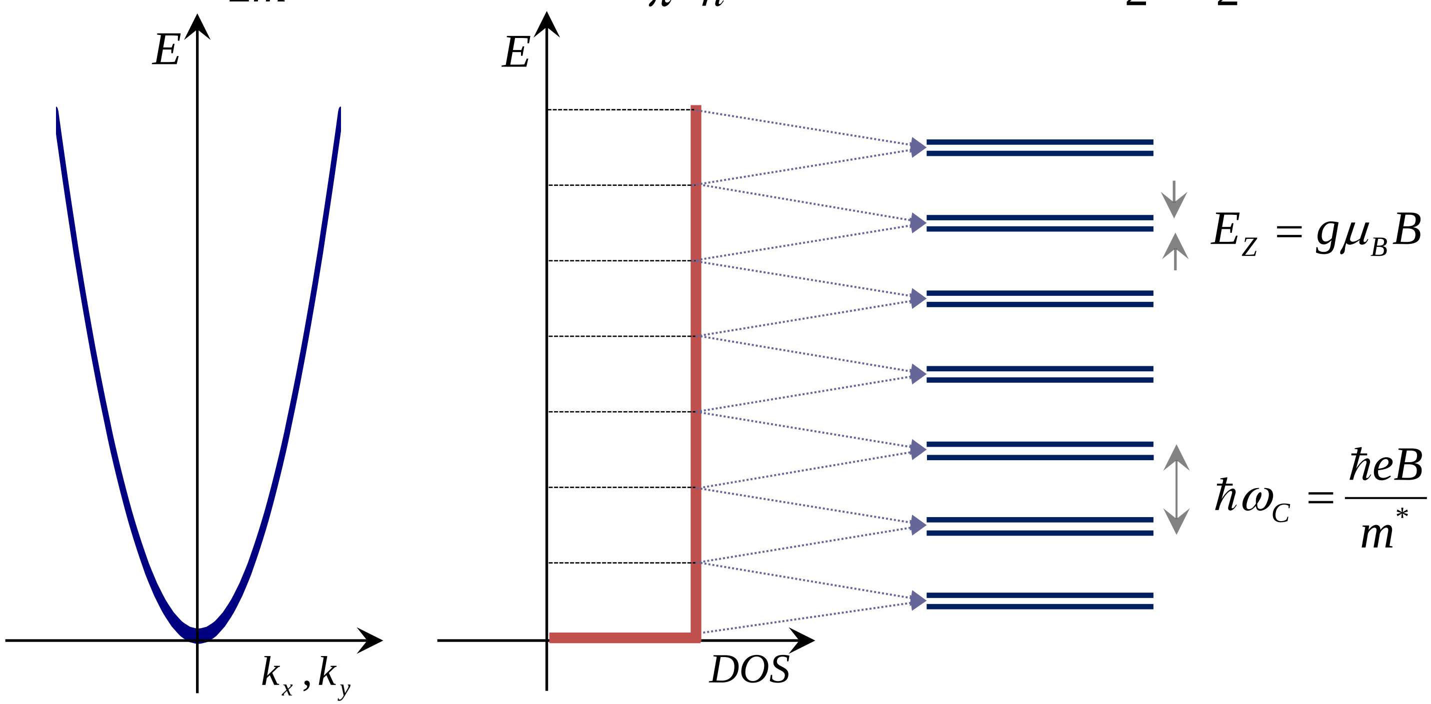
$$\frac{d\vec{\mathbf{p}}}{dt} = e[\vec{\mathbf{v}} \times \vec{\mathbf{B}}]$$

$$\hbar\omega_C = \frac{\hbar eB}{m^*}$$

Two-dimensional electronic systems + magnetic fields =
a fruitful association

Landau quantization into DISCRETE and HIGHLY DEGENERATE levels

$$E(\vec{k}) = \frac{\hbar^2 \vec{k}^2}{2m^*} \qquad DOS = \frac{m^*}{\pi \cdot \hbar^2} \qquad E_n = \hbar\omega_C\left(n + \frac{1}{2}\right) \pm \frac{1}{2} g\mu_B B$$



$$\boldsymbol{B = 0} \qquad \boldsymbol{B > 0}$$

Two-dimensional electronic systems + magnetic fields = a fruitful association

Landau quantization into DISCRETE and HIGHLY DEGENERATE levels

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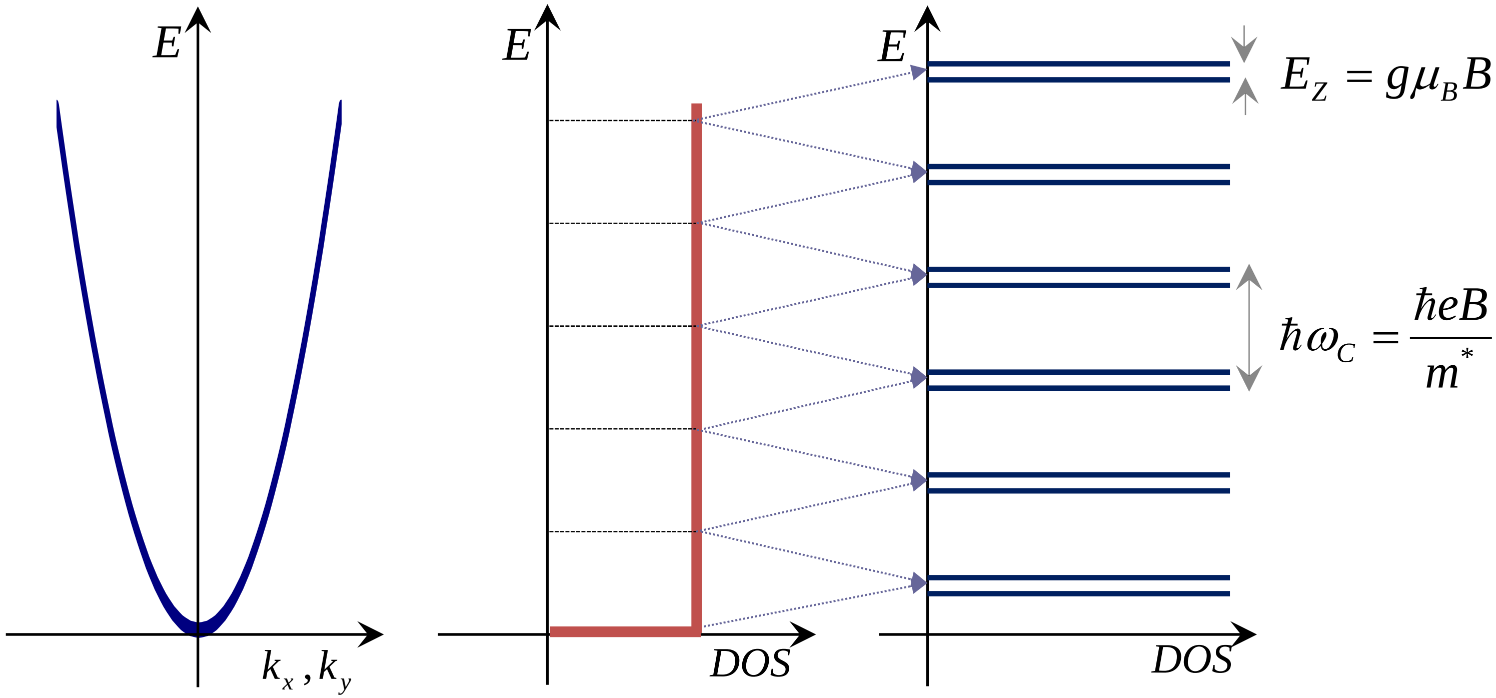
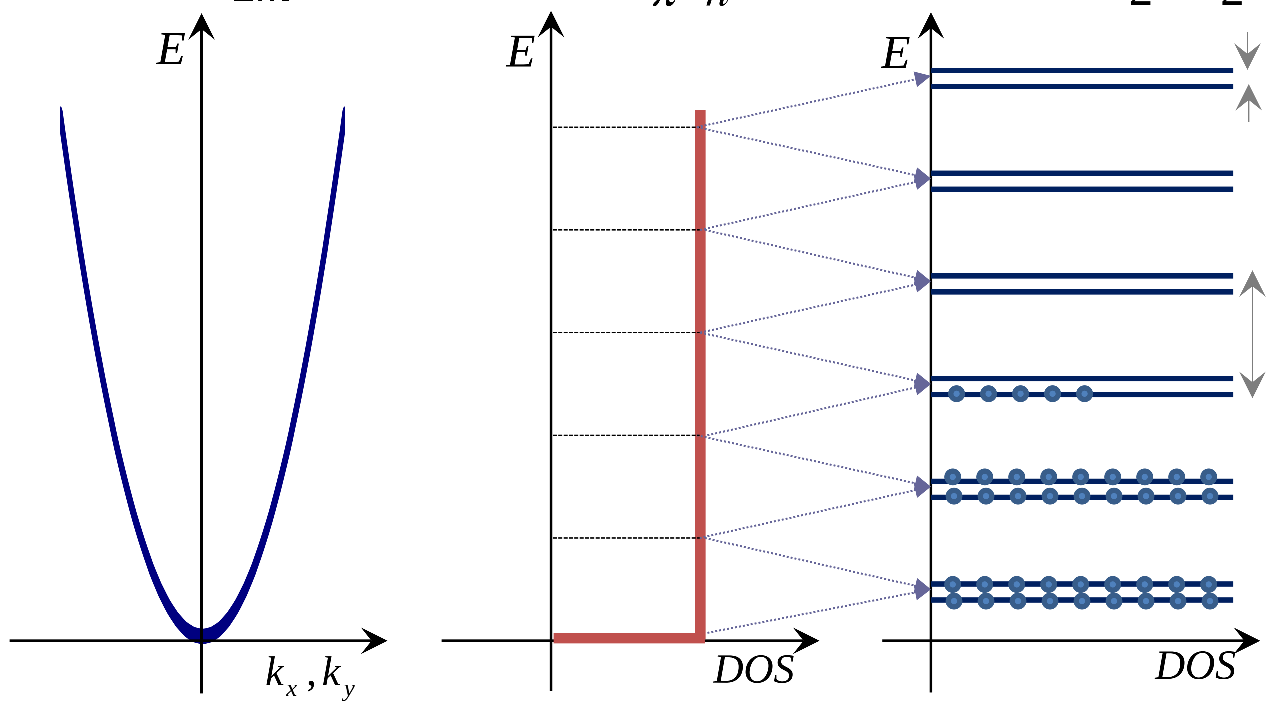


$B = 0$ $\qquad$ $B > 0$

Two-dimensional electronic systems + magnetic fields = a fruitful association

Landau quantization into DISCRETE and HIGHLY DEGENERATE levels

$$E(\vec{k}) = \frac{\hbar^2 \vec{k}^2}{2m^*} \qquad DOS = \frac{m^*}{\pi \cdot \hbar^2} \qquad E_n = \hbar\omega_C(n+\frac{1}{2}) \pm \frac{1}{2} g\mu_B B$$



$$E_Z = g\mu_B B$$

$$\hbar\omega_C = \frac{\hbar eB}{m^*}$$

$$D = \frac{eB}{2\pi \cdot \hbar} \quad \times 2$$
(spin)

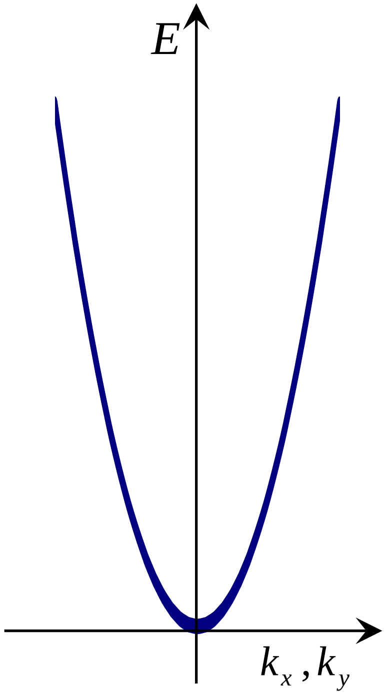
~ 2.41 x 10^{10}
[e- / LL / T]

$B = 0$ $\qquad$ $B > 0$

Dispersion relations and corresponding Landau level fan chart

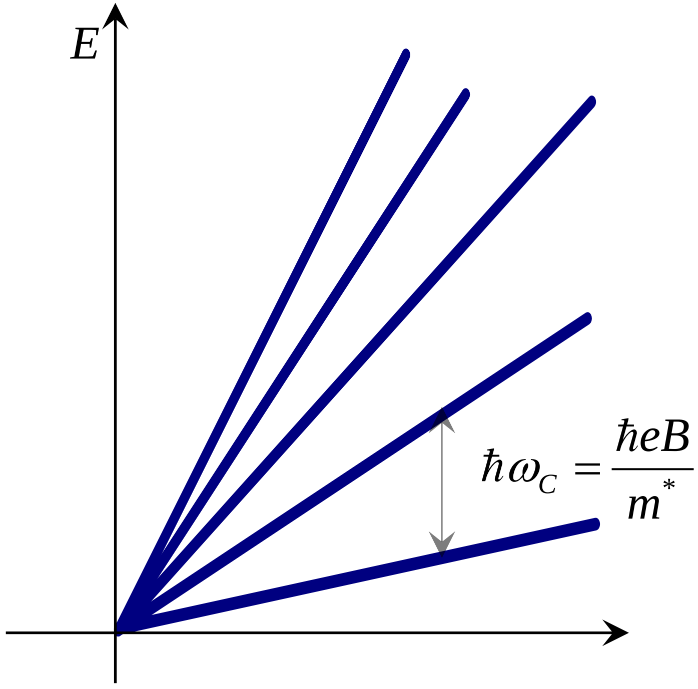
"Parabolic electrons" : conduction band of 2D GaAs

$$E(\vec{k}) = \frac{\hbar^2 \vec{k}^2}{2m^*}$$



$$\boldsymbol{B = 0}$$

$$E_n = \hbar\omega_C (n + \frac{1}{2})$$

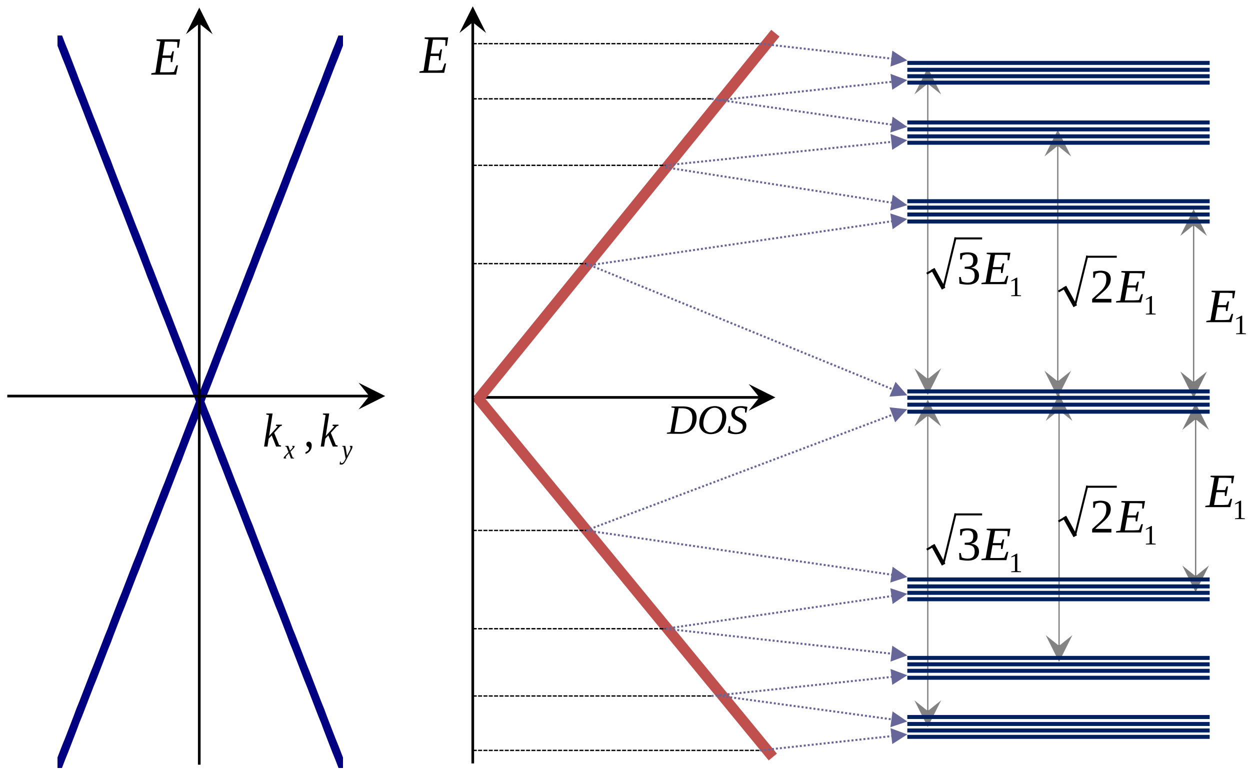


$$\boldsymbol{B > 0}$$

Dispersion relations and corresponding Landau level fan chart

Low energy Dirac electronic states of graphene

$$E(\vec{k}) = \pm v_F \hbar \left| \vec{k} \right| \qquad DOS = \frac{2 \cdot |E|}{\pi \cdot (\hbar v_F)^2} \qquad E_n = \pm v \sqrt{2e\hbar}\sqrt{B n}$$



$$E_1 = v \sqrt{2e\hbar}\sqrt{B}$$

$$D = \frac{eB}{2\pi \cdot \hbar} \times 4$$

(spin and valley)

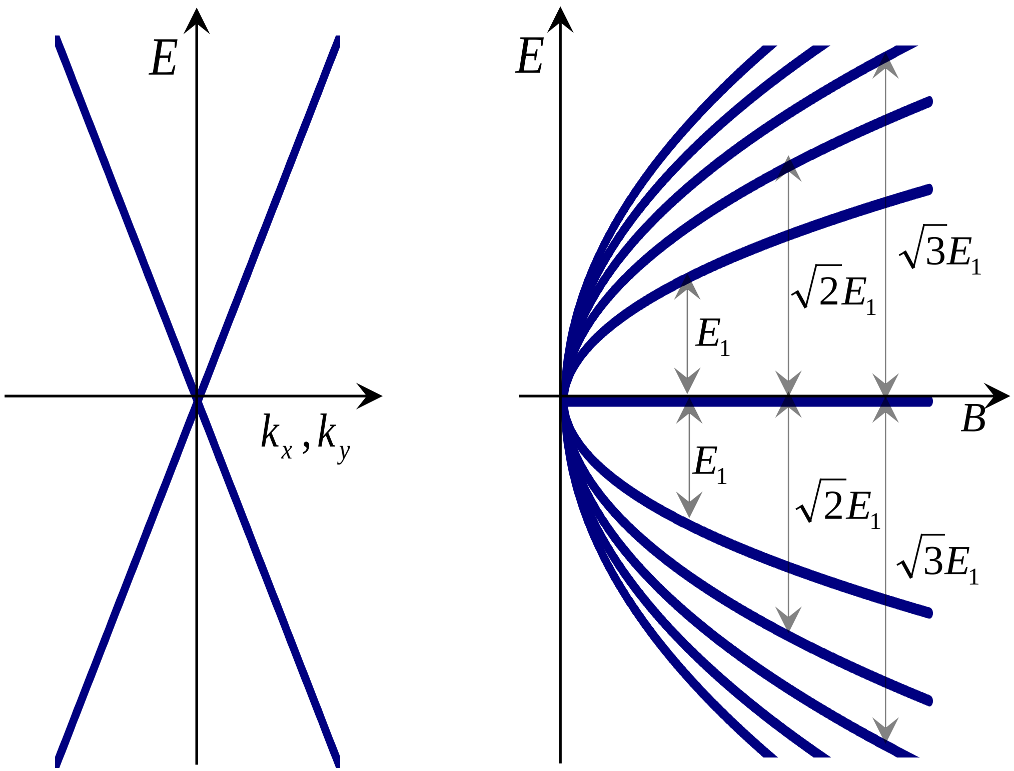
$\boldsymbol{B = 0}$ $\qquad$ $\boldsymbol{B > 0}$

P.R. Wallace, PR, 1947

Dispersion relations and corresponding Landau level fan chart

Dirac cone, "linear electrons" : graphene

$$E(\vec{k}) = \pm v_F \hbar \left| \vec{k} \right| \qquad E_n = \pm v \sqrt{2e\hbar}\sqrt{Bn}$$



$$B = 0 \qquad B > 0$$

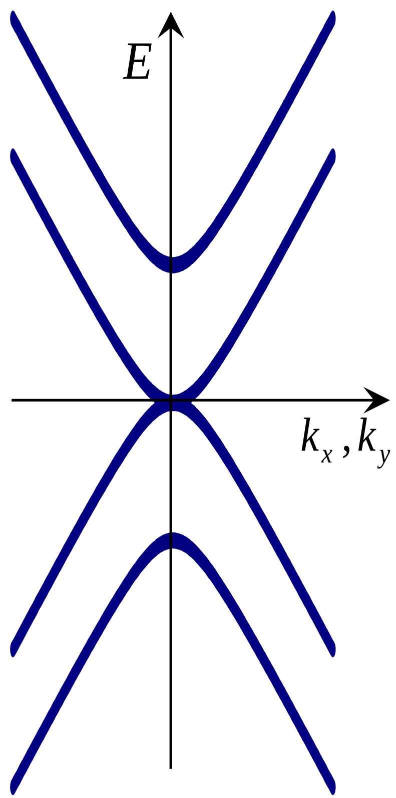
P.R. Wallace, PR, 1947

Dispersion relations and corresponding Landau level fan chart

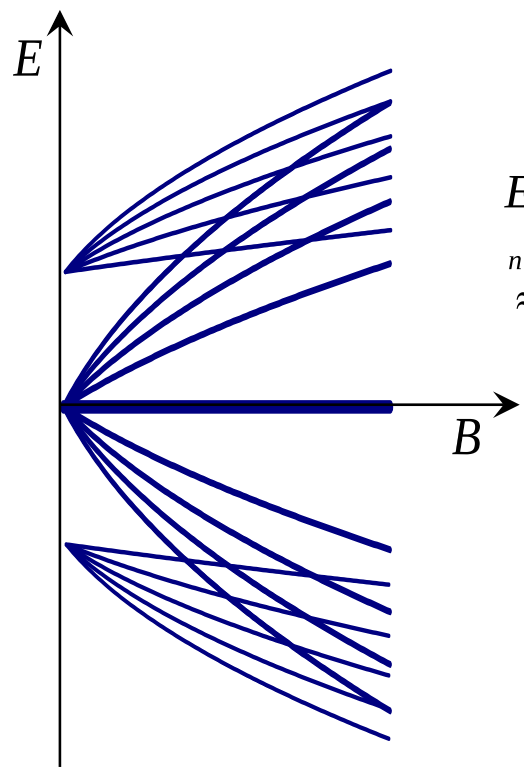
Electronic states of bilayer graphene

$$\sim \quad E(\vec{k}) = \pm\, \hbar^2 \vec{k}^2 / 2m$$

$$m = \gamma_1 / 2v_F^2$$



$B = 0$



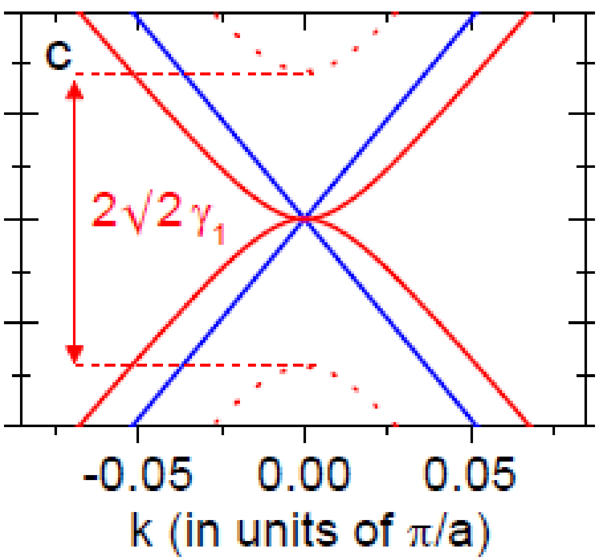
$$E_n \approx \pm\hbar\omega_C \sqrt{n(n+1)} \underset{n\geq 1}{\approx} \pm\hbar \frac{eB}{m}(n+\frac{1}{2})$$

J. Blinowski *et al.*, J.Phys., 1980; E. McCann & V.I. Falko, PRL, 2006

Dispersion relations and corresponding Landau level fan chart

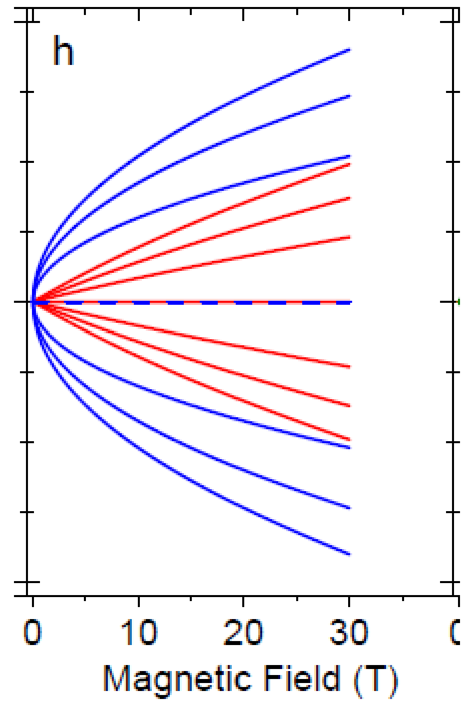
Electronic states in 2D structures of sp[2] carbon ~ graphene + (effective) bilayers

$$E = E(\vec{k})$$



!

?!

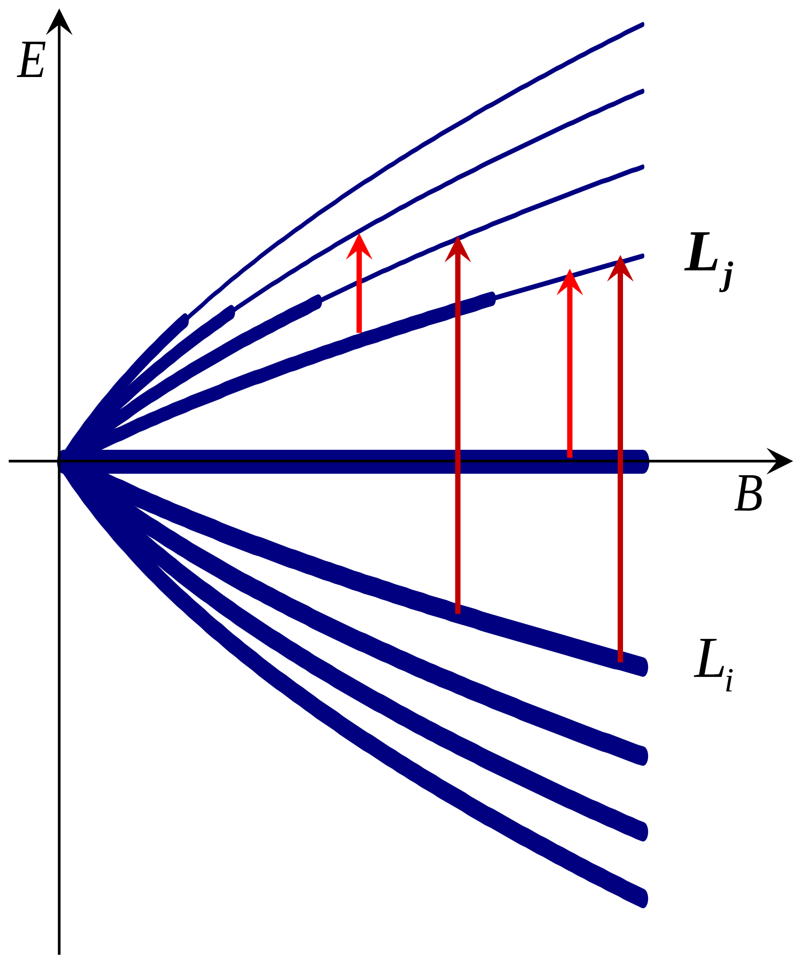


$$E = E_{n_i}(B)$$

B = 0

B > 0

Landau level spectroscopy = Probing inter Landau level excitations $L_i \rightarrow L_j$



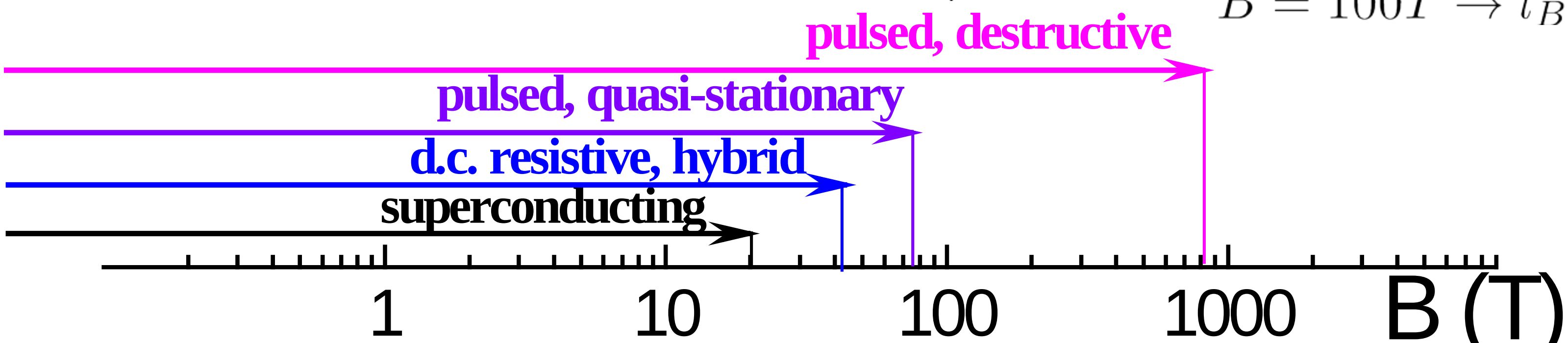
Ideally by **optical means** :

- no electrical contacts
- non invasive
- probe states near and far away from the Fermi energy

The magnetic length, a new characteristic length scale

$$2\pi l_B^2 B = \Phi_0 = h/e \qquad l_B = \sqrt{\frac{\hbar}{eB}} = \frac{25.6nm}{\sqrt{B(T)}}$$

$$B = 10T \rightarrow l_B \sim 10nm$$
$$B = 50T \rightarrow l_B \sim 4nm$$
$$B = 100T \rightarrow l_B \sim 2.5nm$$



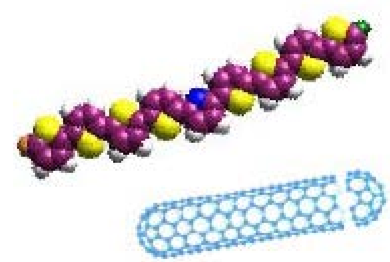
Compare this length to l_{scatt}, l_{loc}, a_b

.. 2DEG, (l_{scatt}) ....→

.. metals, l_{scatt}

.Superconductors, ξ, $d_{interplane}$......→

.. sc quantum dots (l_{loc}) →

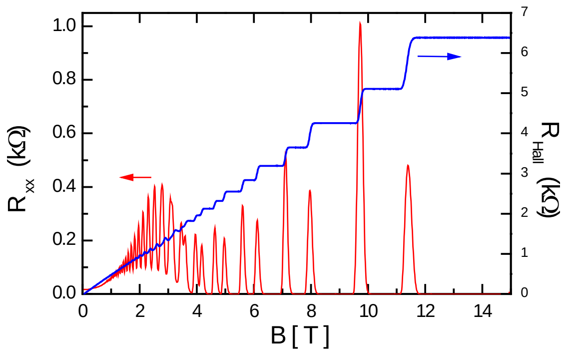


SWCNT ϕ..<1.4 nm.

molecules (a_b) .≤ 1 nm....→

Two-dimensional electronic systems + magnetic fields = a fruitful association

Integer QHE



Nobel Prize, 1985

FQHE, GaAs heterostructure

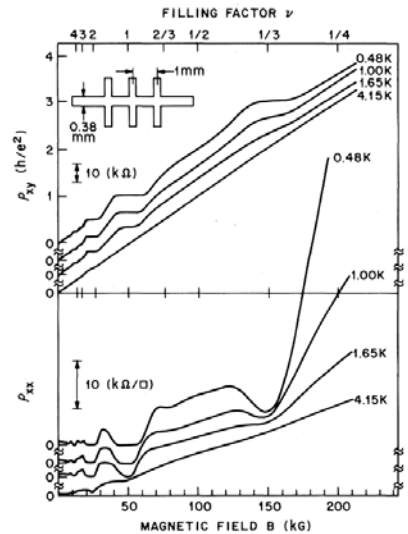
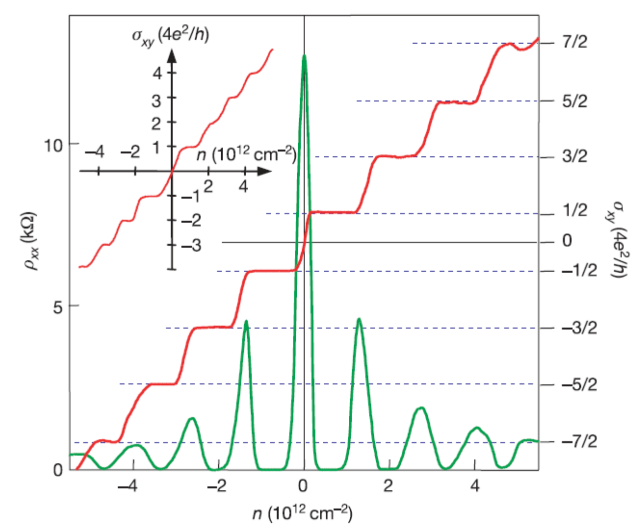


FIG. 1. ρ_{xy} and ρ_{xx} vs B, taken from a GaAs-$Al_{0.3}$-$Ga_{0.7}As$ sample with $n = 1.23\times10^{11}/cm^2$, $\mu = 90\,000$ cm^2/V sec, using $I = 1$ μA. The Landau level filling factor is defined by $\nu = nh/eB$.

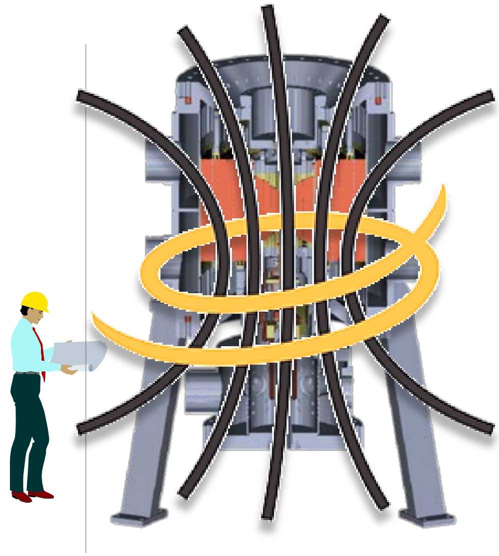
Nobel Prize, 1998

QHE, graphene



Nobel Prize, 2010

Magnetic field is a perfect tool to:



Couple to spin and orbital degrees of freedom

clarify results obtained at B=0, testing models, investigate band structure, etc …

Tune the dimensionality of an electronic system

magnetic length ~ nm

Create new states of matter (FQHE, SC, etc …)

What else ?

Outline:

- Why combining optical spectroscopy with magnetic fields ?

- Experimental techniques

- Dirac fermions in graphene:
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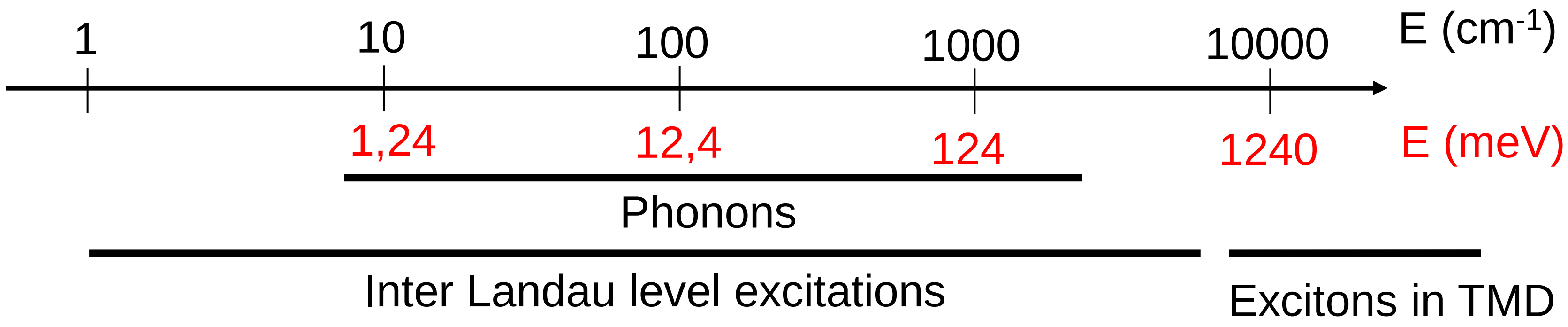
Landau Level Spectroscopy: Experimental techniques

Infrared range of energy



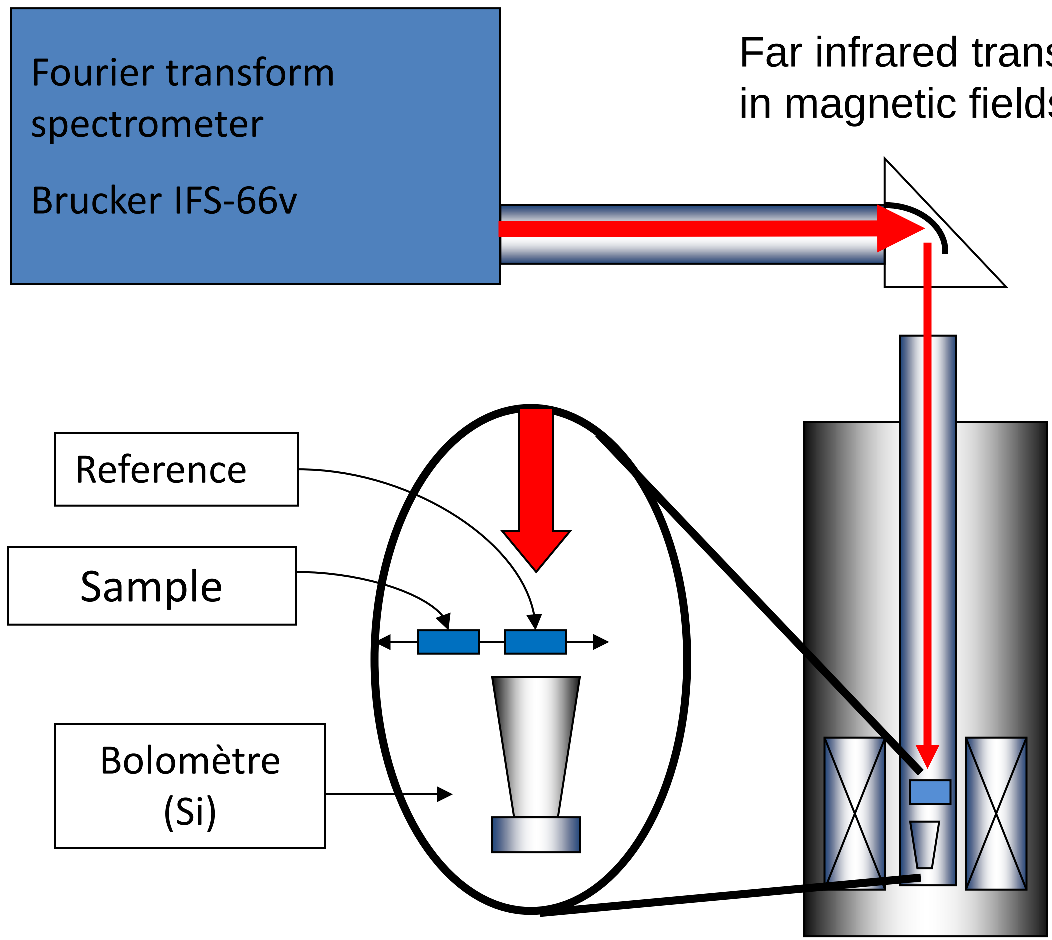
Low energy excitations :

- Fourier transform spectroscopy
- Raman scattering
- Photoconductivity (FIR-MIR laser)

Visible optics :

- Photoluminescence
- Reflectance contrast / Transmission
- Photoluminescence Excitation

Fourier Transform Spectroscopy

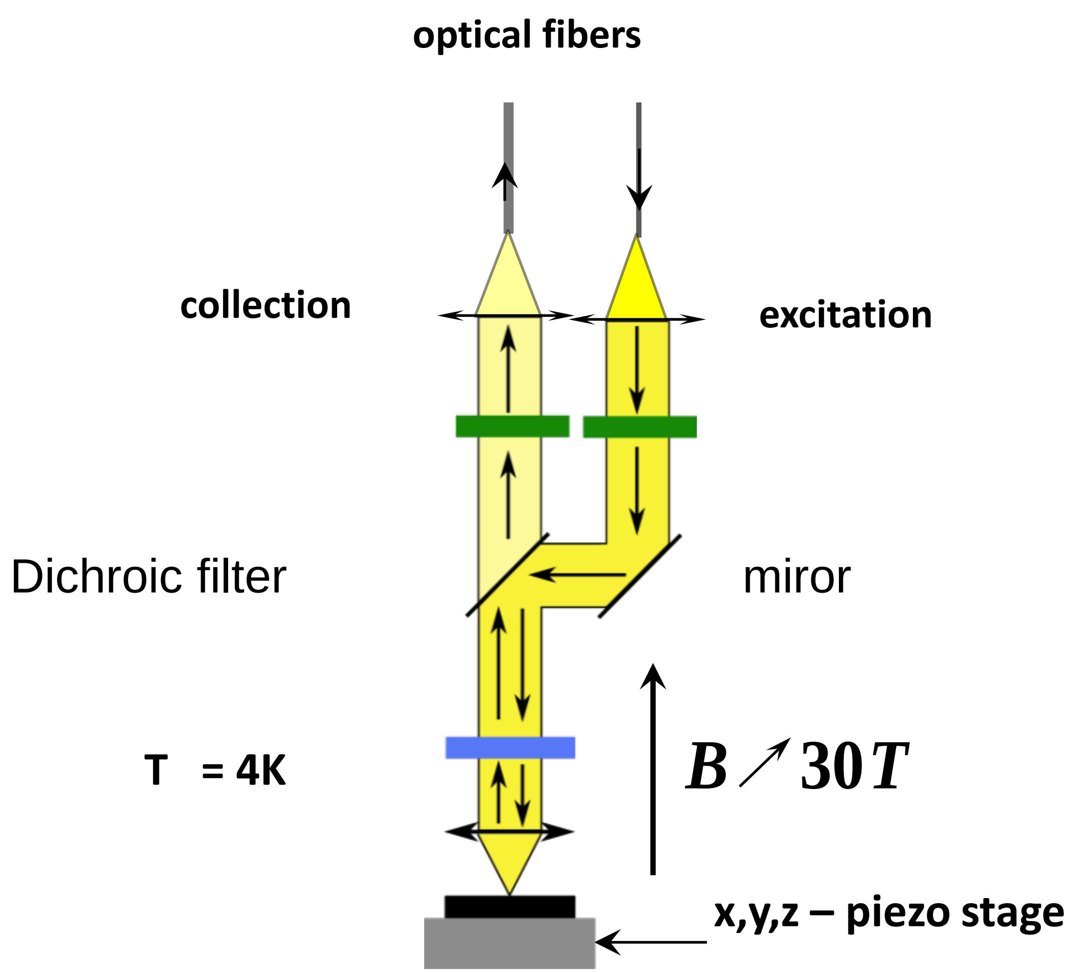


Far infrared transmission spectroscopy in magnetic fields

Relative change of transmission

$$T(\omega, B)/T(\omega, B=0)$$

µ- magneto-Raman scattering or Reflectance spectroscopy



miniaturized optical bench

Pros and cons

IR magneto-transmission

Broad range of energy, from 1-2 meV to ~1 eV

Absolute measurement
(gives access to the oscillator strength)

Selection rules well defined
(dipole allowed excitations)

Requires macroscopic samples (>1 mm)

Polarization optics not well developped

Si bolometers

Magneto-Raman scattering

Micrometer scale probing

Polarization optics

Si-CCD detectors

Not an absolute measurement

Requires high quality specimens

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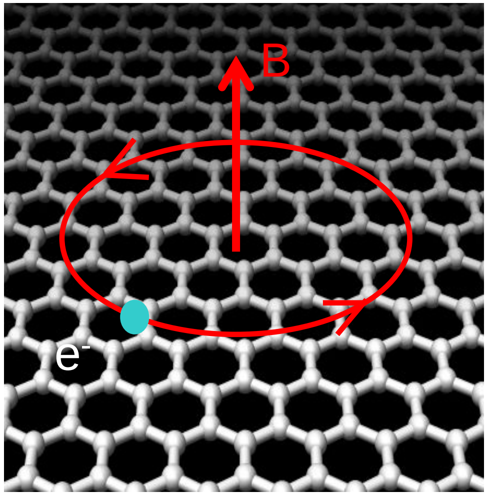
Cyclotron motion of massless Dirac fermions (classical regime)

Equation of motion for a charged particle in magnetic field (2D):

$$\frac{d\vec{\mathbf{p}}}{dt} = e[\vec{\mathbf{v}} \times \vec{\mathbf{B}}]$$

Cyclotron motion at frequency: $$\omega_c = \frac{eB}{\underbrace{(E/v_F^2)}}$$



"Effective" effective mass
of massless particle (i.e. Einstein relation)

Linear in magnetic field

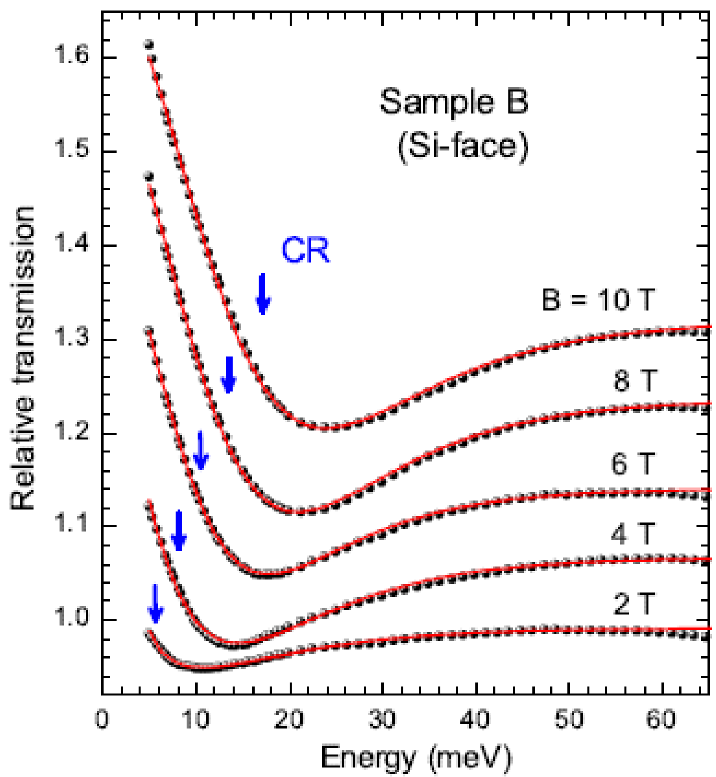
Energy dependent…

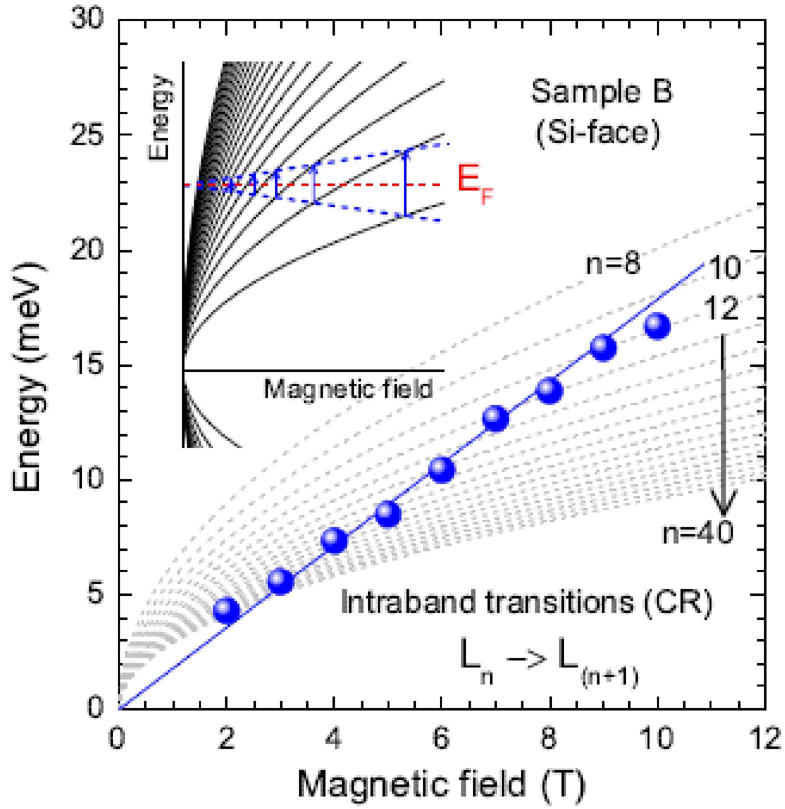
For conventional particles $\omega_c = \dfrac{eB}{m^*}$

A. M. Witowski et al., Phys. Rev. B, 82, 165305 (2010)
I. Crassee et al., Nature Physics 7, 48 (2011)

Cyclotron motion of massless Dirac fermions (classical regime)

Highly doped (~10^{13} cm^{-2}) monolayer on Si face SiC





Intra-bande
$L_n \rightarrow L_{n+1}$
absorbtions

$$\sigma_{\pm}(\omega, B) = \sigma_0 \frac{i\gamma}{\omega \pm \omega_c + i\gamma}$$

A. A. M. Witowski, M. Orlita, et al., Phys. Rev. B, 82, 165305 (2010)

Cyclotron resonance of massless Dirac fermions (quantum regime)

LL spectrum:

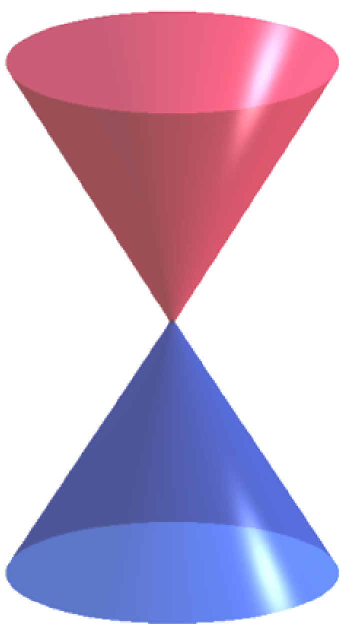
$$E_n = \pm v_F \sqrt{2e\hbar|nB|} = \pm E_1 \sqrt{|n|}$$

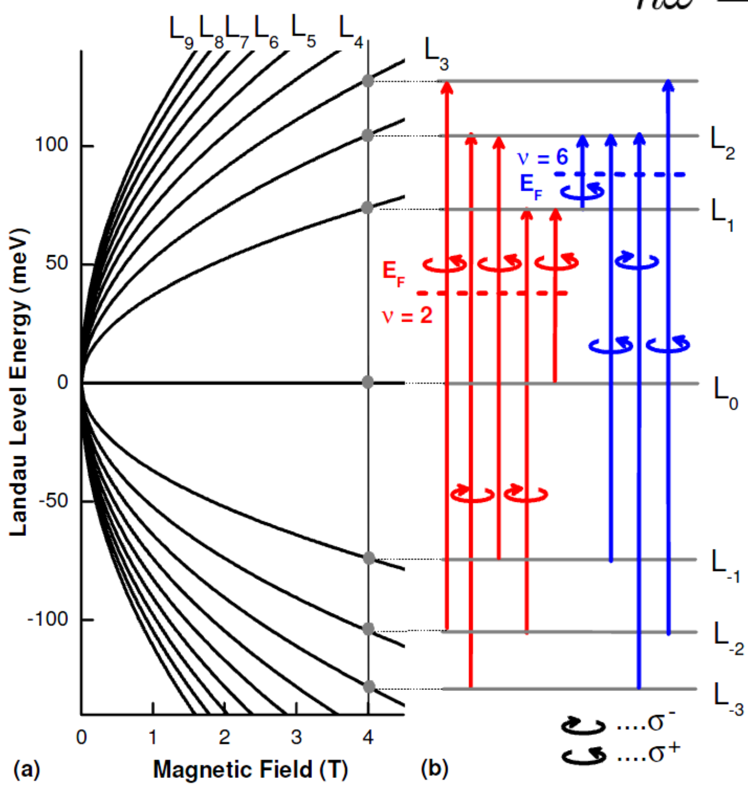
Selection rules (inter- and intra-band resonances):

$$|n| \rightarrow |n| \pm 1$$

Energy of optical transitions:

$$\hbar\omega = E_1(\sqrt{|n+1|} \pm \sqrt{|n|})$$





Multi-mode response (especially at higher T)

Typical $\sqrt{B}$ scaling of absorption lines
(single particle picture…)

M.L. Sadowski et al., SSC 2007
M. Orlita et al., SST 25 063001 (2010)

Cyclotron resonance of massless Dirac fermions (quantum regime)

Absorption in Kubo approach:

$$\mathrm{Re}(\sigma^{\pm}(\omega,B)) = \frac{4e^2}{\omega}\underbrace{\frac{|eB|}{h}}_{\text{LL degeneracy}}\frac{\gamma}{\pi}\sum_{m,n}\underbrace{|\langle m|\hat{v}_{\pm}|n\rangle|^2}_{\text{Velocity operators Independent of B}}\frac{f_n - f_m}{(E_m - E_n - \hbar\omega)^2+\gamma^2}$$

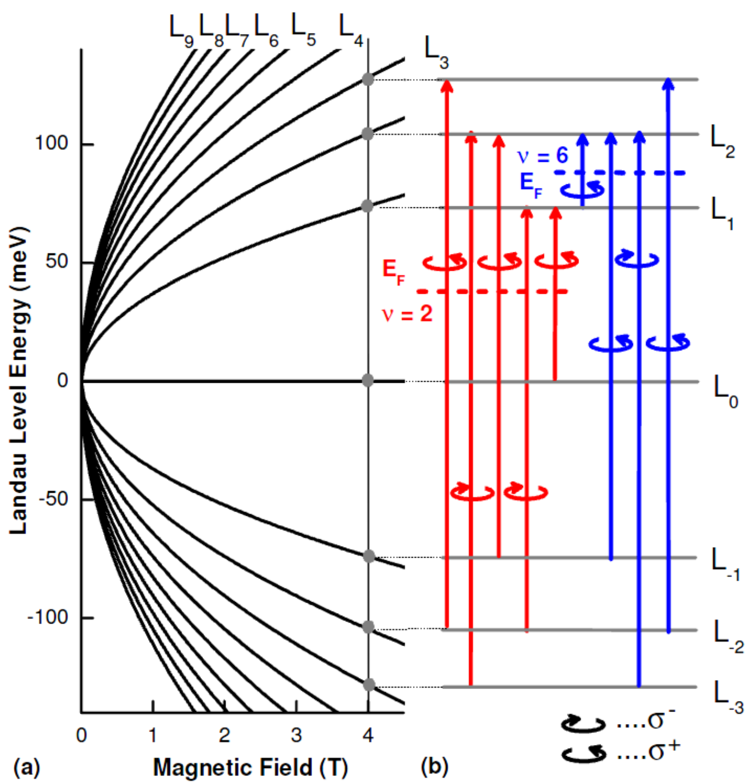
LL degeneracy

Velocity operators
Independent of B

$$|\langle m|\hat{v}_{\pm}|n\rangle|^2 = (v_F^2/4)\delta_{|m|,|n|\pm 1}$$

for $m \neq 0, n \neq 0$

otherwise $(v_F^2/2)\delta_{|m|,|n|\pm 1}$



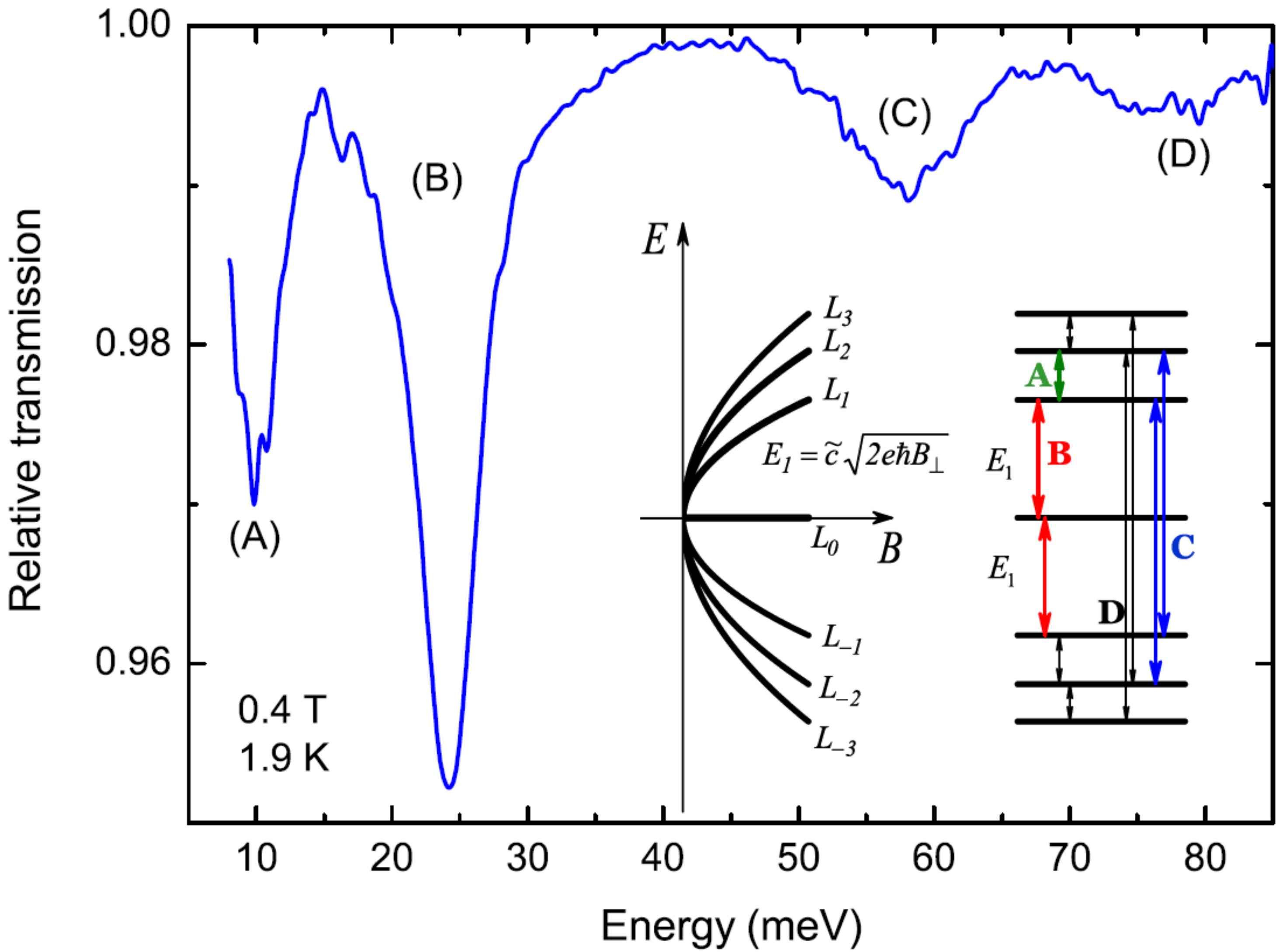
$$\int_0^{\infty}\mathrm{Re}[\sigma_{\pm}(\omega,B)]d\omega \propto \underline{\sqrt{B}}$$

for one particular transition and constant occupation factors

For "parabolic electrons" :

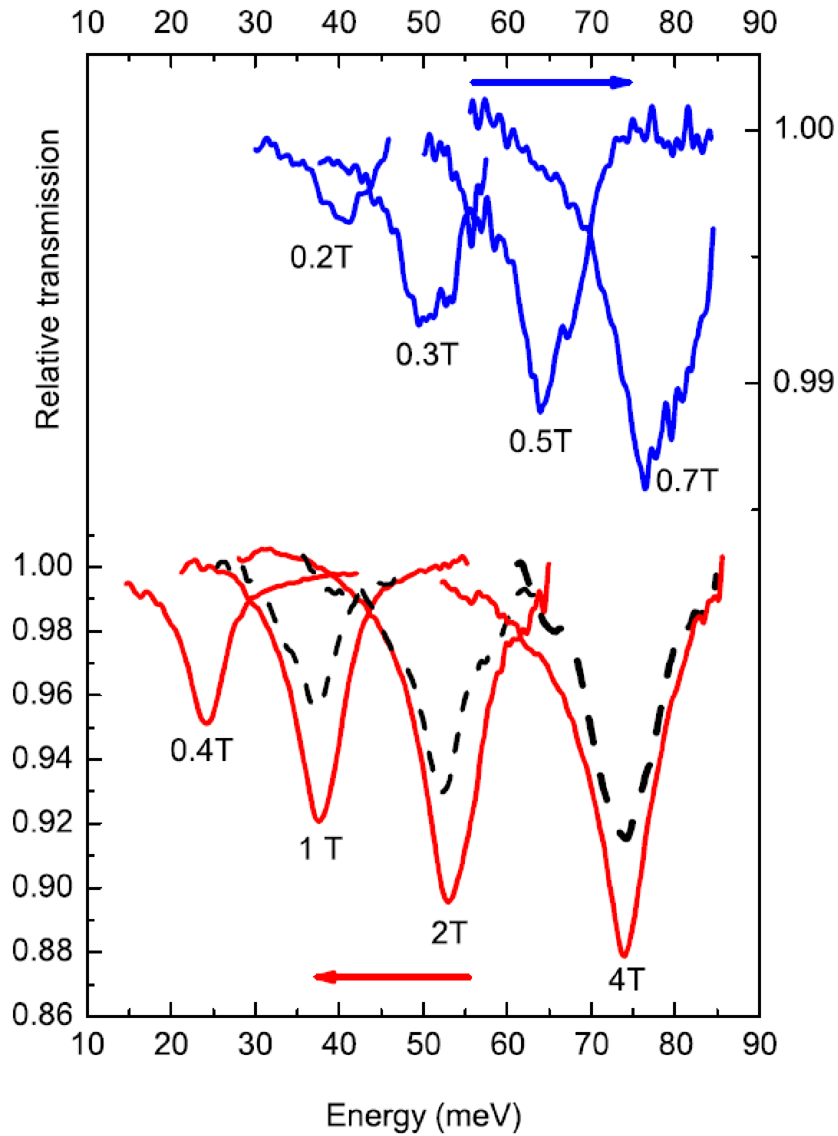
$$\int_0^{\infty}\mathrm{Re}[\sigma_{\pm}(\omega,B)]d\omega \propto \underline{n_0/m}$$

Cyclotron resonance in (multilayer epitaxial) graphene



M. L. Sadowski et al., Phys. Rev. Lett. 97, 266405 (2006)
M. Orlita et al., Phys. Rev. Lett. 101, 267601 (2008)

Cyclotron resonance in (multilayer epitaxial) graphene



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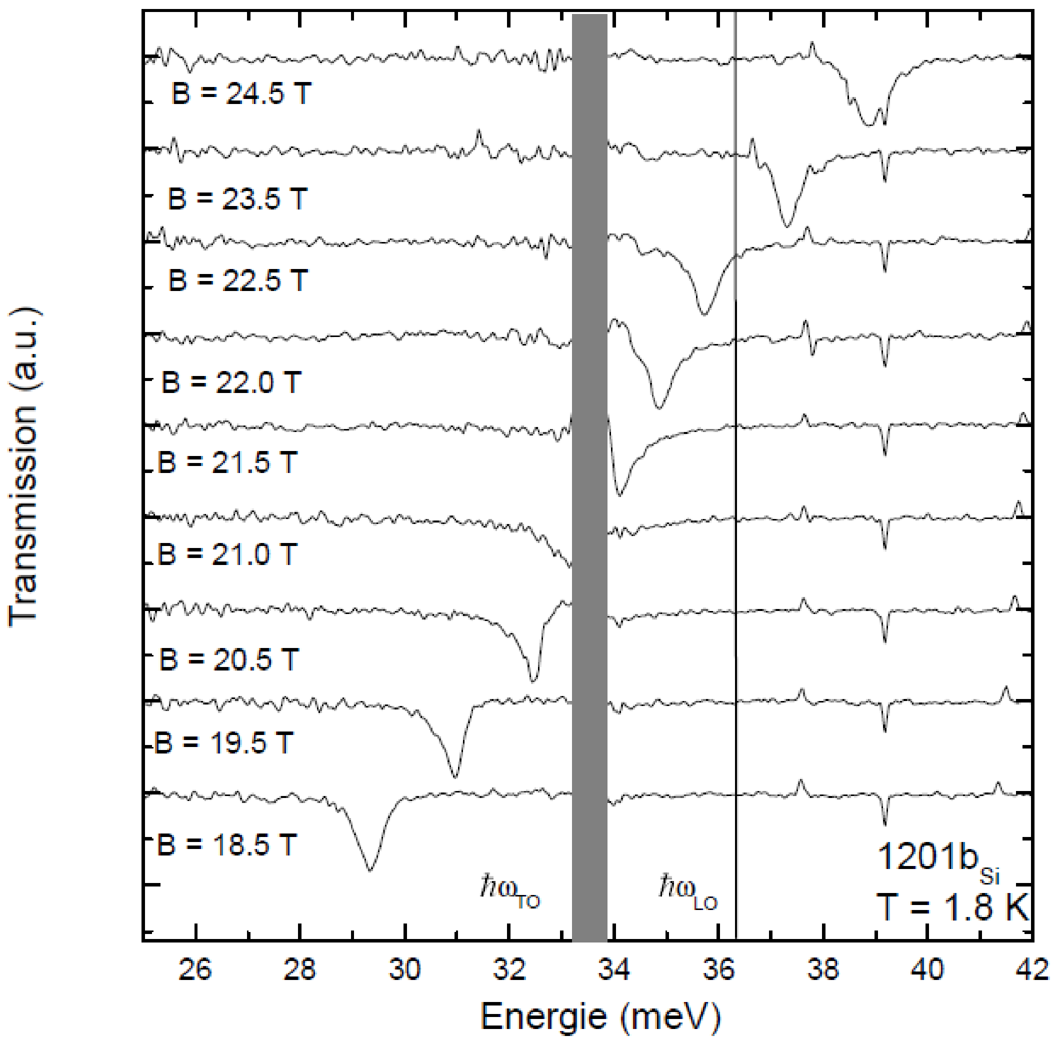
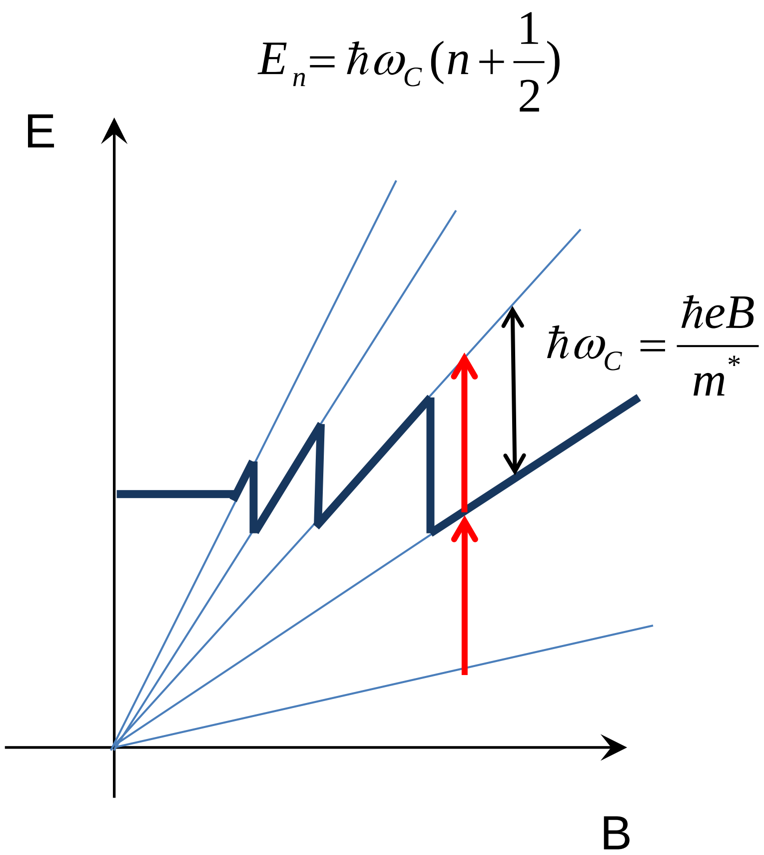
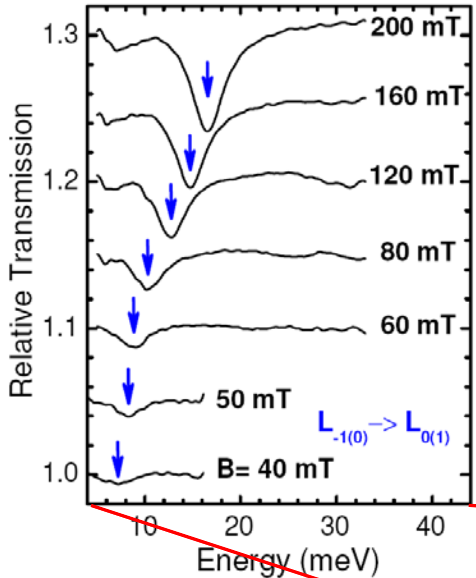
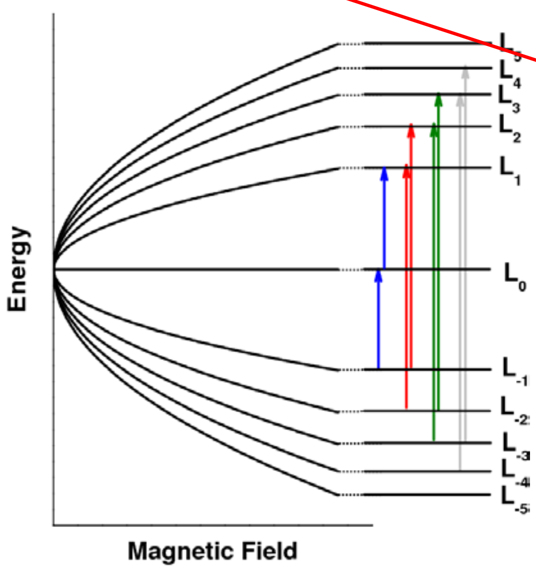


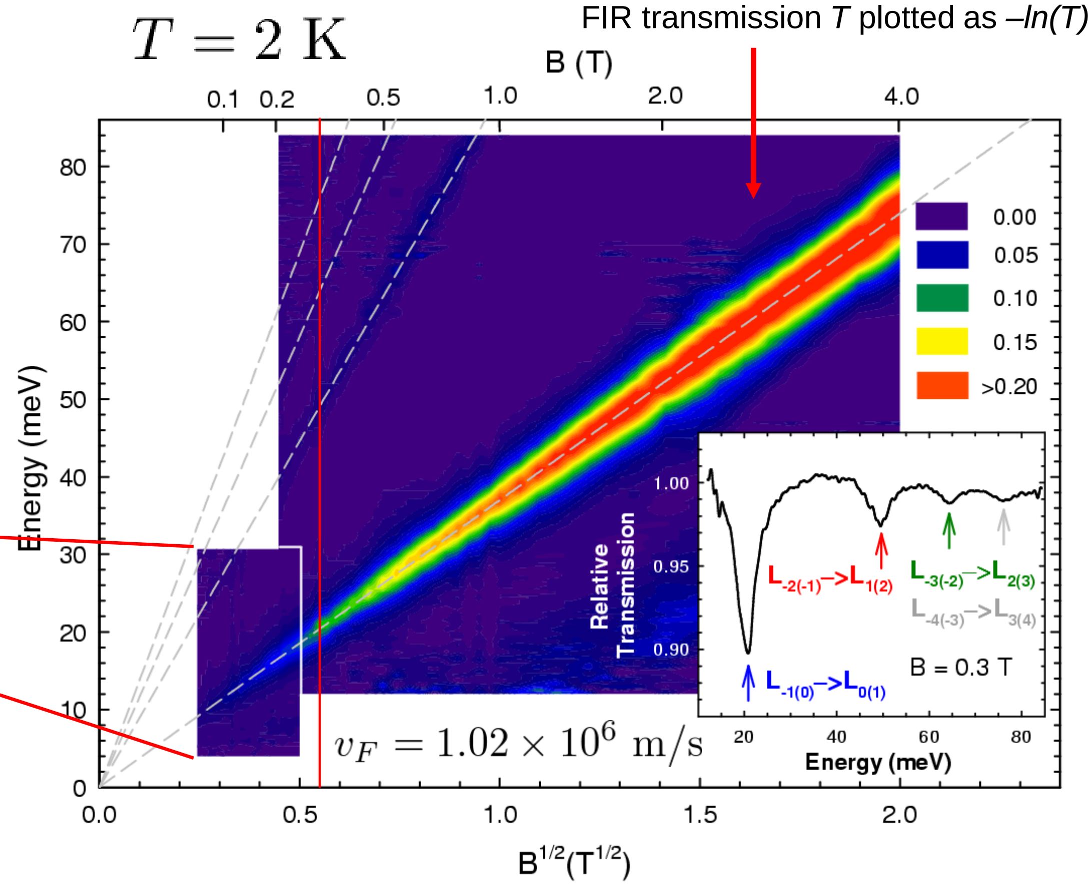


GaAs single QW

Cyclotron resonance in (multilayer epitaxial) graphene







Energy spectrum:

$$E_n = \pm v_F \sqrt{2e\hbar|Bn|}$$

Selection rules:

$$|n| \rightarrow |n| \pm 1$$

M. L. Sadowski et al., Phys. Rev. Lett. 97, 266405 (2006)
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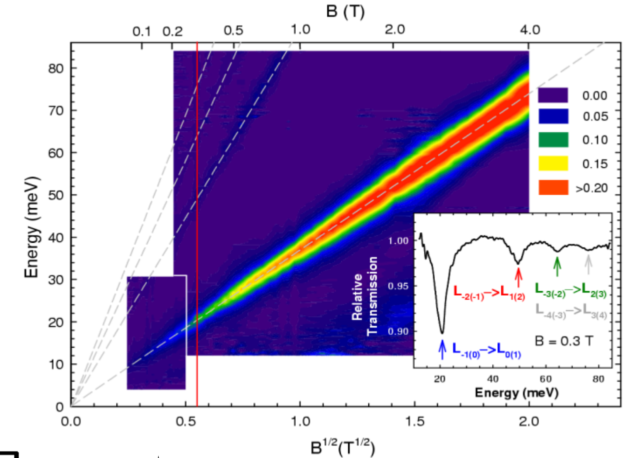
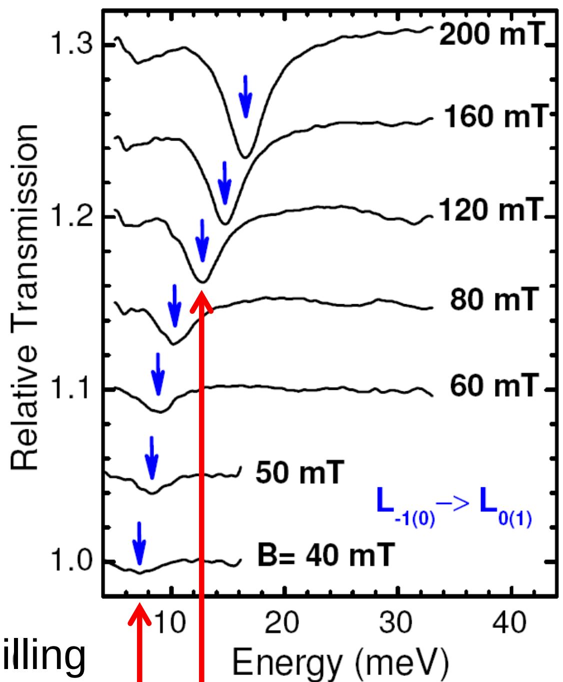
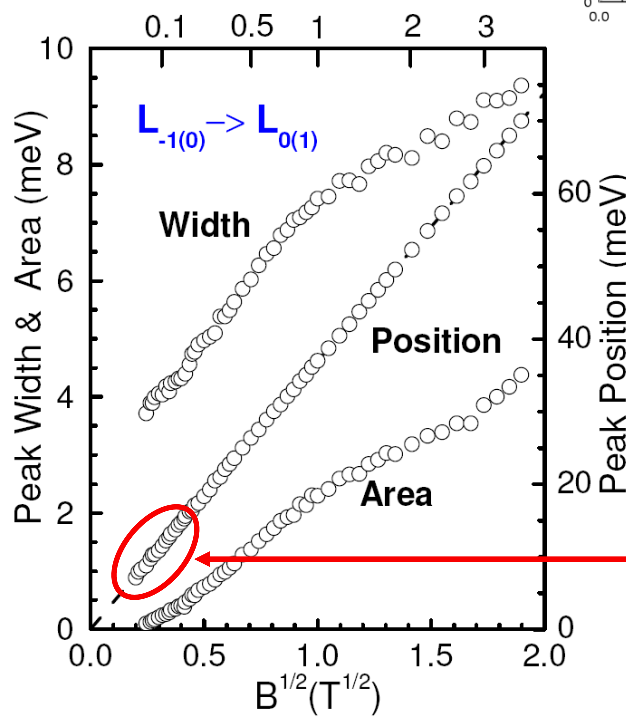
Analysis of low magnetic field data

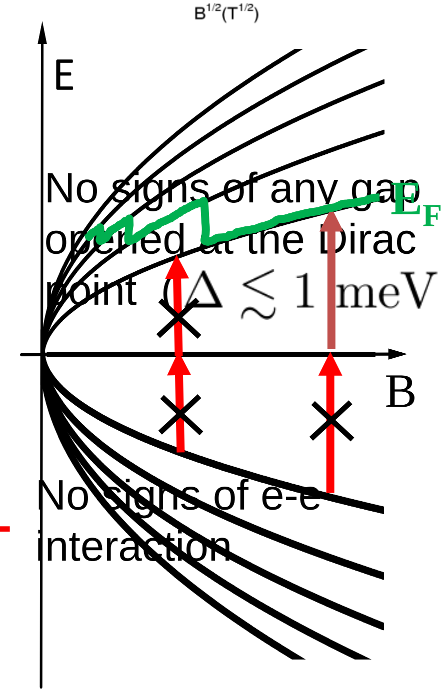


Focus on $L_{-1(0)} \rightarrow L_{0(1)}$ line
(vicinity of Fermi level)

Well-defined line down to $B \sim 40$ mT at ~ 7 meV







No signs of any gap opened at the Dirac point ($\Delta \lesssim 1$ meV)

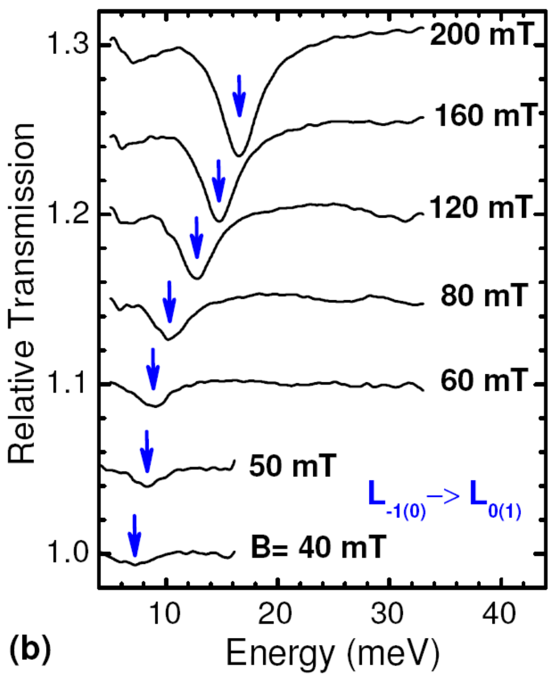
No signs of e-e interaction

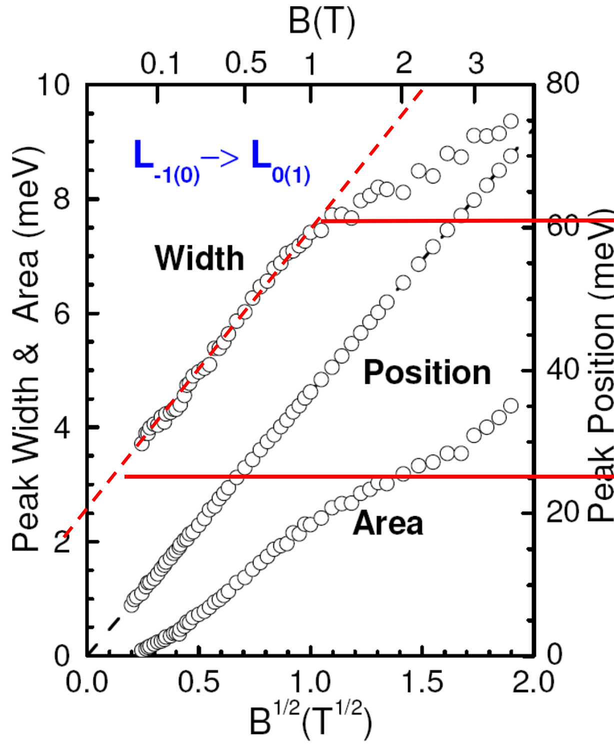
Filling factor $\nu \approx 2$ $\nu \approx 6$

Estimation of carrier density $n_0 \approx 5 \times 10^9$ cm^{-2}

$$\varepsilon_F = \tilde{c}\hbar\sqrt{\pi n_0} \approx 8 \text{ meV}$$

Analysis of data (lineshape, scattering time, mobility...)





Scattering time from the linewidth:

$$\tau \sim 150 \text{ fs}$$

$$\tau = 2\hbar/\delta E$$

$$\tau \sim 300 \text{ fs}$$

Mean free path

$$l = v_F \tau \approx 300 \text{ nm}$$

Linewidth $\propto \sqrt{B}$ $\Longrightarrow$ Short-range scattering

N. H. Shon and T. Ando, J. Phys. Soc. Jap. 67, 2421 (1998)

Carrier mobility?

$$\tau\omega_c > 1 \Rightarrow \mu B > 1$$

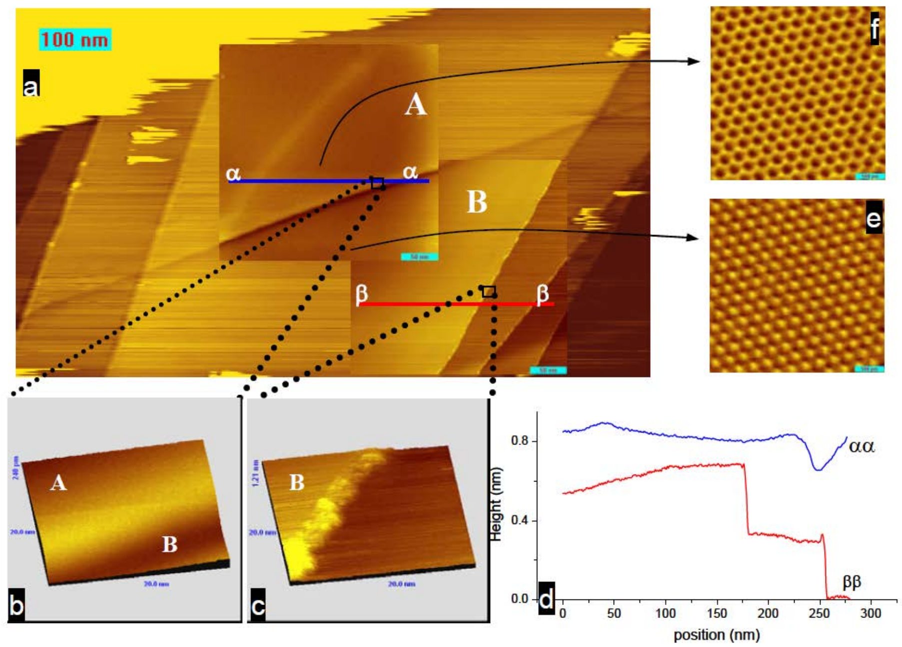
$$\mu > 250000 \text{ cm}^2/(\text{V.s})$$

↑

Main line down to $B = 40$ mT

Graphene flakes on the surface of natural graphite

STM



Li et al, PRL **102** 176804, (2009)

Graphene flakes on the surface of natural graphite

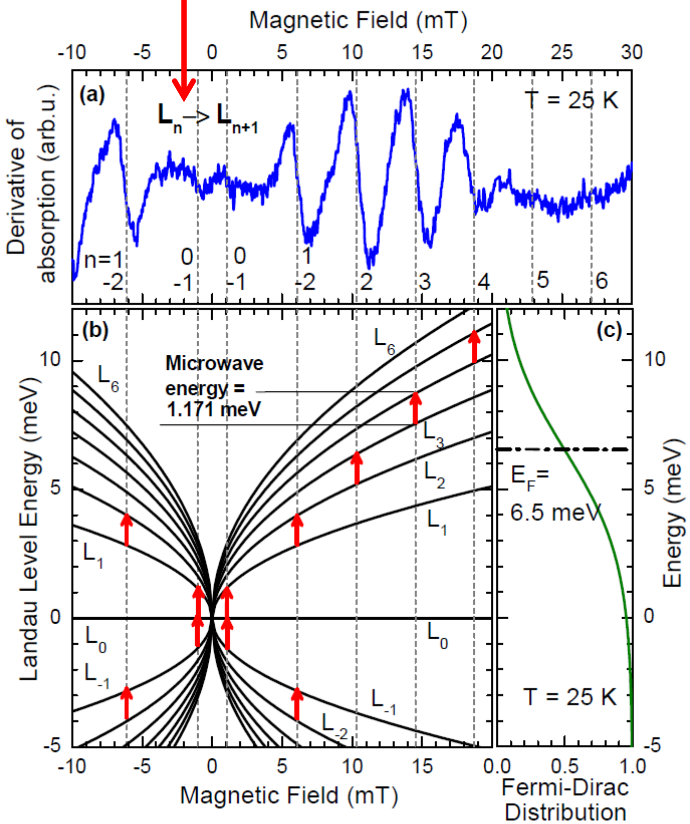
EPR-like

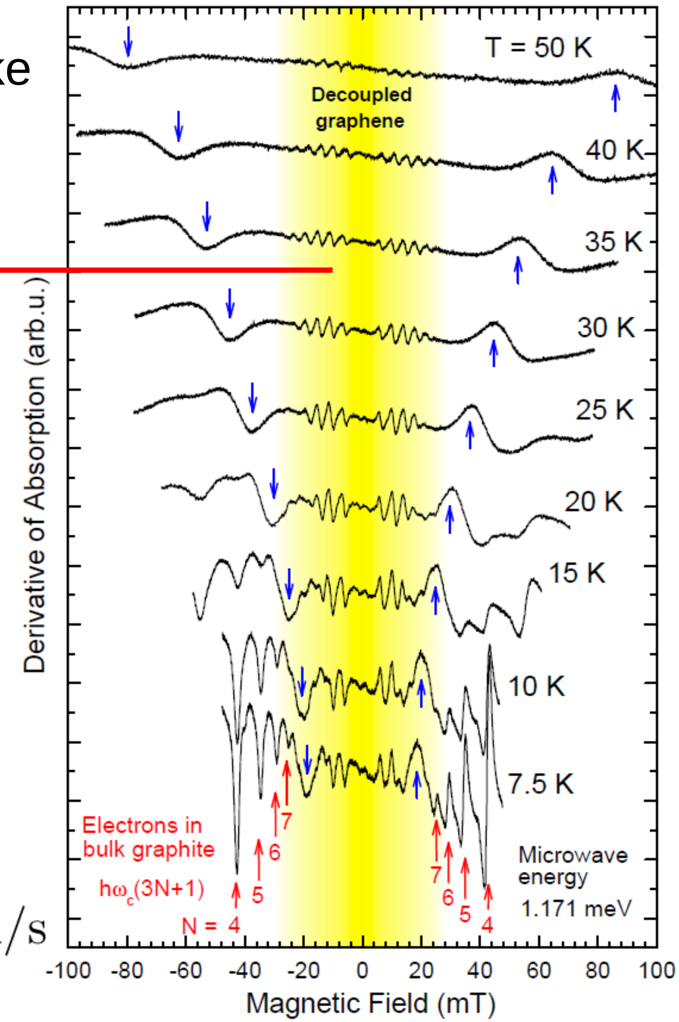
Landau level quantization down to $B = 1$ mT

LL width temperature independent

$\Gamma \approx 40\ \mu\mathrm{eV}$

$(\tau \approx 20\ \mathrm{ps})$





Fermi velocity

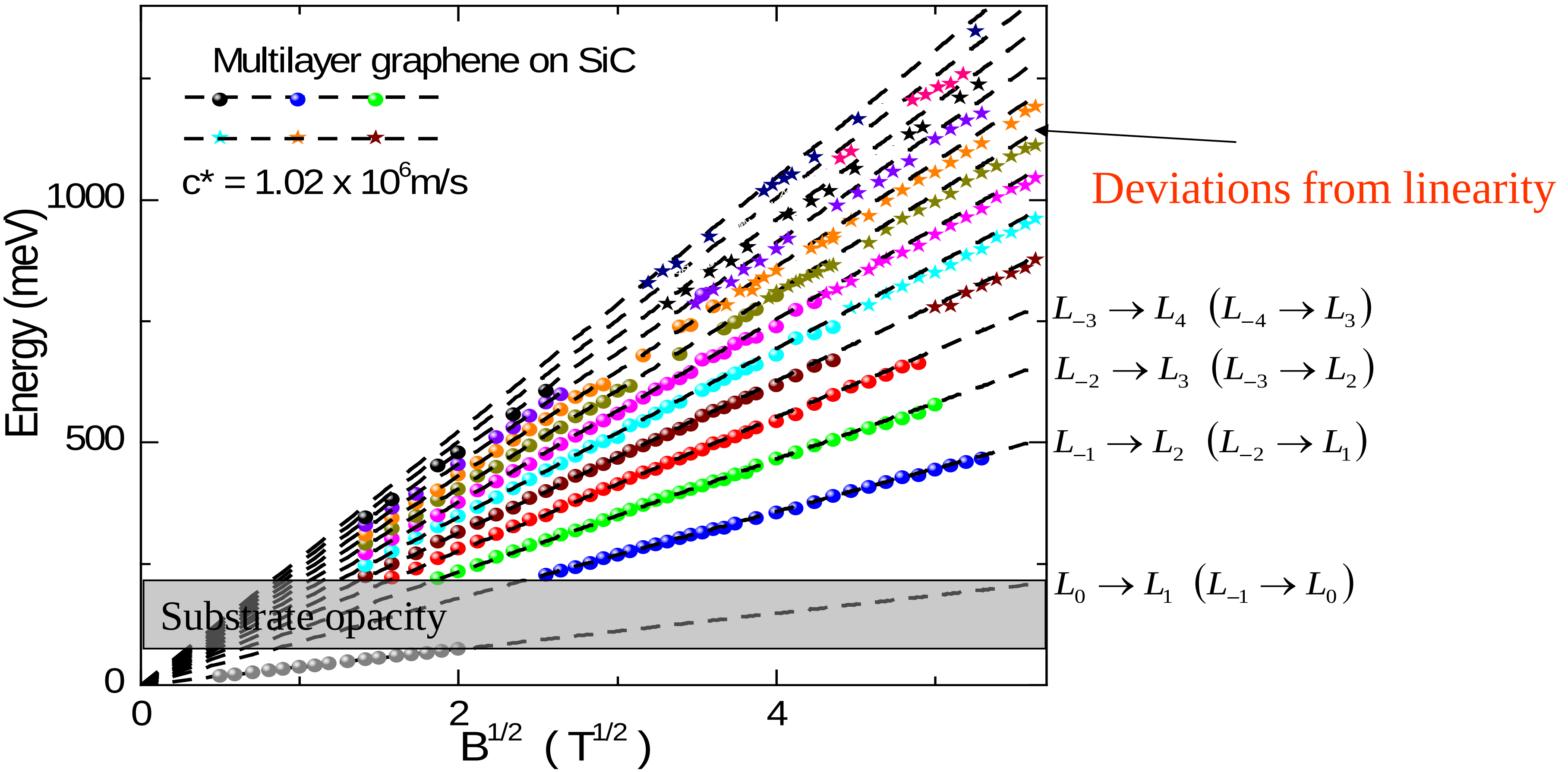
1.00×10^6 m/s

$10^7\ \mathrm{cm^2/(V.s)}$

P. Neugebauer, M. Orlita et al., Phys. Rev. Lett. 103, 136403 (2009)

Accurateness of the “ Dirac cone” ? How far does it continue

Landau Level spectroscopy from the Far Infrared to the Near Visible



P. Plochocka et al., Phys. Rev. Lett. **100**, 087401 (2008)

High energy limits of “Dirac like electron dispersions”

+ next nearest neighbor hopping

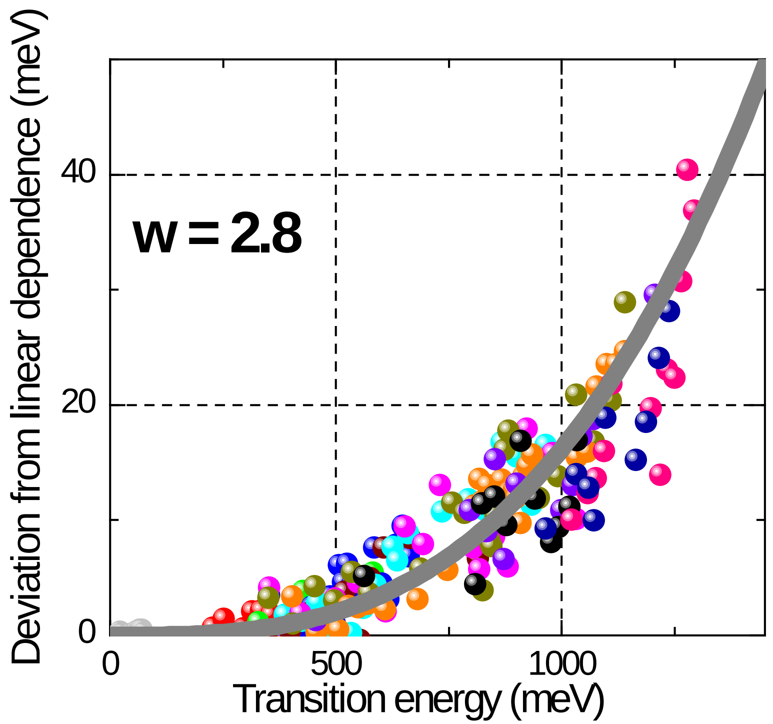
$$E_s(\mathbf{k}) = \pm\hbar v_F \sqrt{k^2 + \frac{a^2}{16}k^4 + \frac{a}{2}s\left(k_x^3 - 3k_xk_y^2\right)},$$

In magnetic fields :

graphene :

tight binding (t)

next nearest neighbor (t`/t ~ 0.1)



$$\mathbf{E}_{\pm,n} = \pm\mathbf{E}_0\sqrt{\mathbf{n}} \mp \mathbf{E}_0\sqrt{\mathbf{n}}\left\{\frac{3\mathbf{w}^2}{8}\left(\frac{\tilde{\mathbf{a}}}{\mathbf{l}_B}\right)^2\mathbf{n}\right\} + \mathbf{E}_0\frac{3\mathbf{t}'}{\sqrt{2}\mathbf{t}}\frac{\tilde{\mathbf{a}}}{\mathbf{l}_B}\mathbf{n}$$

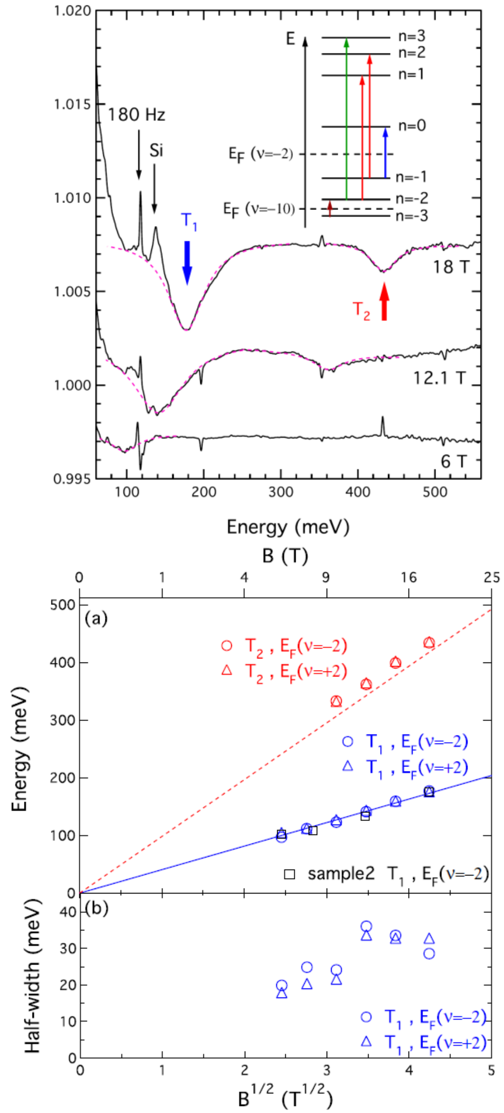
$$\Delta E^{\pm} = \mp\frac{9t'}{2}\left(\frac{\tilde{a}}{l_B}\right)^2 + \frac{3\tilde{a}w^2}{64\hbar^2 v_F}\left(\Delta_n^0\right)^3$$

Electron-hole asymmetry: small and not seen !

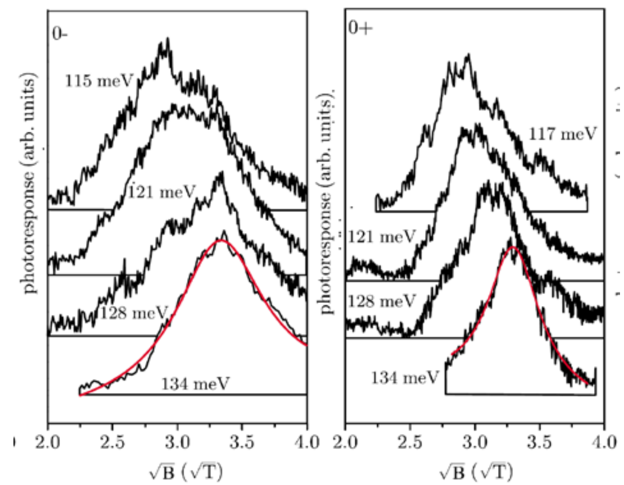
P. Plochocka et al., Phys. Rev. Lett. **100**, 087401 (2008)

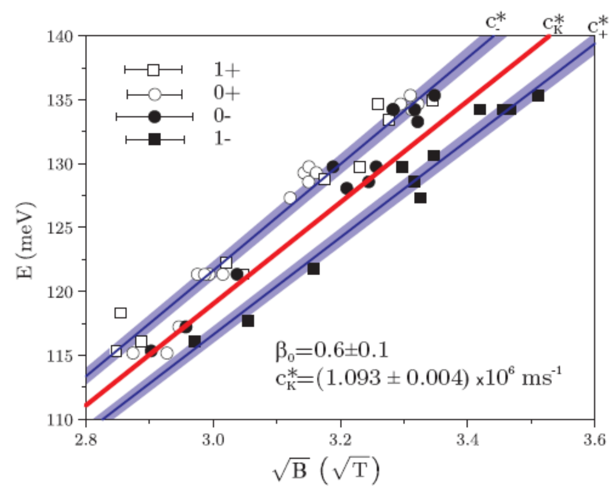
FIR experiments with exfoliated graphene

Z. Jiang et al., PRL (2007)



R.S. Deacon et al., PRB (2007)

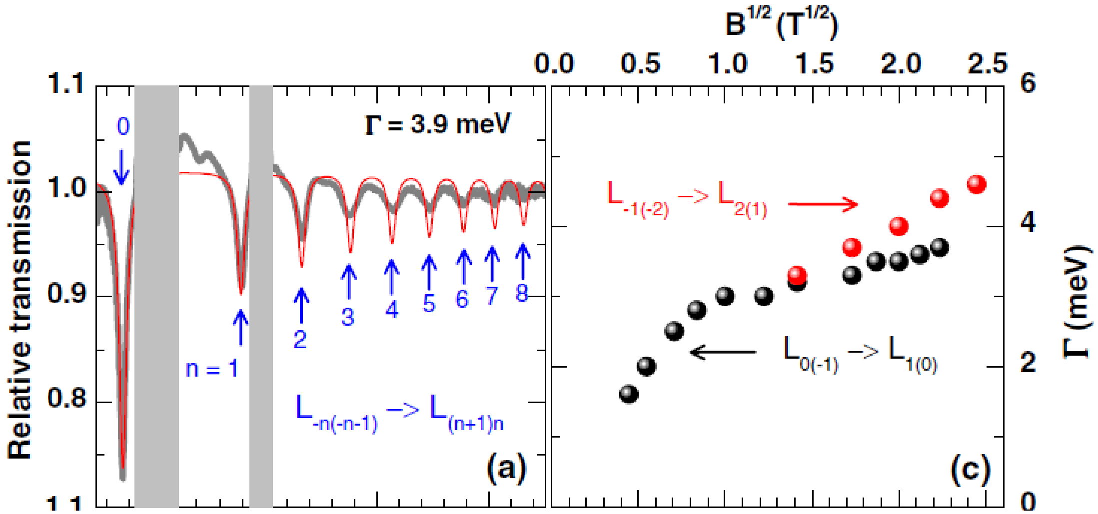




Energy dependence of scattering time in graphene

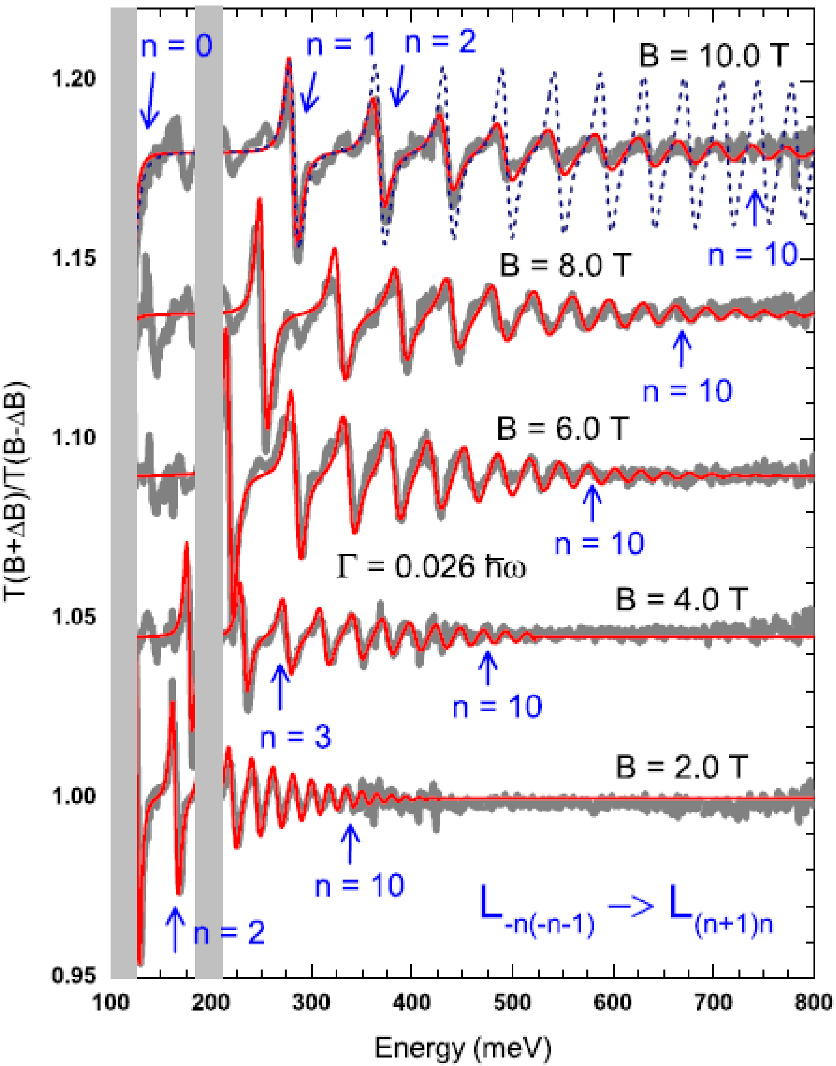
Modelling data with Kubo-Greenwood formula

$$\mathrm{Re}(\sigma^{\pm}(\omega, B)) = \frac{4e^2}{\omega}\frac{|eB|}{h}\frac{\gamma}{\pi}\sum_{m,n}|\langle m|\hat{v}_{\pm}|n\rangle|^2 \frac{f_n - f_m}{(E_m - E_n - \hbar\omega)^2 + \gamma^2}$$



M. Orlita et al. PRL 107, 216603, (2011)

Energy dependence of scattering time in graphene



Scattering rate increases linearly with energy !

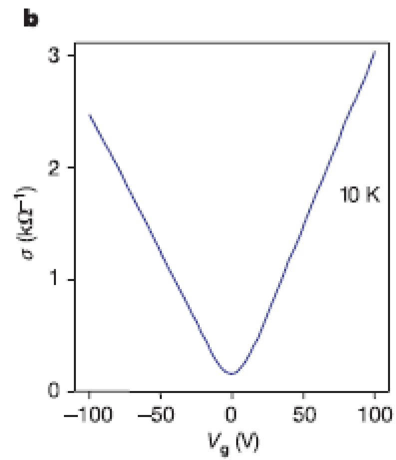
$$1/\tau \propto E$$

$$\sigma = v_F^2.\tau(E_F).DOS(E_F)$$

$$\sigma \neq f(n_s)$$

Experimentally (transport)

$$\sigma(n_s) \propto |n_s|$$



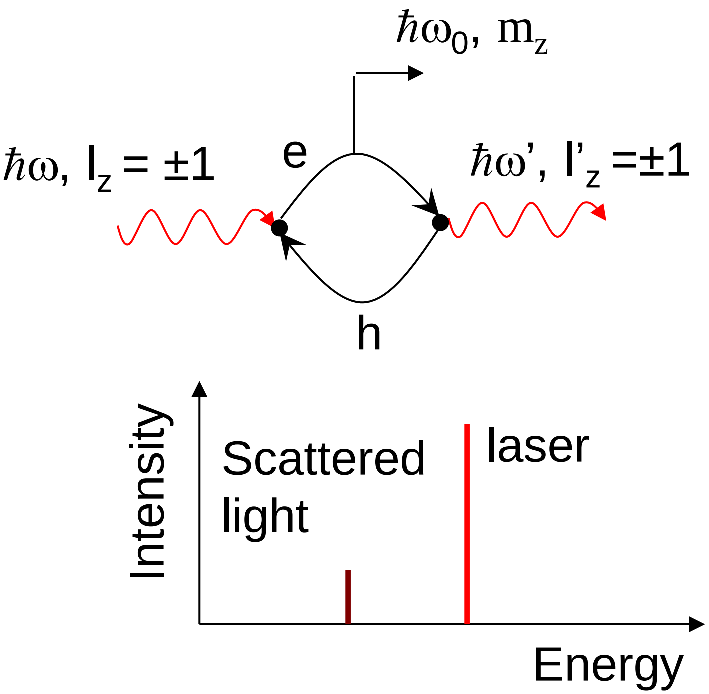
Protected graphene with
“conventional” scatterers

M. Orlita et al. PRL 107, 216603, (2011)

Outline:

- Why combining optical spectroscopy with magnetic fields ?
- Experimental techniques
- Dirac fermions in graphene:
  - Cyclotron motion/resonance & Landau levels
  - Magneto-Raman scattering
  - Interaction effects (electron-phonon and electron-electron)
- Semiconducting transition metal dichalcogenides
  - Excitonic properties
  - Zeeman spectroscopy
  - Magnetic brightening
- Summary

Raman or inelastic light scattering

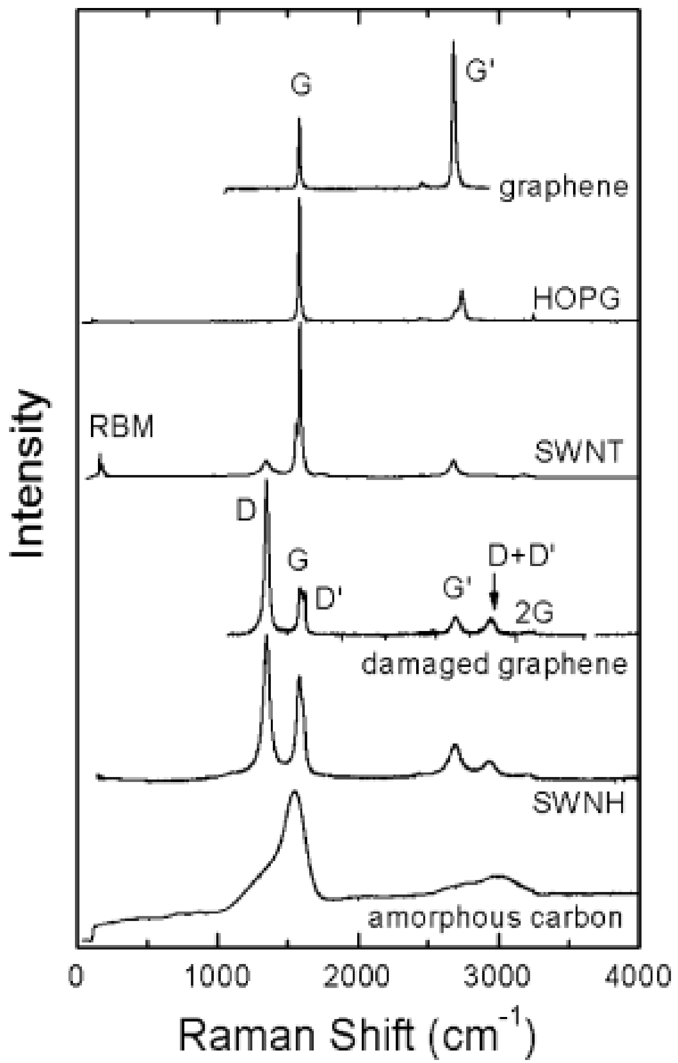


$\hbar\omega_0 = \hbar\omega - \hbar\omega'$

$m_z = \Delta l_z = l'_z - l_z$

"co – pol" $\sigma^{+/+}$ / $\sigma^{-/-}$ $\Delta l_z = 0$

"cross – pol" $\sigma^{+/-}$ / $\sigma^{-/+}$ $\Delta l_z = \pm 2$



M. Dresselhaus et al., NanoLett. **10,** 751, (2010)

Reviews:
A.C. Ferrari and D.M. Basko, Nature Nanotech. (2013)
L.M. Malard et al, Physics reports (2009)

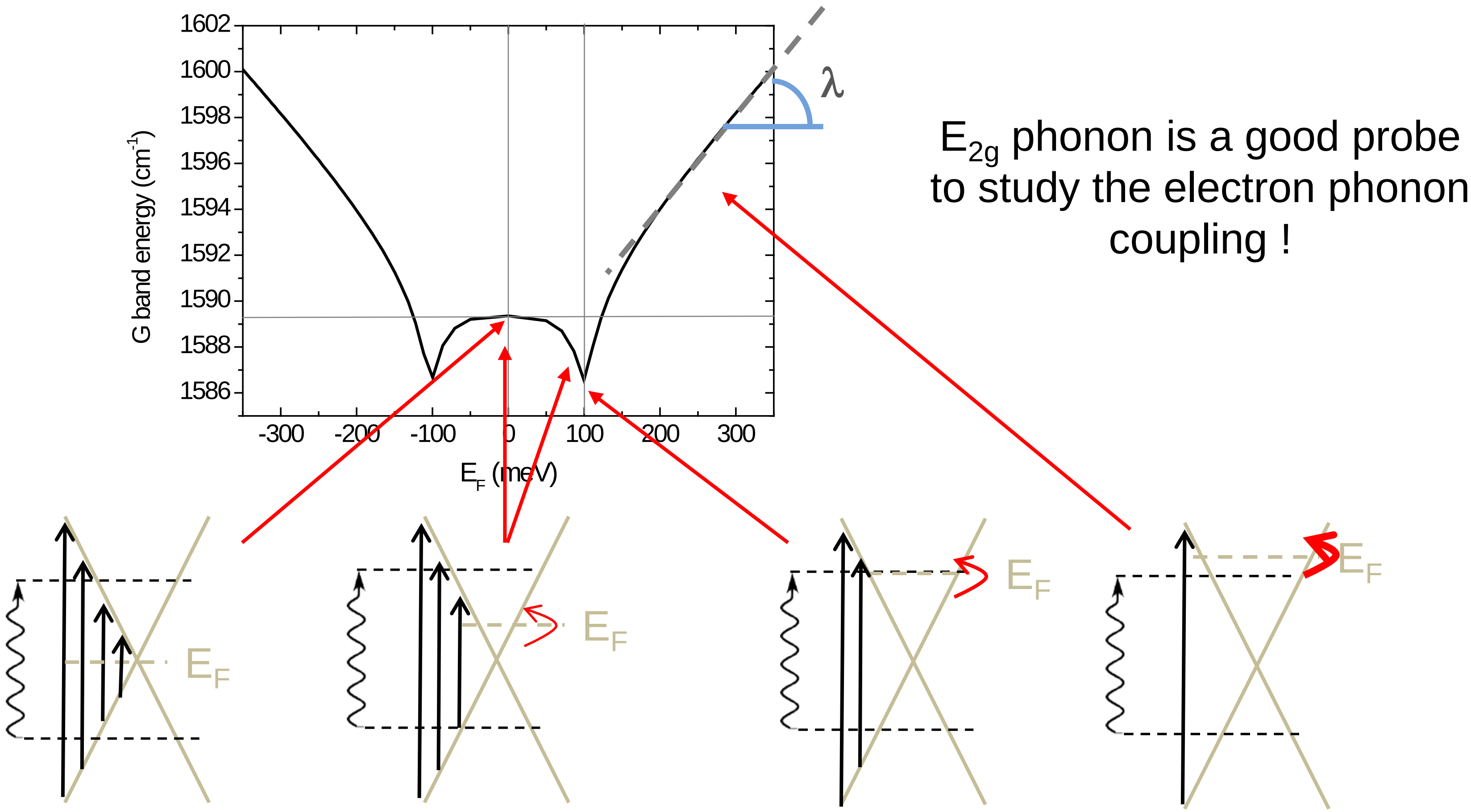
Interaction effects I :

Electron-phonon interaction

and

the magneto-phonon resonance

Tuning the e-ph coupling with electric fields

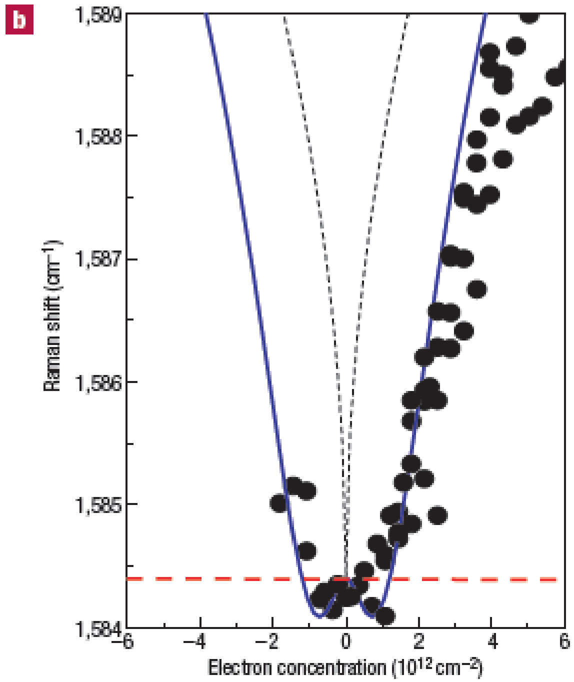


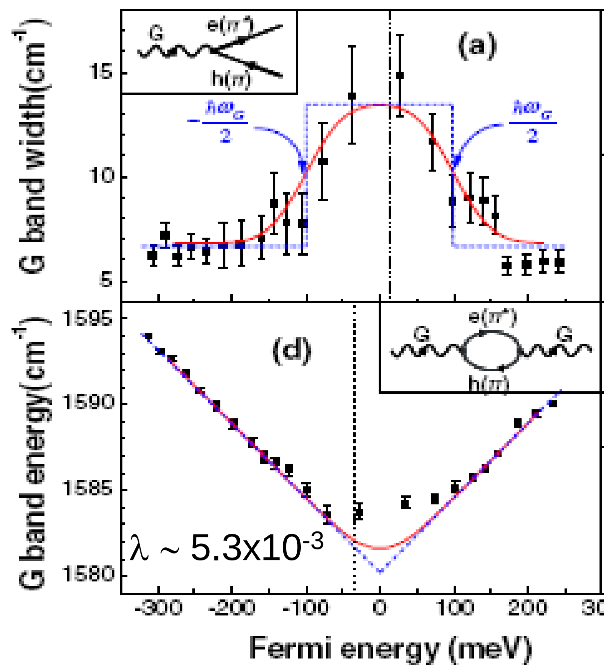
E_{2g} phonon is a good probe to study the electron phonon coupling !

$$\Pi(\boldsymbol{q},\omega) = \lambda\varepsilon_{\mathrm{F}} - \frac{1}{4}\lambda(\hbar\omega + \mathrm{i}\delta)\left(\ln\frac{\hbar\omega + 2\varepsilon_{\mathrm{F}}^{0} + \mathrm{i}\delta}{\hbar\omega - 2\varepsilon_{\mathrm{F}}^{0} + \mathrm{i}\delta} + \pi\mathrm{i}\right)$$

T. Ando, J. of Phys. Soc. of Jpn **75**, 124701, (2006)

Tuning the e-ph coupling with electric fields

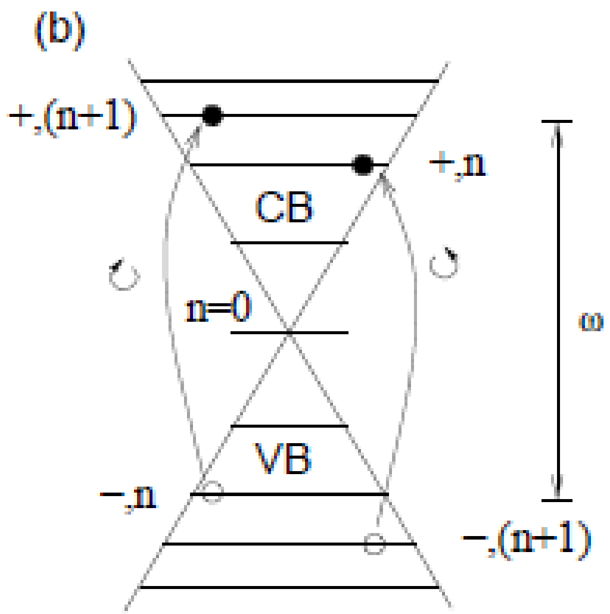


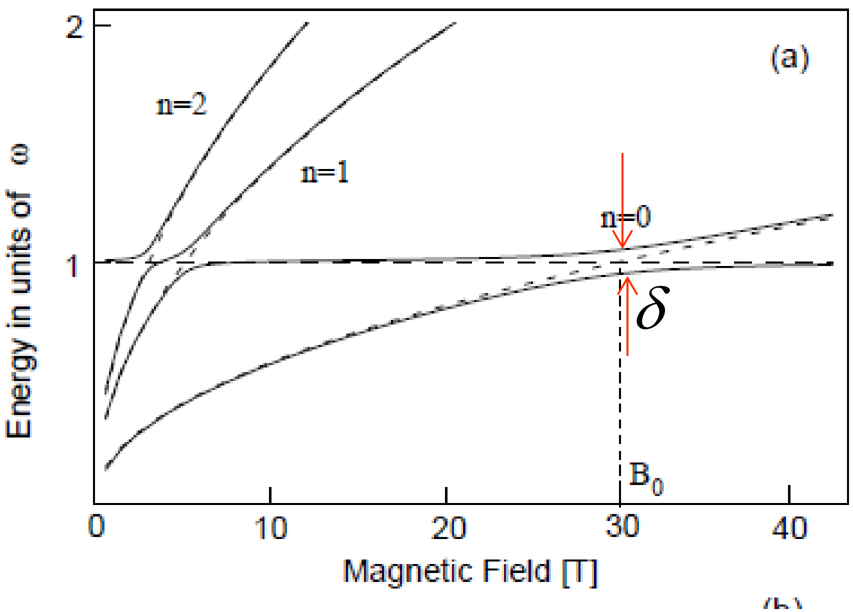


Pisana et al., Nature Mat.**6**, 201, (2006)

J. Yan et al., PRL **98** 166802 (2007)

…. or with magnetic fields





LL spectrum:

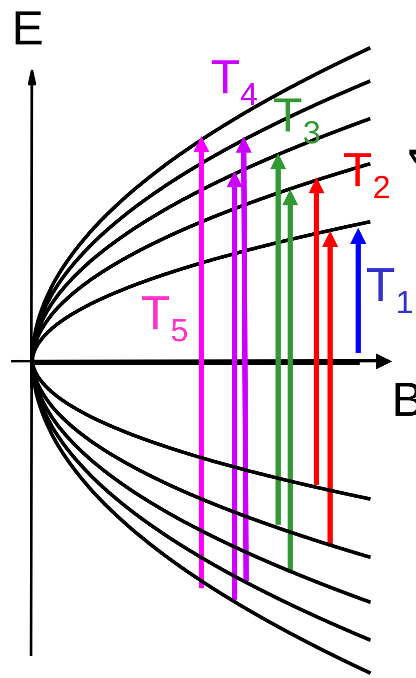
$$E_n = \mathrm{sgn}(n)\tilde{c}\sqrt{2e\hbar B|n|}$$

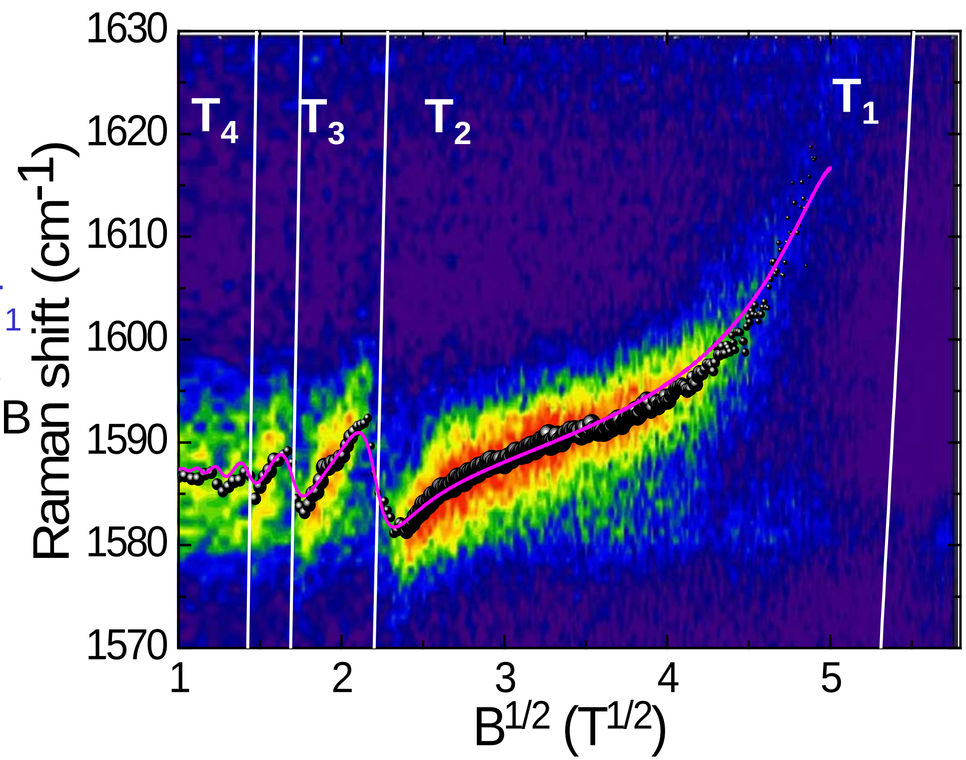
Δ|n| = ±1

$$\delta \propto \lambda.\sqrt{B_{res}}\sqrt{(1-f_f)f_i}$$

M. O. Goerbig, J. N. Fuchs, K. Kechedzhi, and V. Fal'ko, Phys. Rev. Lett. **99,** 087402 (2007)
T. Ando, J. Phys. Soc. Jpn. **76**, 024712 (2007)

Magneto-phonon resonance in MEG

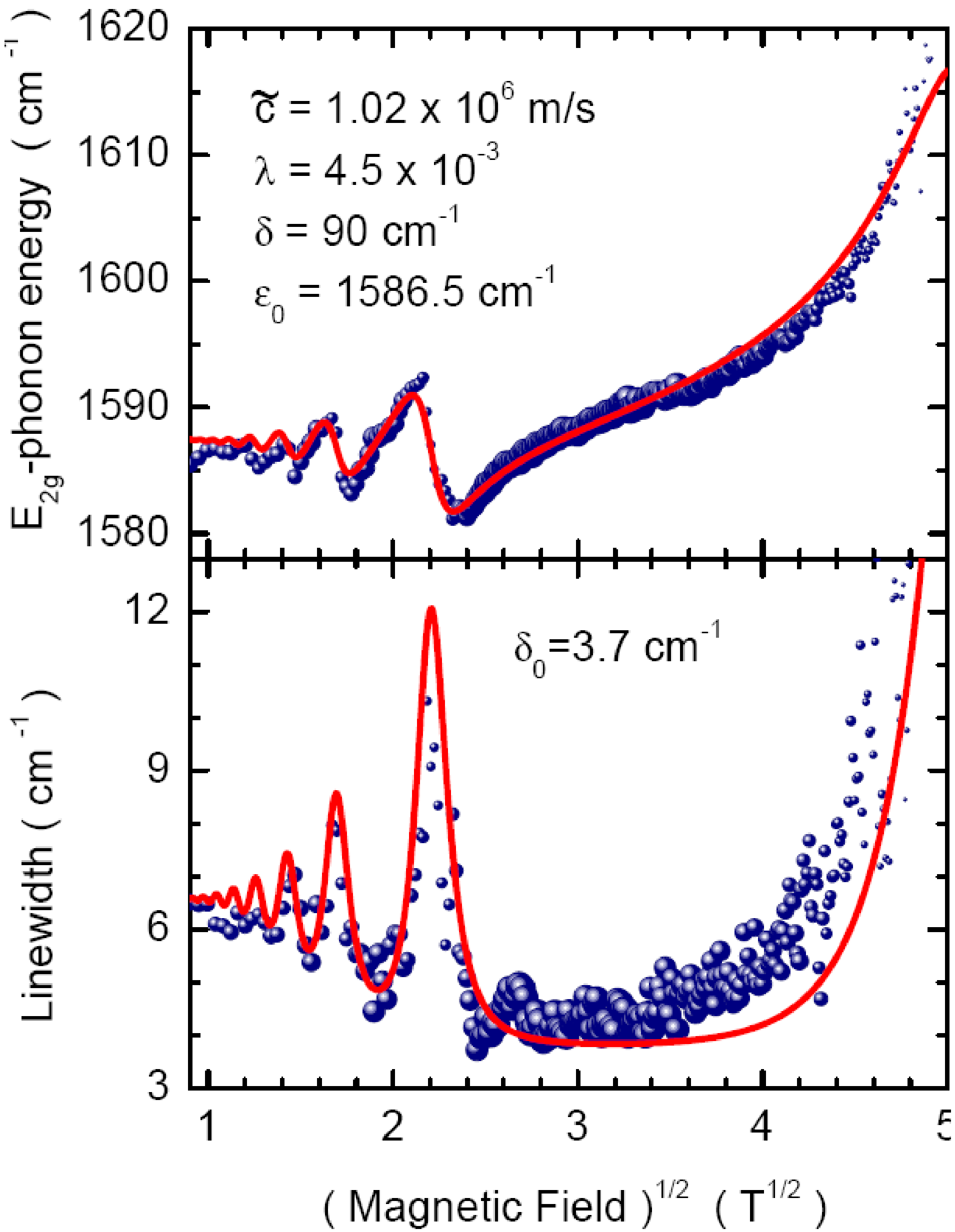




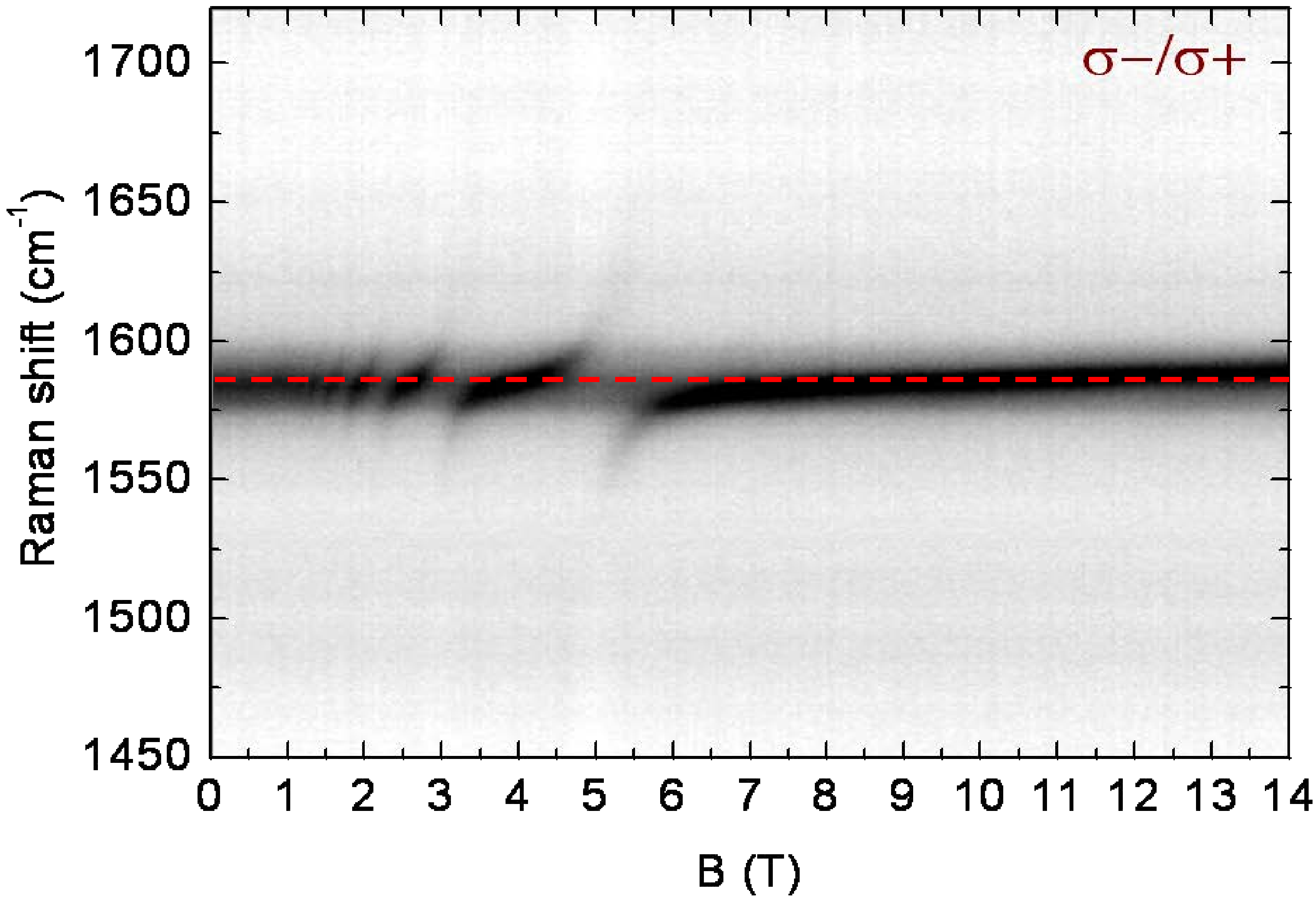
Δ|n| = ±1

$$\tilde{\epsilon}^2 - \epsilon_0^2 = 2\epsilon_0 \lambda E_1^2 \sum_{k=0}^{\infty} \{ \frac{f_k T_k}{(\tilde{\epsilon} + i\delta)^2 - T_k^2} + \frac{1}{T_k} \}$$

C. Faugeras et al., PRL **103**, 186803, (2009)
T. Ando, J. Phys. Soc. Jpn. **76**, 024712 (2007)
M.O. Goerbig et al., PRL **99**, 087402, (2007)

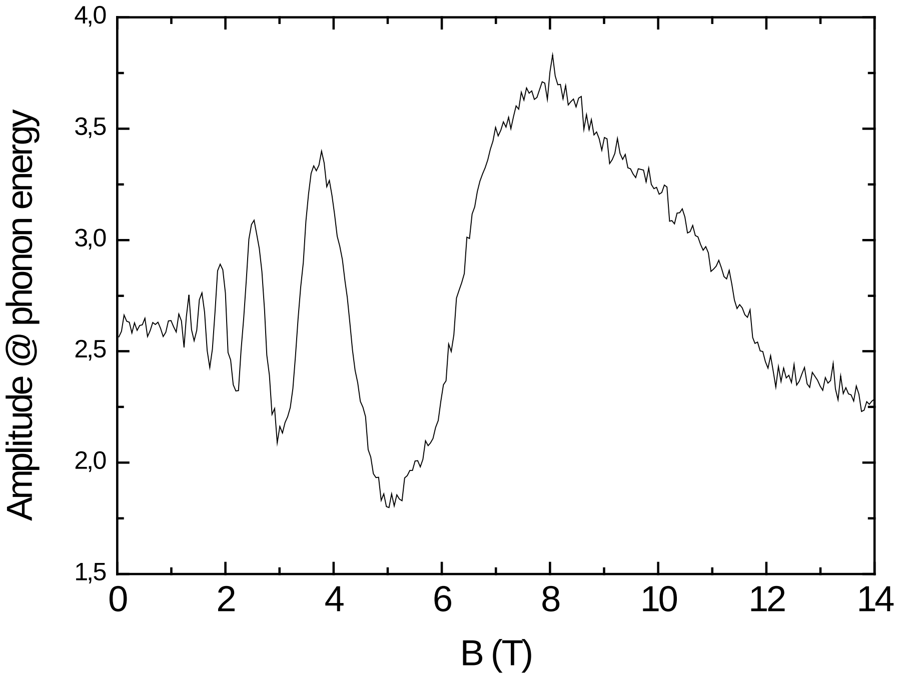


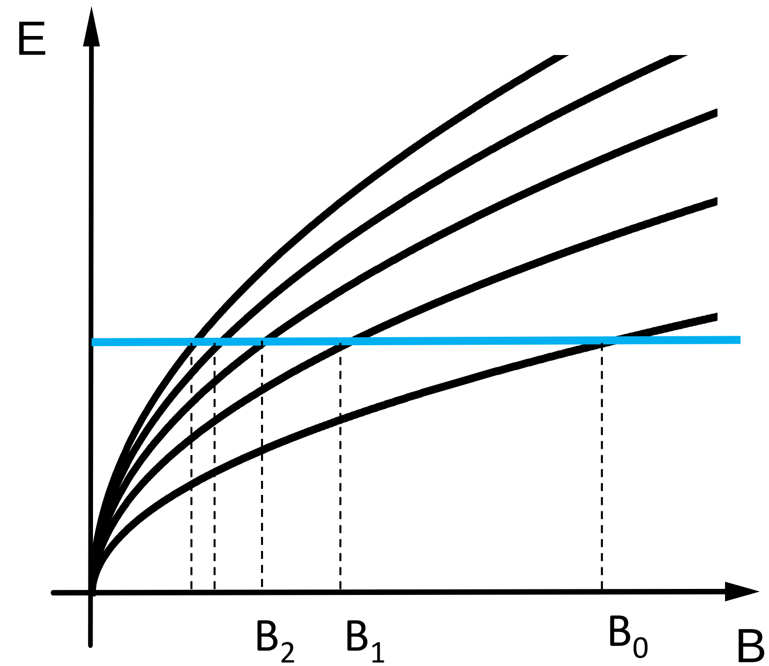
$\tilde{c}$ = 1.02 x 10^6 m/s
λ = 4.5 x 10^{-3}
δ = 90 cm^{-1}
ε_0 = 1586.5 cm^{-1}
δ_0=3.7 cm^{-1}
E_{2g}-phonon energy (cm^{-1})
Linewidth (cm^{-1})
(Magnetic Field $)^{1/2}$ ($T^{1/2}$)
1620
1610
1600
1590
1580
12
9
6
3
1
2
3
4
5



σ−/σ+
Raman shift (cm^{-1})
1700
1650
1600
1550
1500
1450
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
B (T)

Frequency analysis





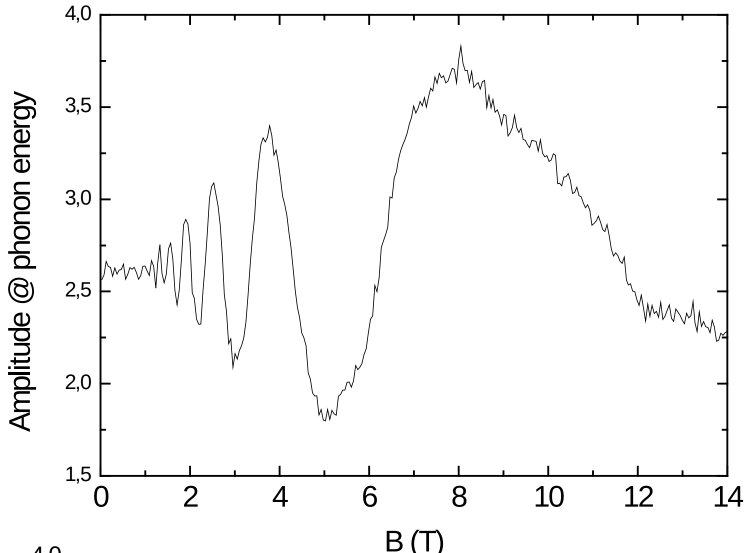
$$E_{elec} = E_{ph}$$

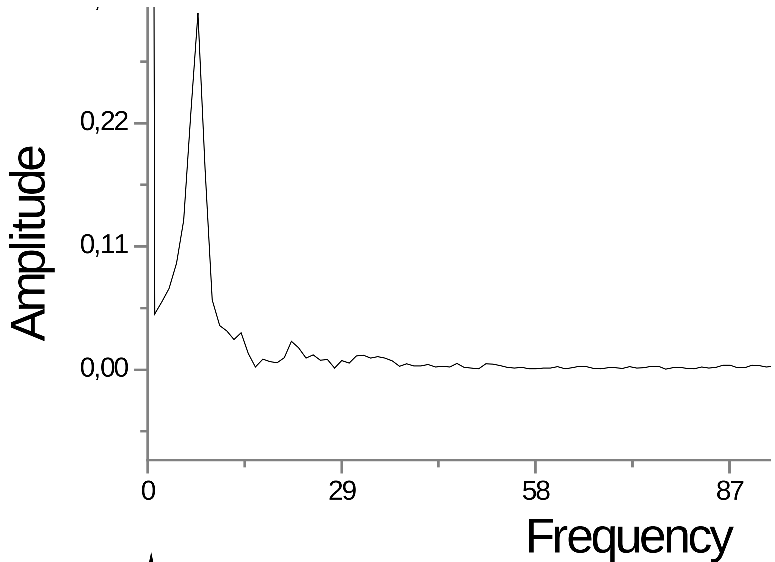
$$E_{n+1} + E_n = \hbar\omega_{ph}$$

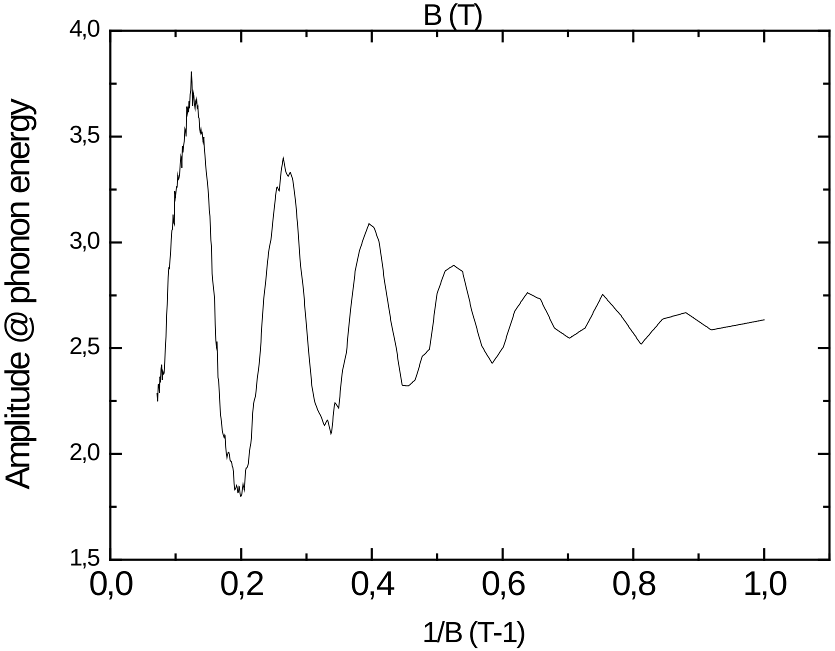
$$v\sqrt{2e\hbar B}(\sqrt{n} + \sqrt{n+1}) = \hbar\omega_{ph}$$

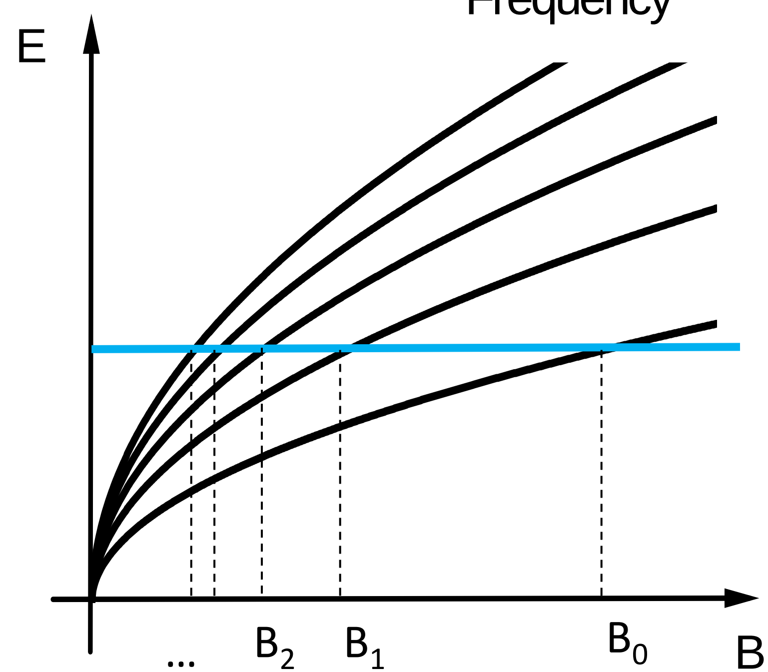
$$\frac{1}{B_n} = \frac{8v^2 e\hbar}{\omega_{ph}^2}(n + 1/2)$$

Frequency analysis



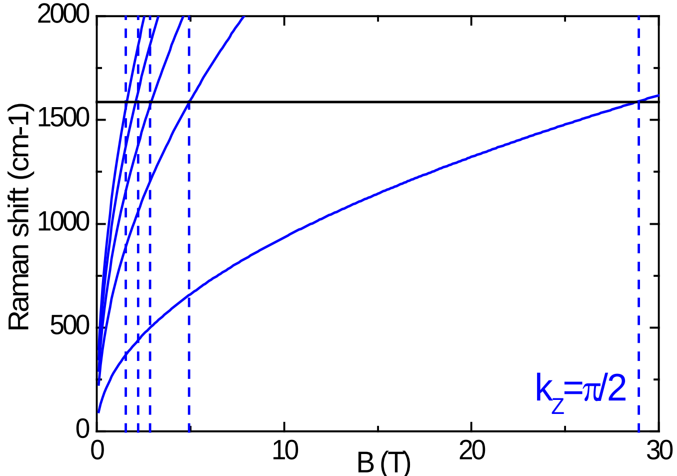




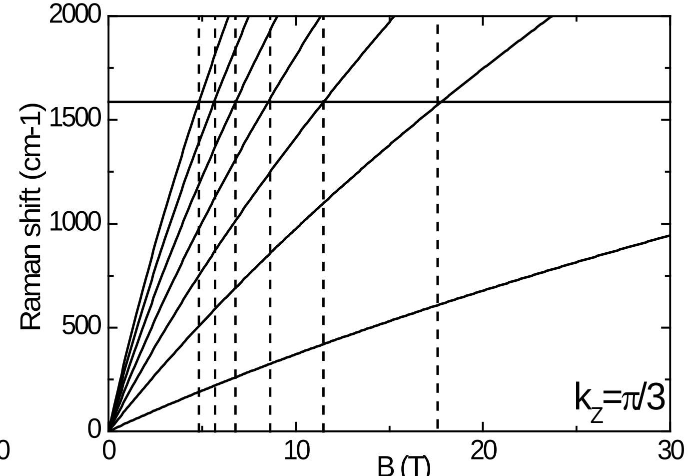


Magneto Phonon Resonance as a tool for Landau level spectroscopy

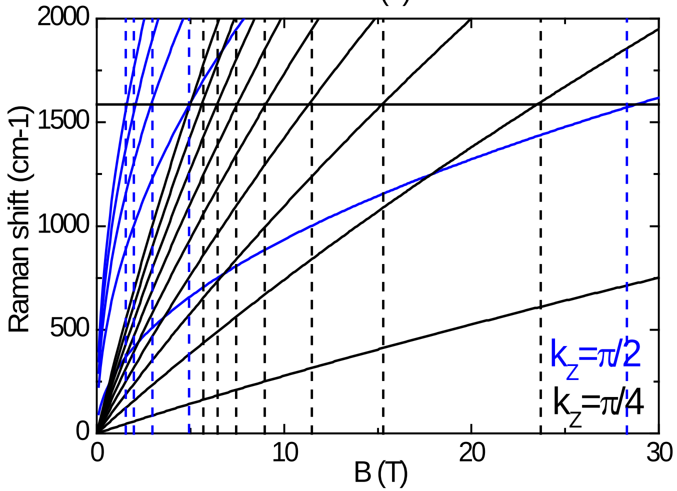
monolayer



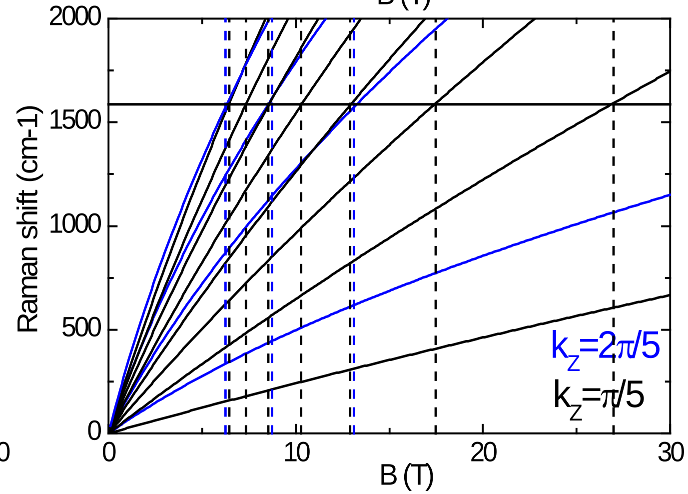
bilayer



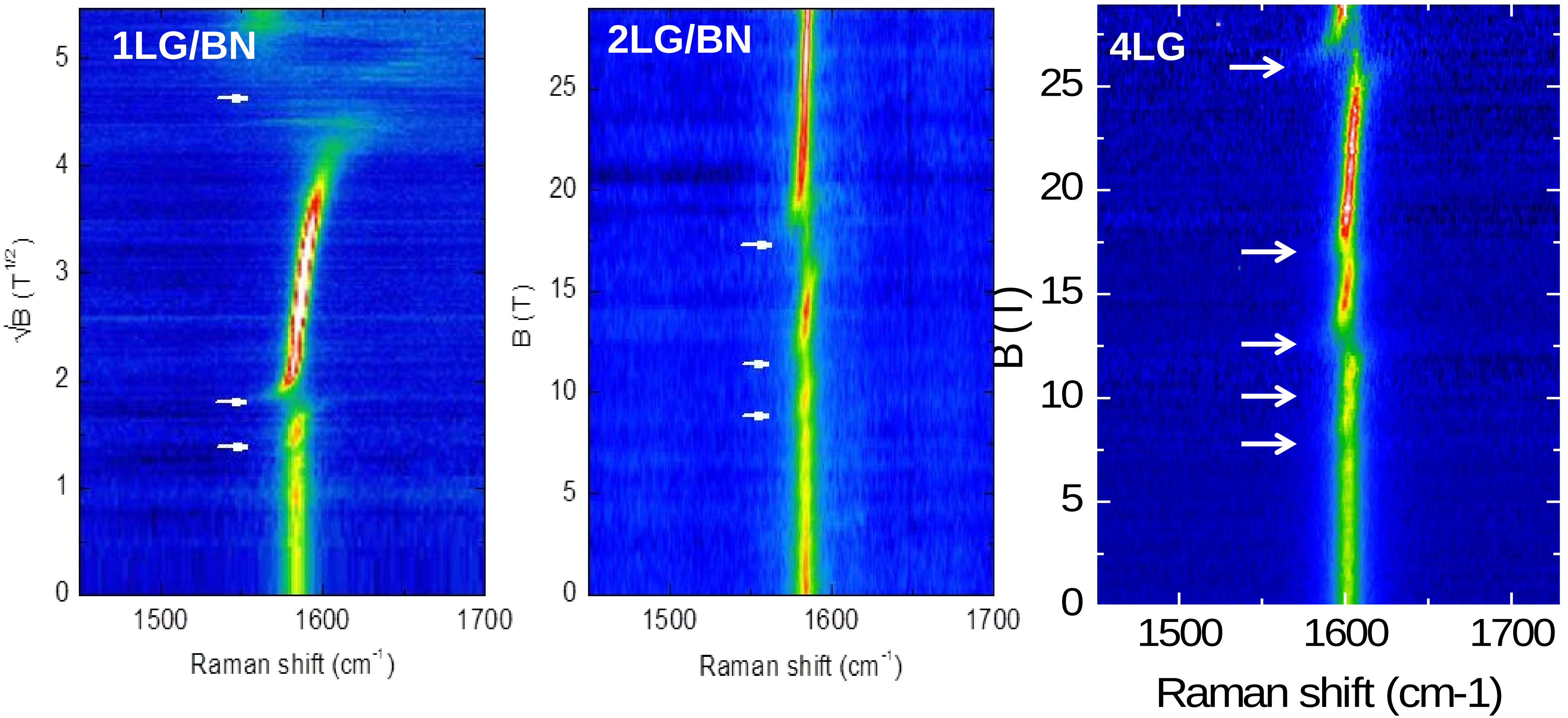
trilayer



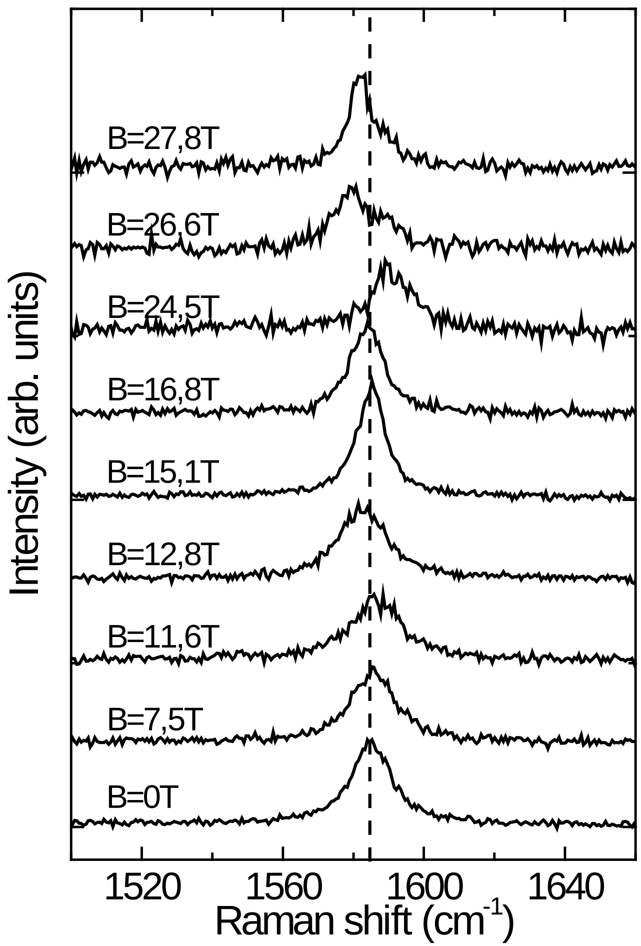
quadrilayer

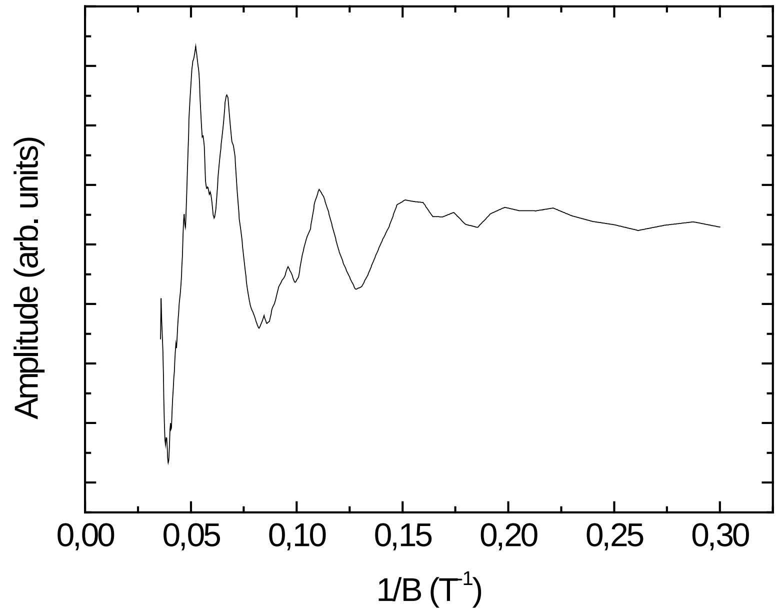


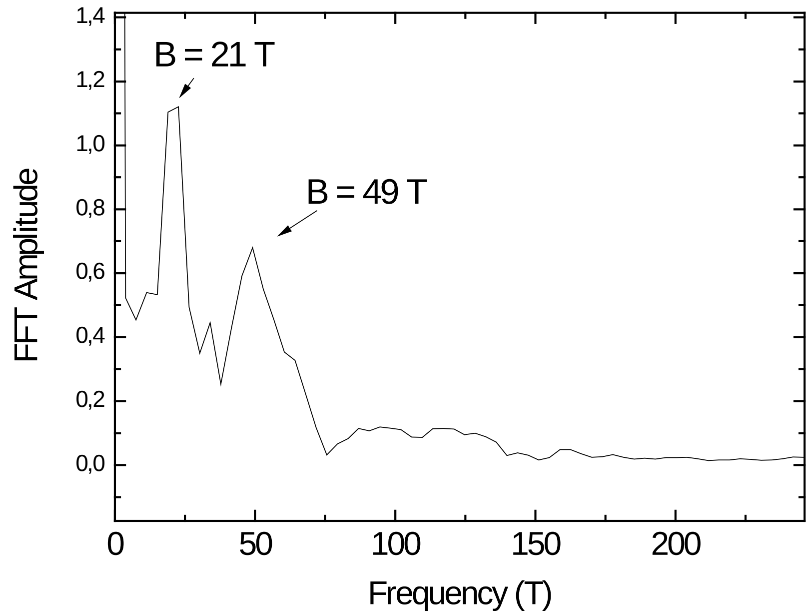
MPR as a tool to perform the Landau level spectroscopy



Frequency analysis for 4LG



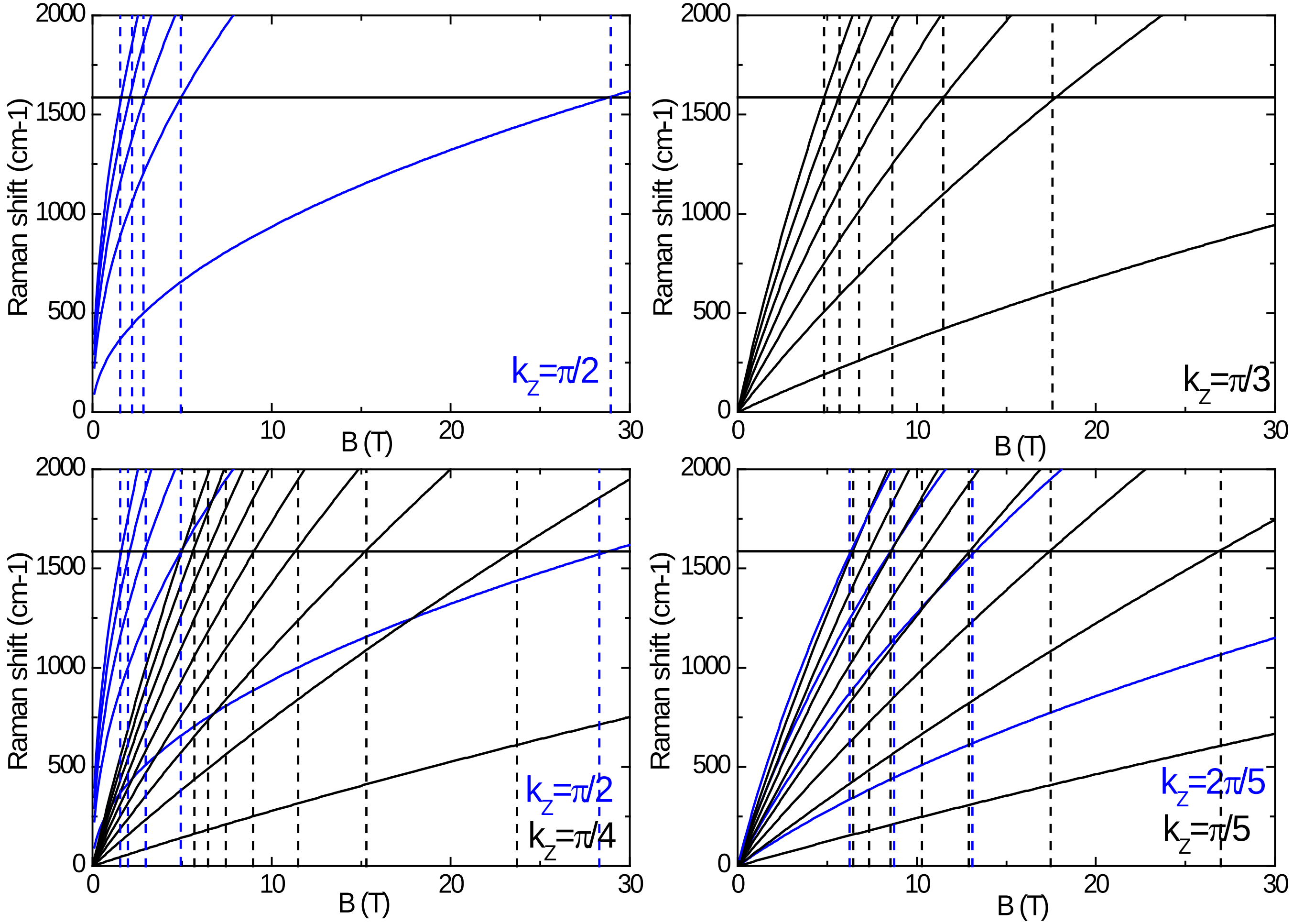




Magneto Phonon Resonance as a tool for Landau level spectroscopy

monolayer

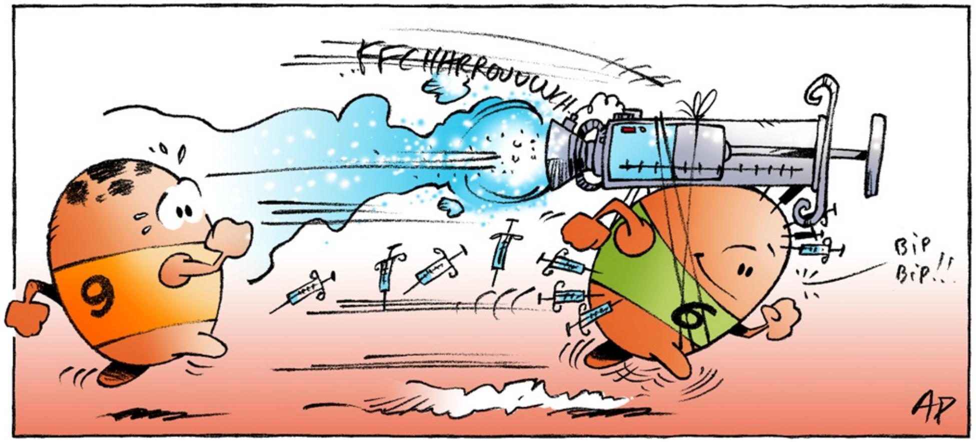
bilayer



trilayer

quadrilayer

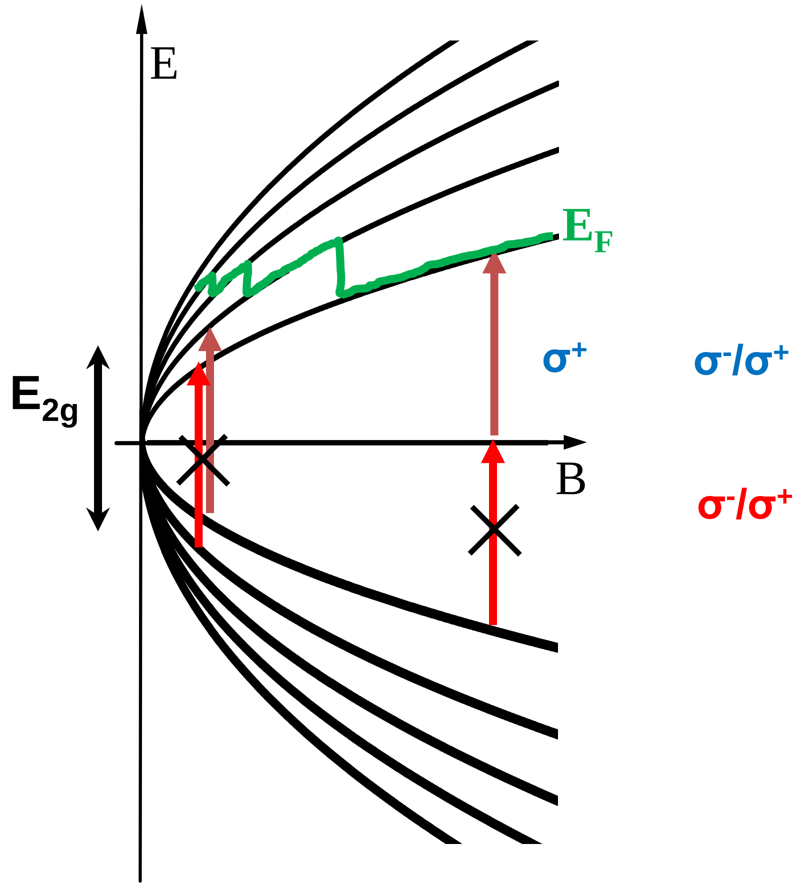
Effect of doping

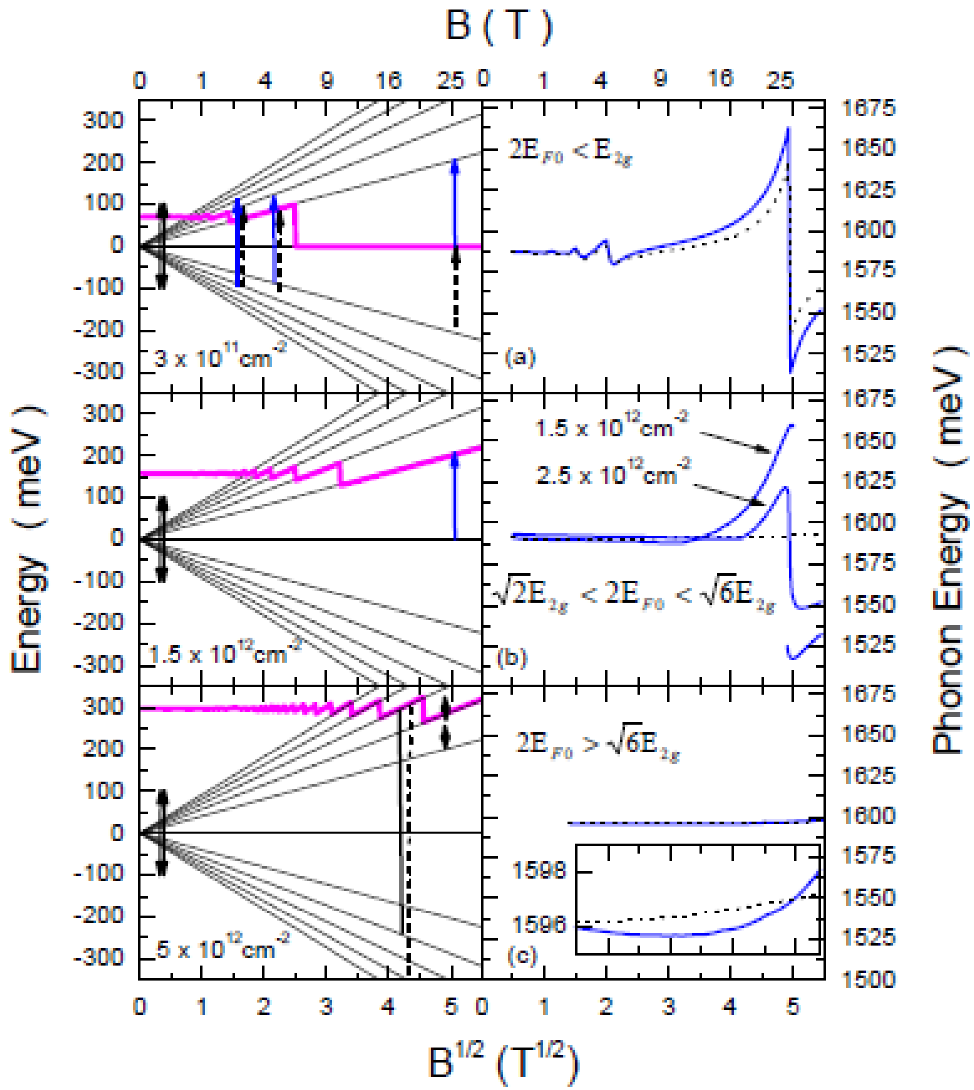


The case of doped graphene

Coupling only between

E_{2g} and $E_{0\to1}(\sigma^+)$



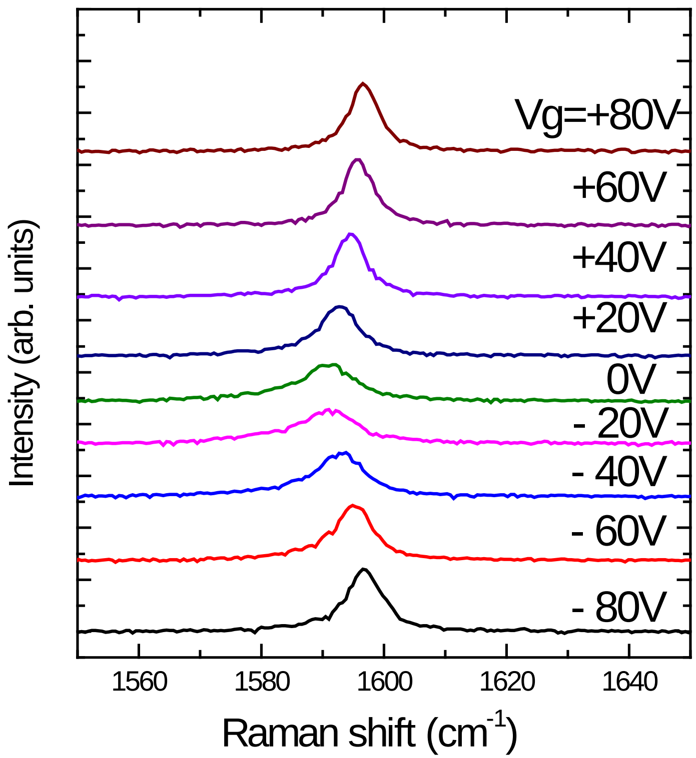


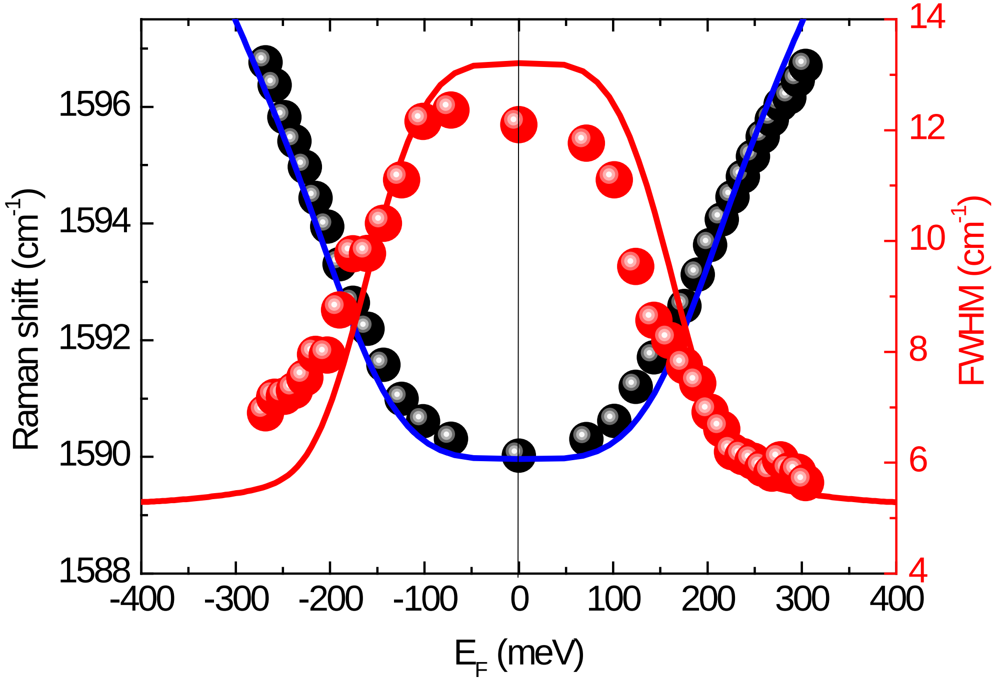
P. Kossacki et al. PRB 86, 205431, (2012)

$$\delta \propto \lambda . \sqrt{B_{res}} \sqrt{(1 - f_f) f_i}$$

M. O. Goerbig, J. N. Fuchs, K. Kechedzhi, and V. Fal'ko, Phys. Rev. Lett. 99, 087402 (2007).

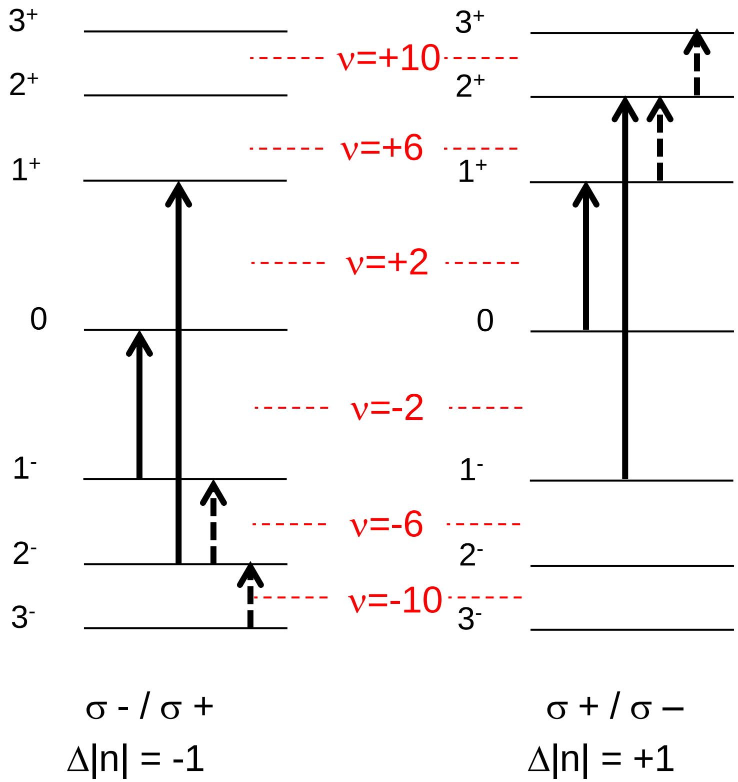
CVD graphene on SiO_2 B=0T
Density dependence

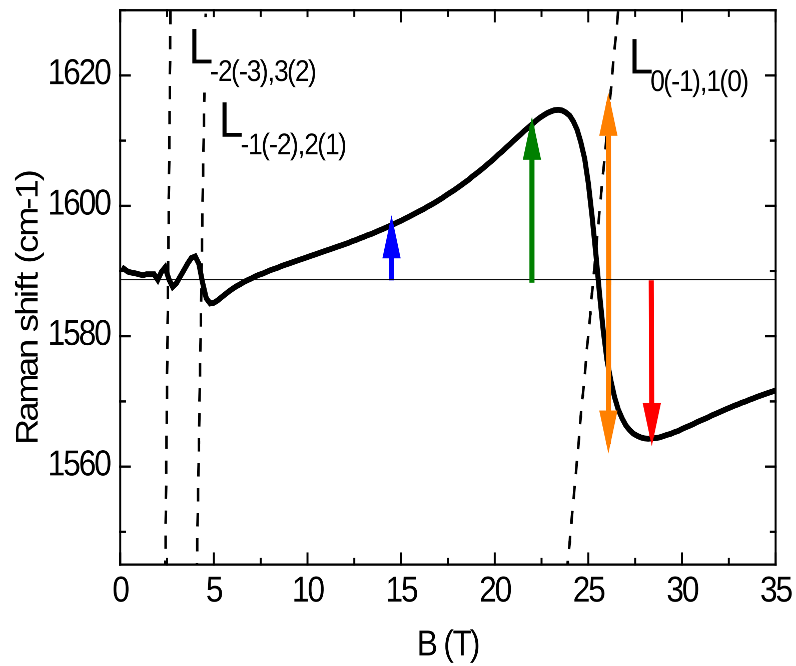




Gaussian convolution of the carrier density with $\sigma = 1.27 \times 10^{12}$ cm^{-2} and $\lambda = 4{,}0 \times 10^{-3}$

Aims of the experiment



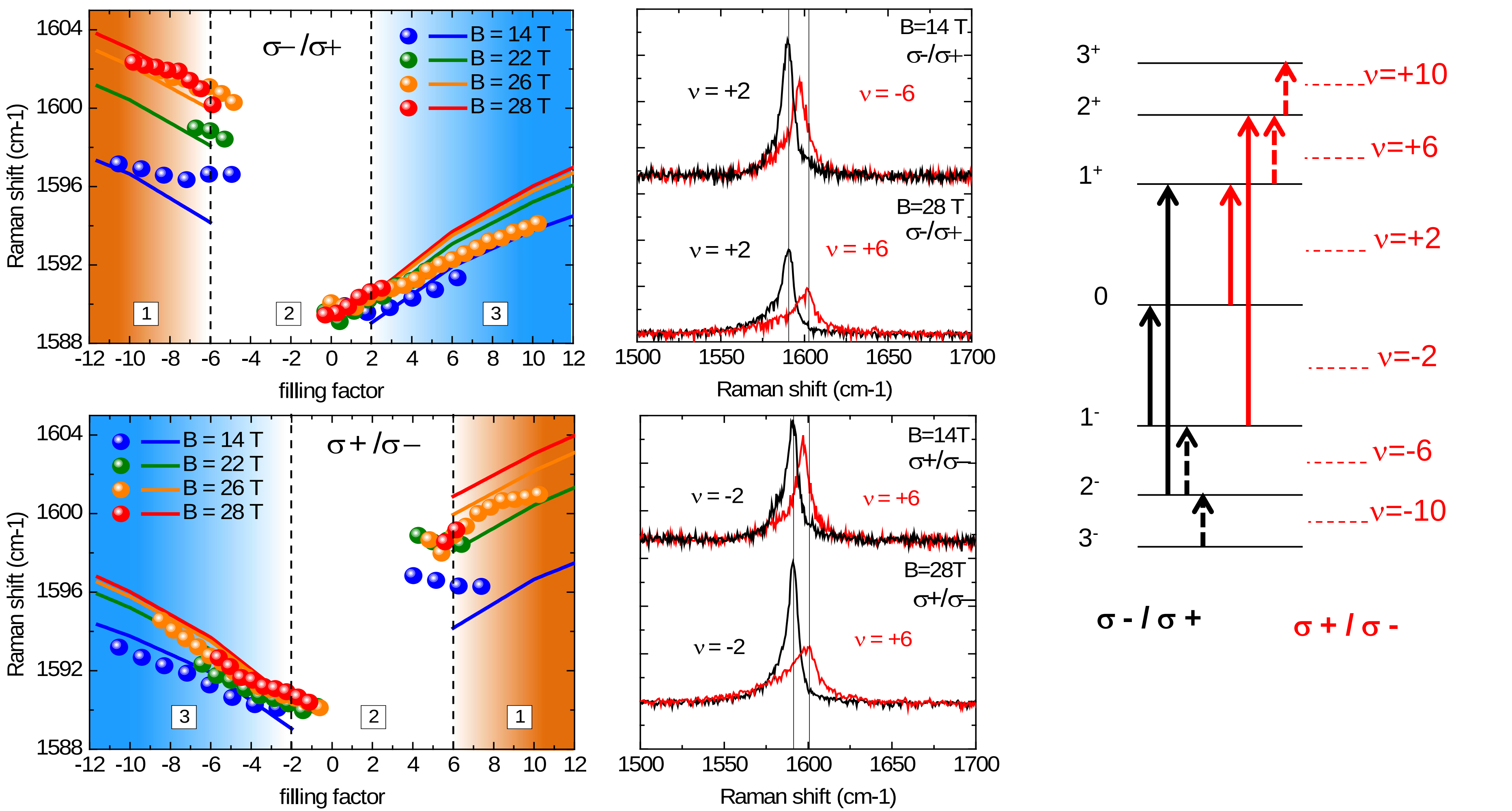


neutral graphene

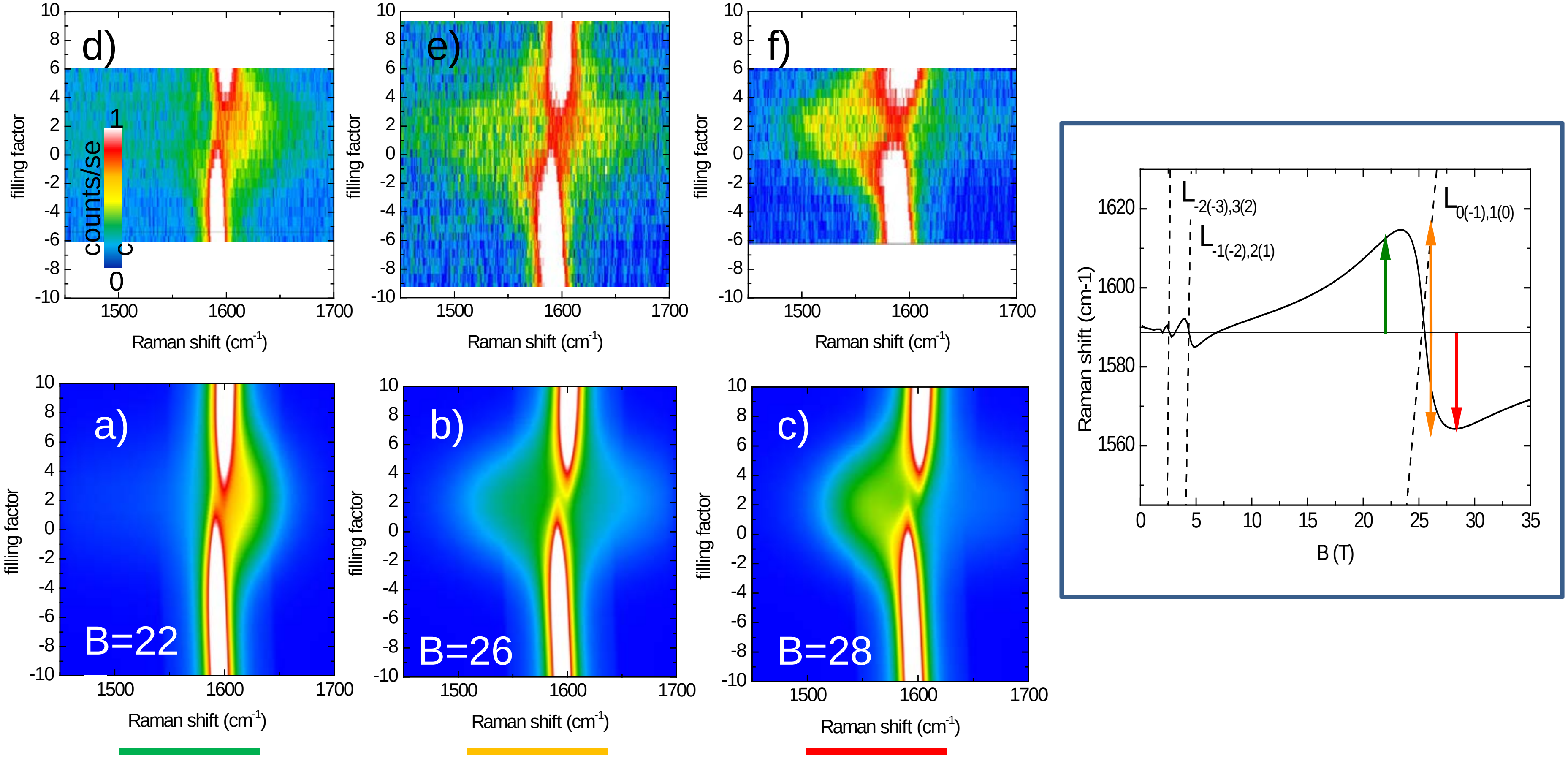
Selecting the inter LL excitations with polarized Raman scattering

Search for effects related to intraband excitations AND tuning the occupation factor close to the resonance

Signature of cyclotron resonance in MPR



The resonant case



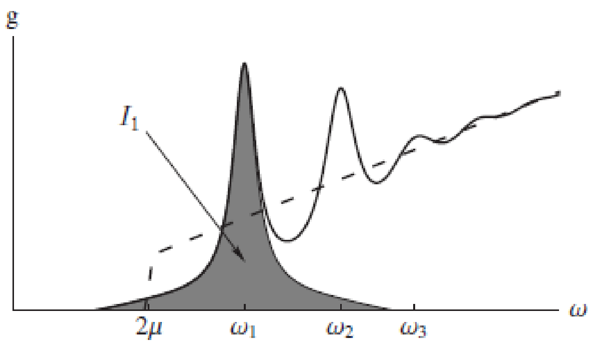
Calculations performed with $\lambda = 4x10^{-3}$

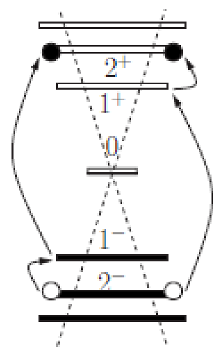
$v_F = 1{,}08x10^6\ m.s^{-1}$

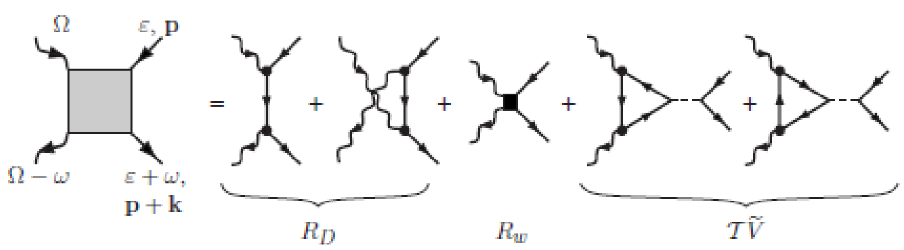
$\sigma = 1{,}27x10^{12}\ cm^{-2}$

P. Leszczynski et al., NanoLett. **14**, 1460, (2014)

Electronic Raman scattering



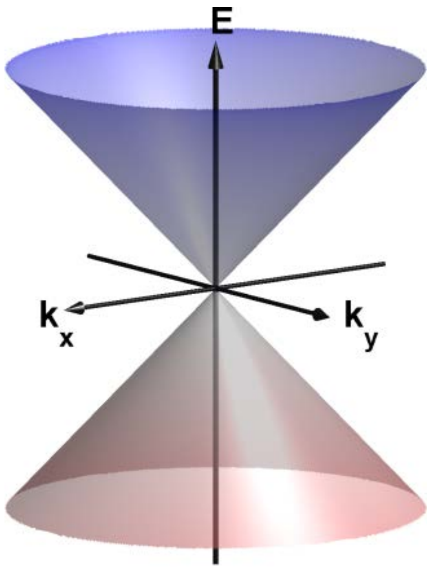


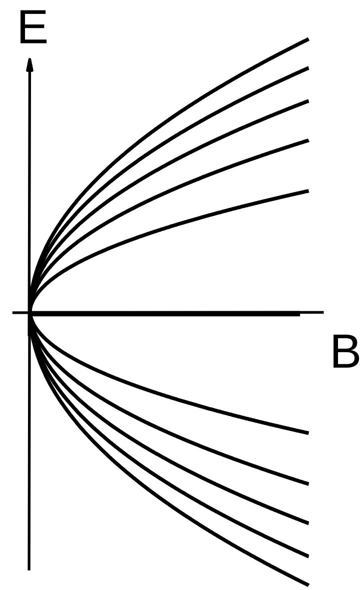


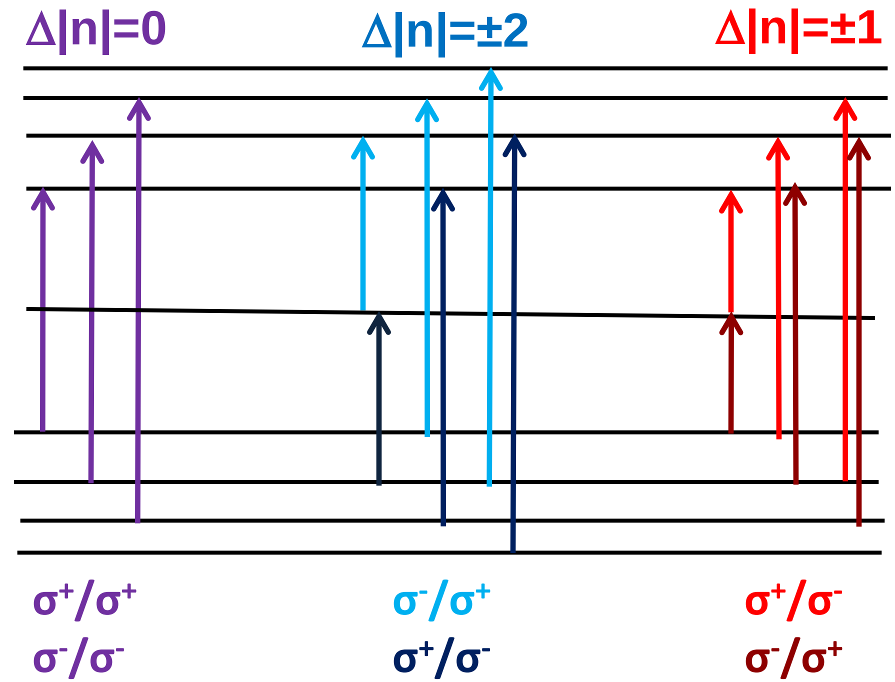
O. Kashuba and V. Falko, Phys. Rev. B 80, 241404(R), (2009)

Electronic excitations in Raman scattering

Graphene







O. Kashuba and V. Falko. PRB **80**, 241404R (2009)

Roldan et al. SST **25**, 034005, (2010)

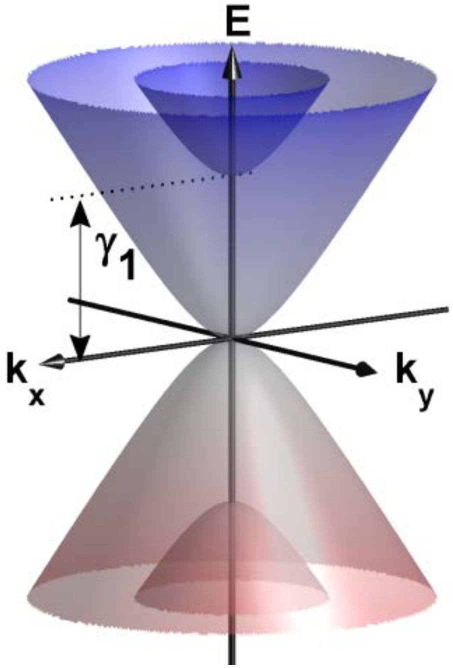
Δ|n| = 0 - dominant contribution (symmetric transitions)

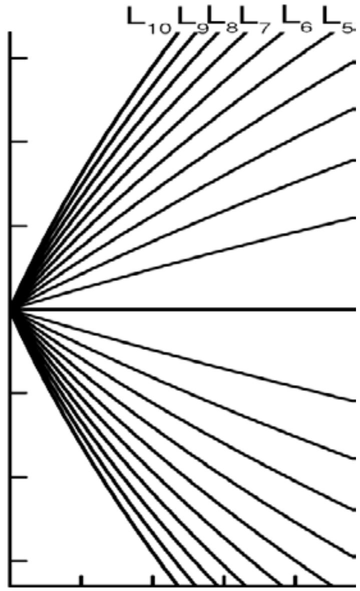
Δ|n| = ±2 - weaker transitions

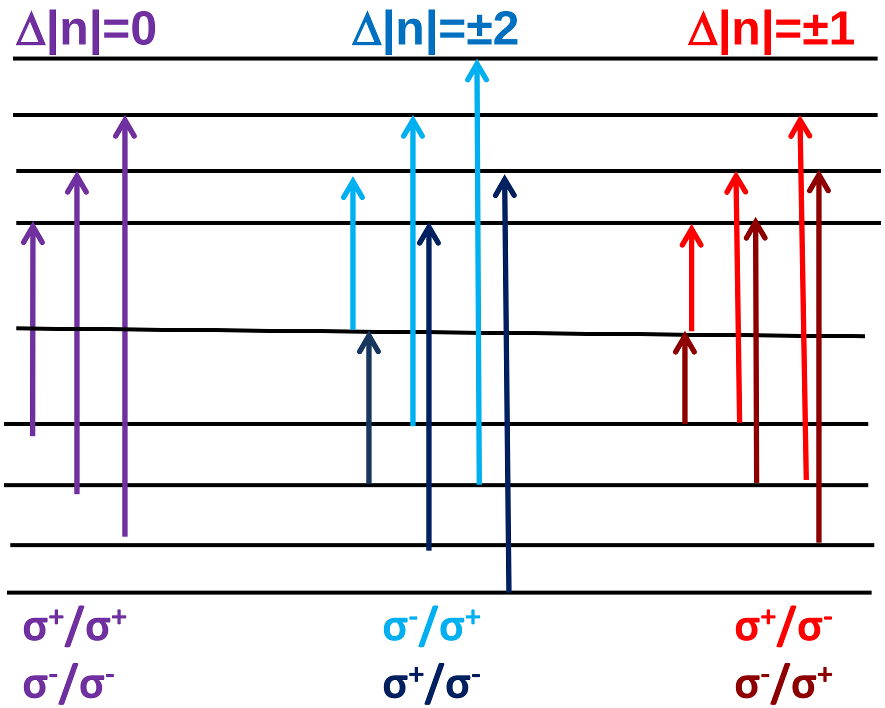
Δ|n| = ±1 - weak transitions, except at magneto-phonon resonance

Electronic excitations in Raman scattering ?

Graphene bilayer

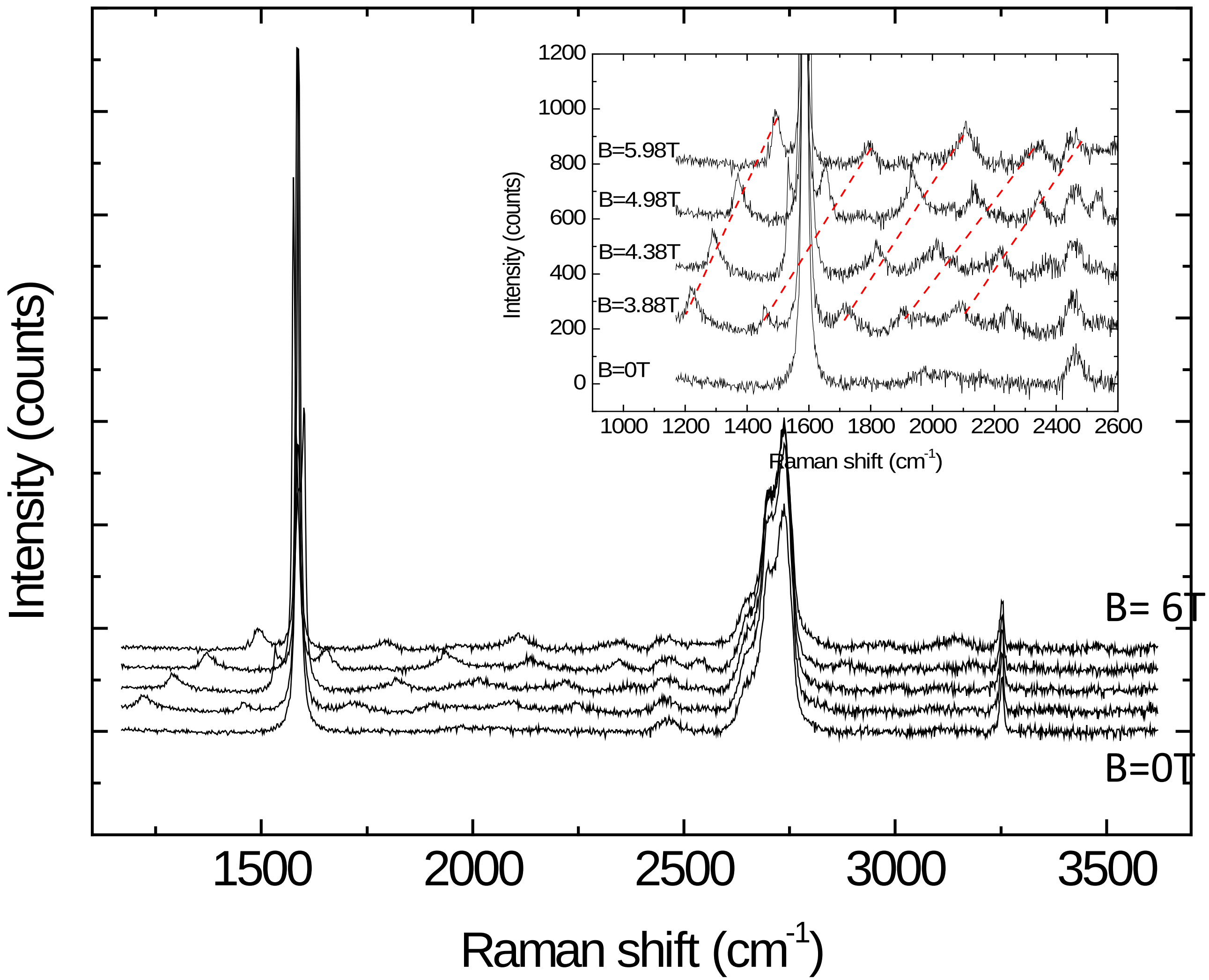






$$E(p) \approx \pm p^2/2m \qquad E_n \approx \pm\hbar\omega_c\sqrt{|n|(|n|+1)} \overset{n\geq 1}{\approx} \pm\hbar\omega_c\left(|n|+\frac{1}{2}\right)$$

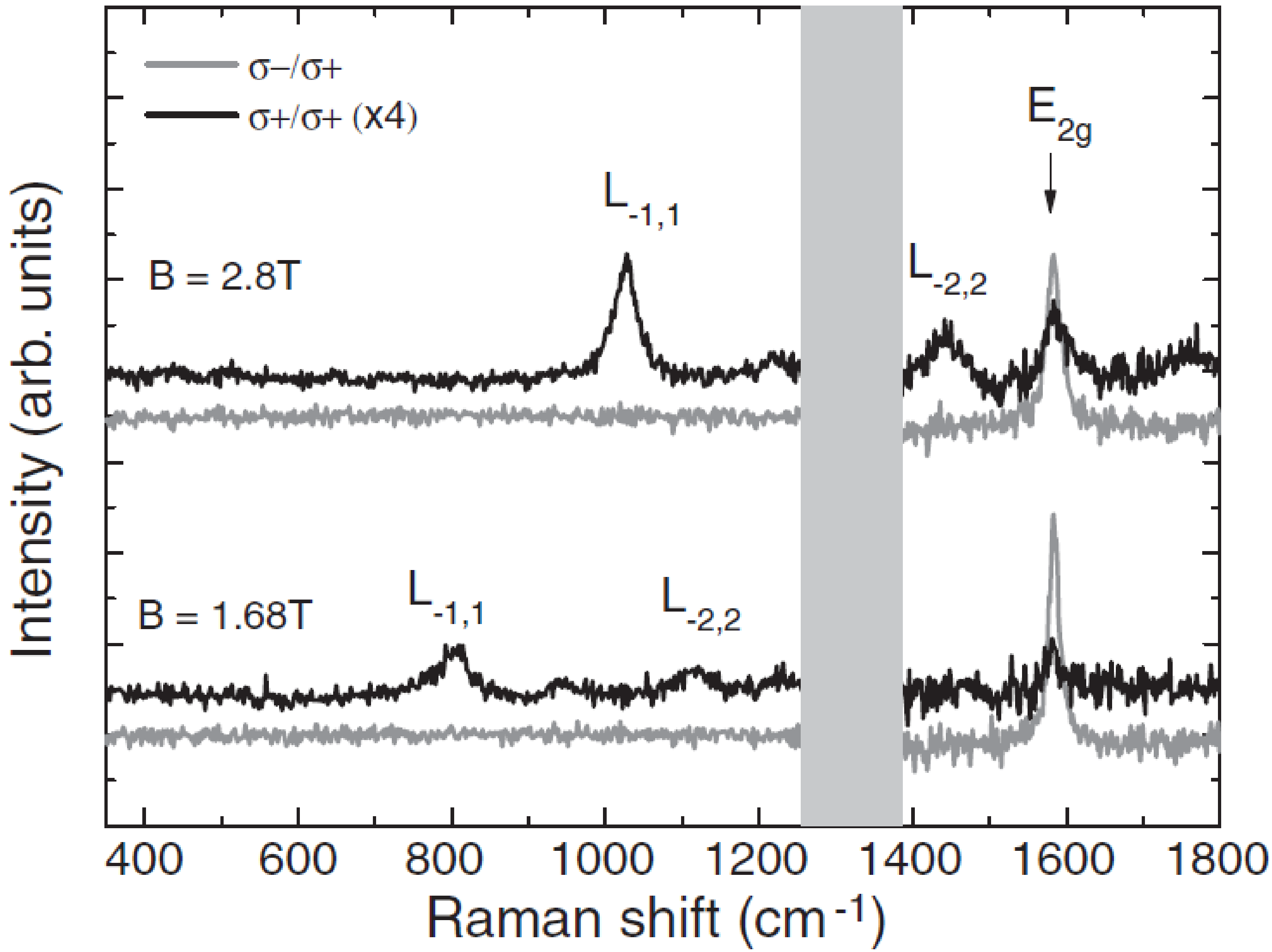
Mucha-Kruczynski et al, PRB **82** 045402 (2010)



Electronic excitations can be observed with magneto-Raman scattering

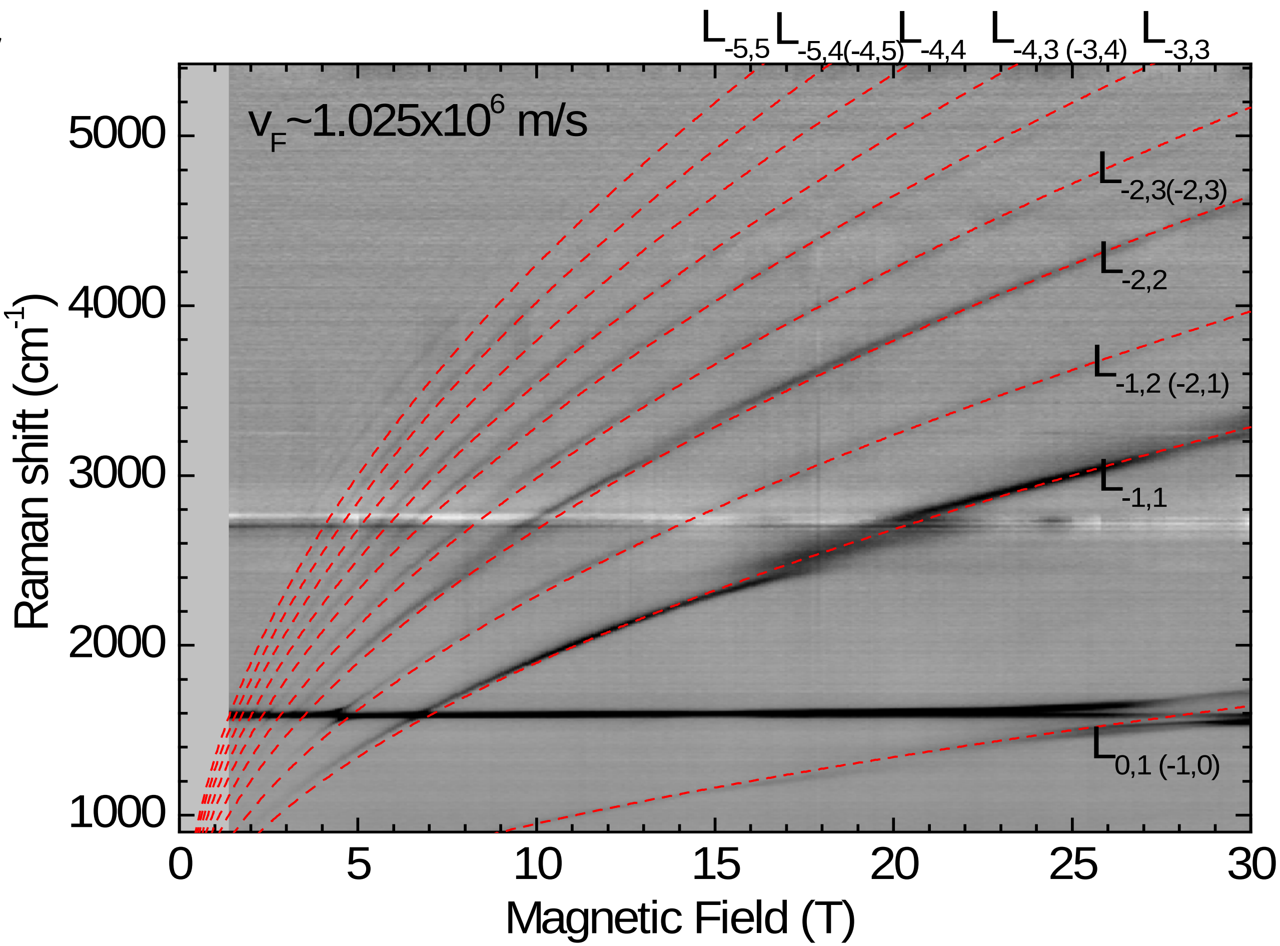
→ well adapted technique for « small » graphene samples

Checking the selection rules



C. Faugeras et al., Phys. Rev. Lett. 107, 036807, (2011)
M. Kuhne et al., Phys. Rev. B 85, 195406, (2012)

620 meV

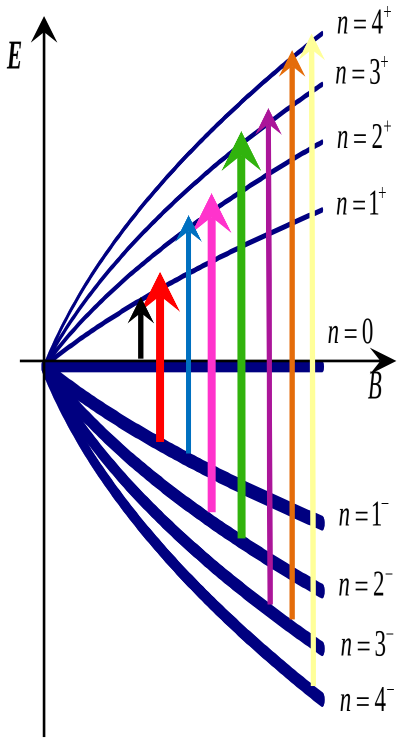


120 meV

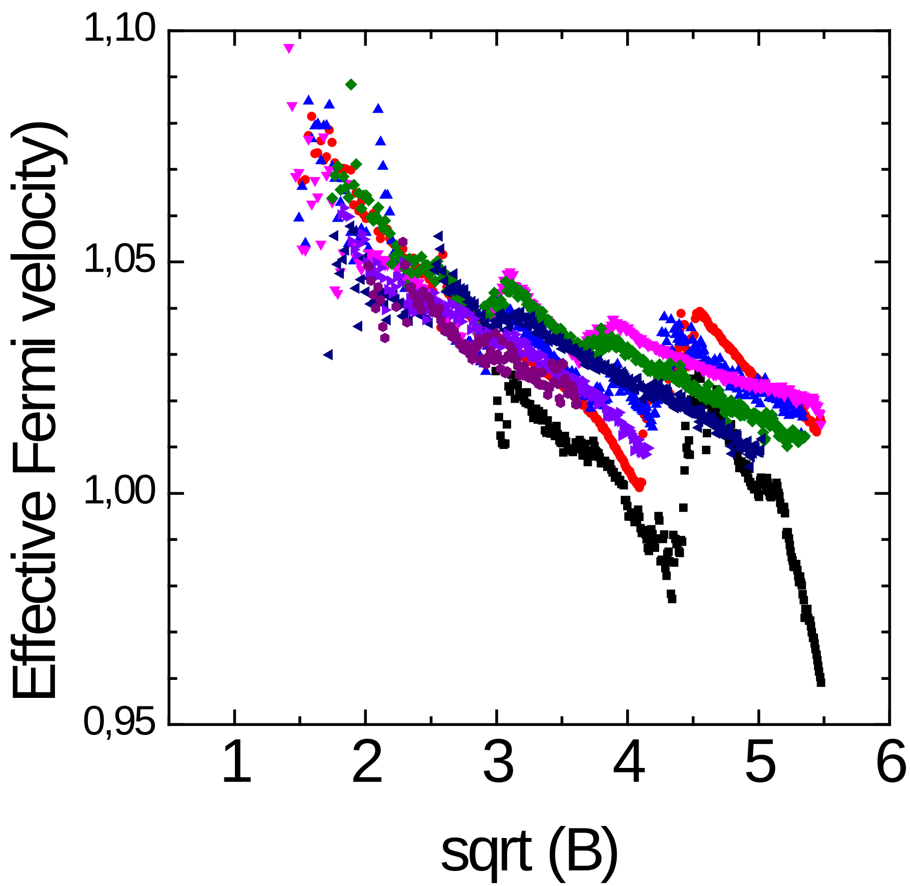
$$E_{-n,m} = v_F \sqrt{2e\hbar}\sqrt{B}\,\left(\sqrt{|n|}+\sqrt{|m|}\right)$$

$$<v_F> = 1.025 \cdot 10^6\, m.s^{-1}$$

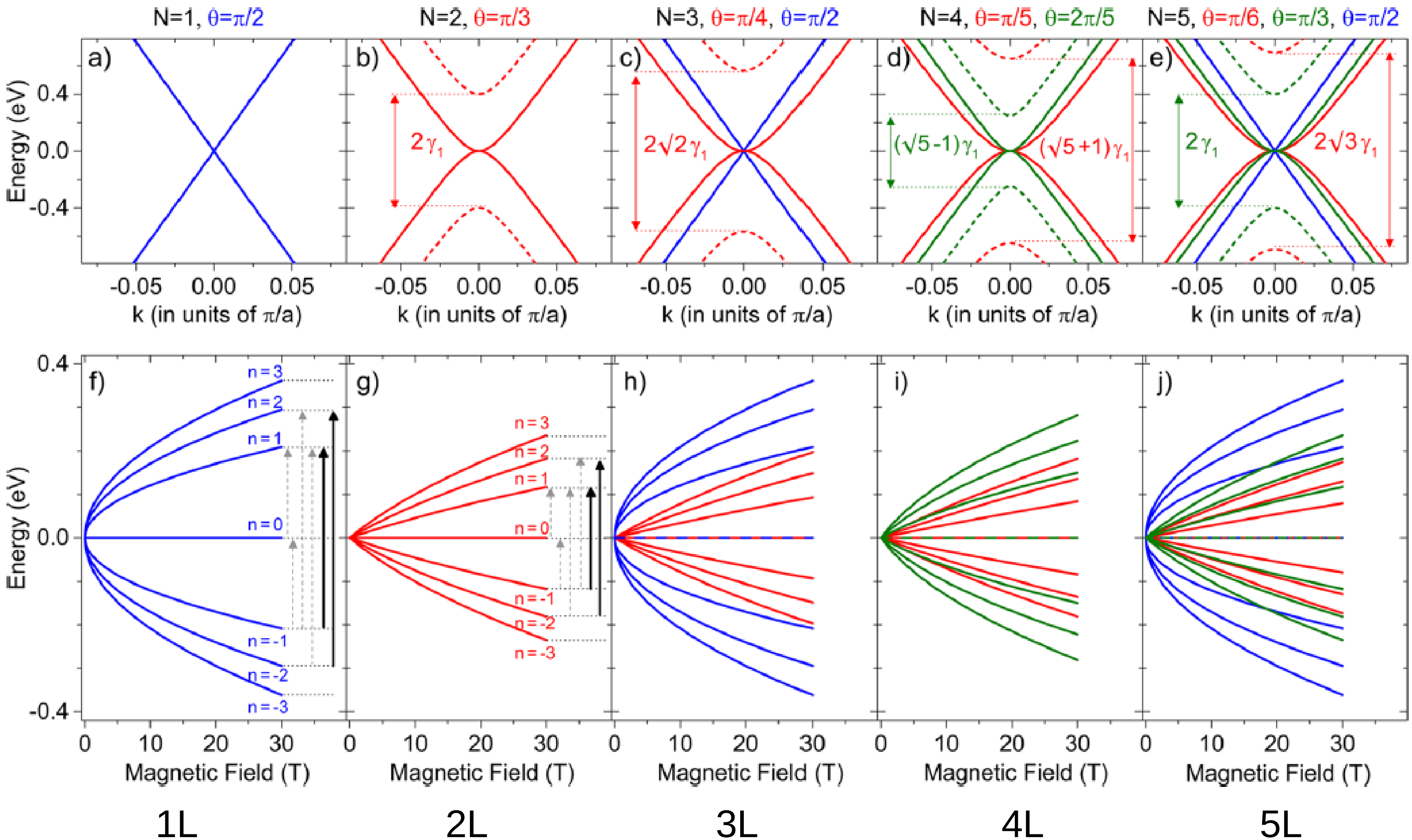
Graphene on graphite: accuracy of LL fanchart ?



$$\frac{E_{-n,m}}{\sqrt{2e\hbar}\sqrt{B}\,(\sqrt{|n|}+\sqrt{|m|})} = v_F\ ?$$



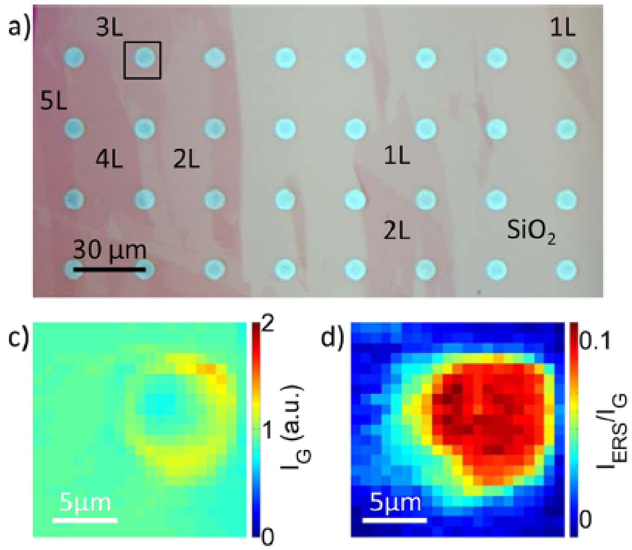
Investigating the electronic band structure with magneto-Raman scattering



B. Partoens and F. M. Peeters, Phys. Rev. B 75, 193402 (2007)
M. Koshino and T. Ando, Phys. Rev. B 77, 115313 (2008)
K.F. Mak et al., PNAS (2010)

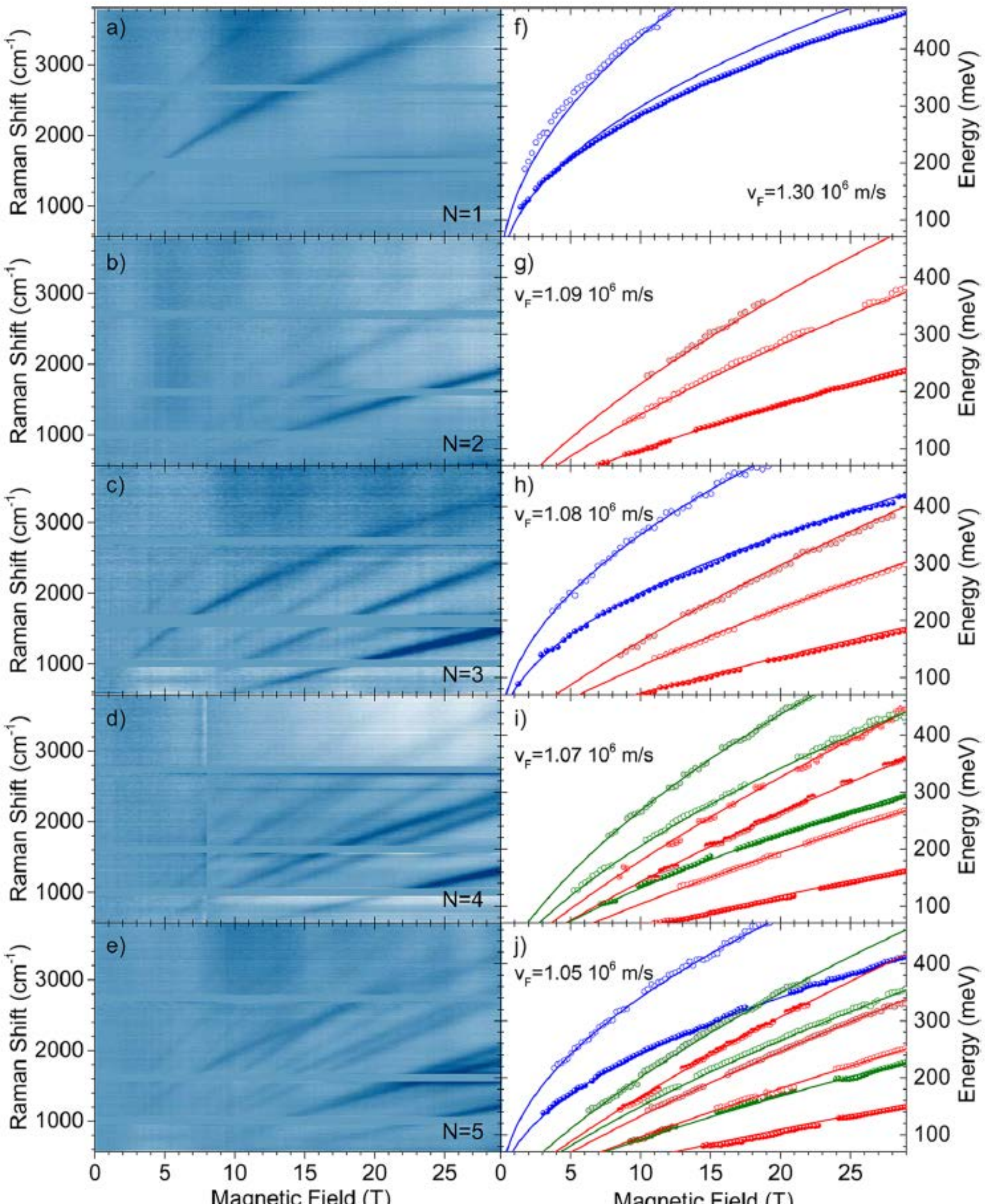
S. Berciaud, et al. NanoLetters (2014)

Investigating the electronic band structure with magneto-Raman scattering



S. Berciaud et al. NanoLetters (2014)

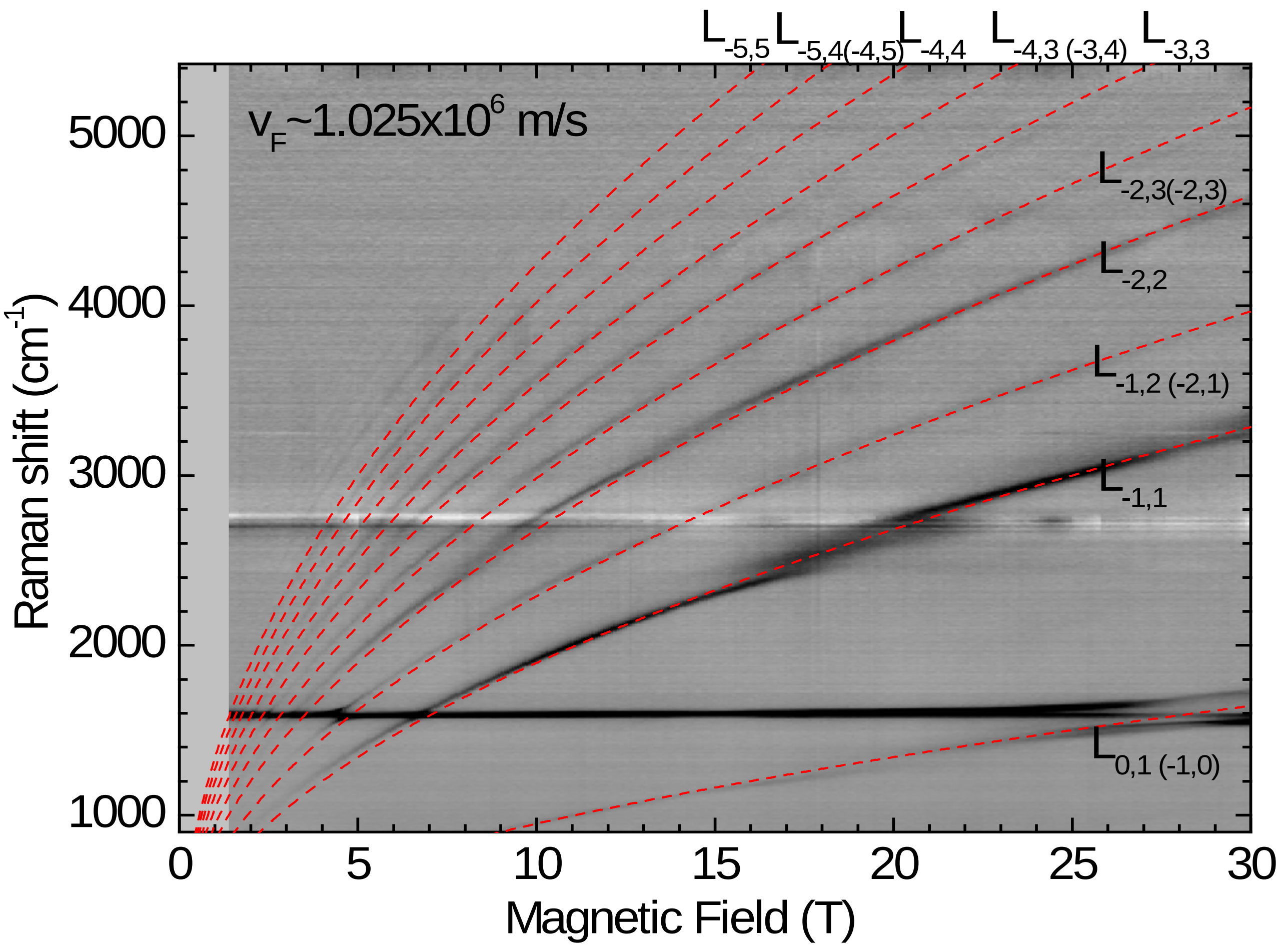
Investigating the electronic band structure with magneto-Raman scattering



S. Berciaud et al., NanoLetters (2014)

620 meV

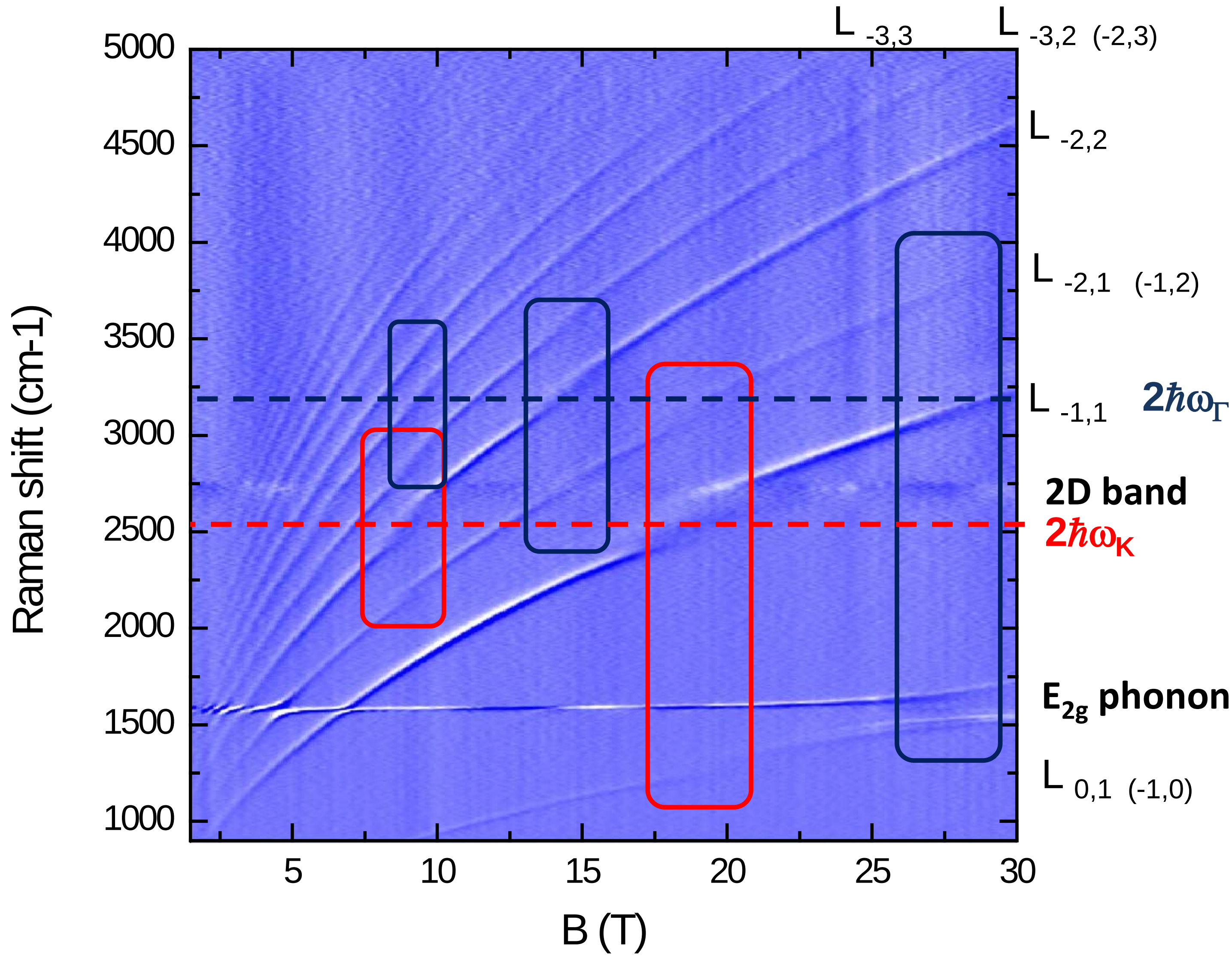
120 meV



$$E_{-n,m} = v\sqrt{2e\hbar}\sqrt{B}\ (\sqrt{|n|}+\sqrt{|m|})$$

$$v = 1.025\cdot 10^{6}\, m.s^{-1}$$

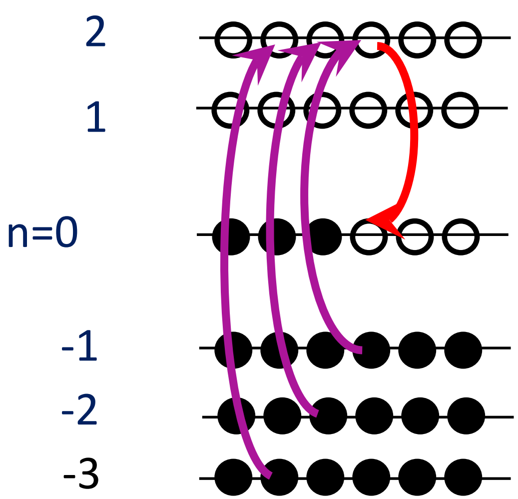
Electron-phonon interaction from the view point of electronic excitations



D.M. Basko et al., 2D Materials **3**, 015004, (2016)

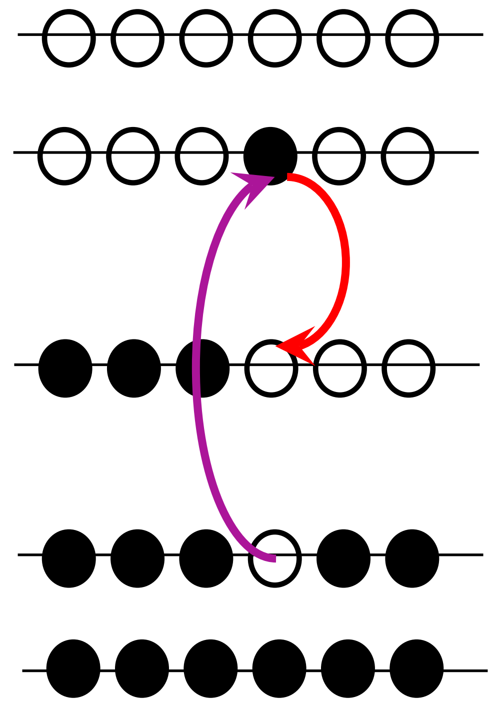
New class of magneto-phonon resonances:

- accelerated relaxation, shortening of the final/initial states lifetime



$E_{ph} = E_{0,2}$

$E_{ph} = E_{0,1}$

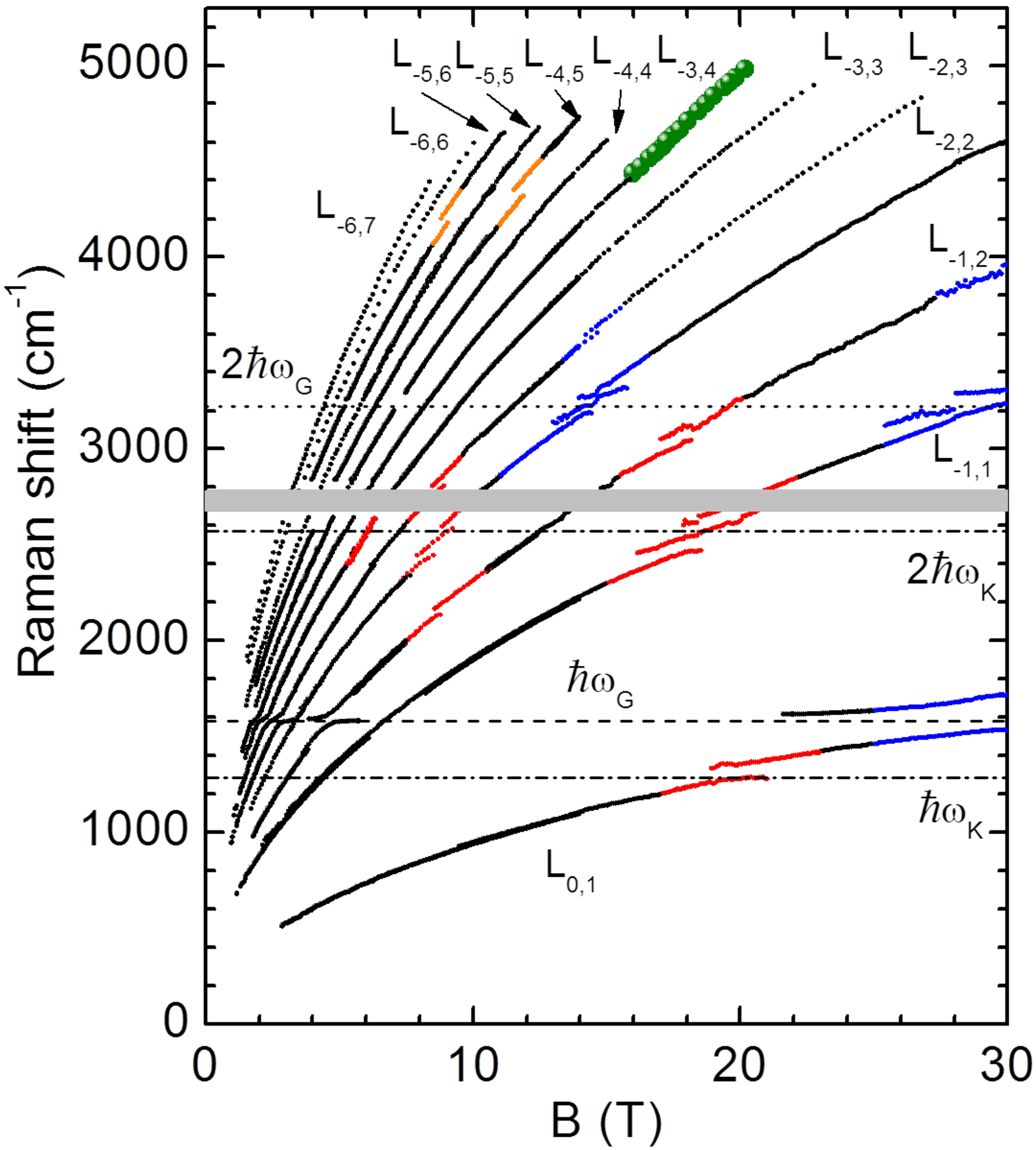


$$E_{-1,2} = E_{-1,0} + E_{ph}$$
$$E_{-3,2} = E_{-3,0} + E_{ph}$$
$$E_{-2,2} = E_{-2,0} + E_{ph}$$
$$E_{k=0} = E_{K,K} + E_{\Gamma}$$
$$E_{k=0} = E_{K,K'} + E_{K}$$

“ruling out” momentum conservation

$$E_{-1,1} = E_{-1,0} + E_{ph} = 2 \times E_{ph}$$

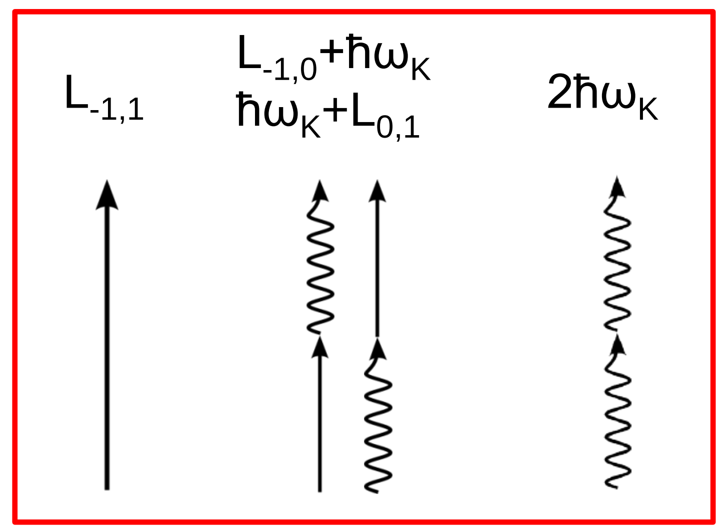
both K- and Γ-phonons involved
two-particle excitations, triple resonances
intra and inter-valley scattering
- learning more on carrier dynamics



Γ point phonons

K point phonons

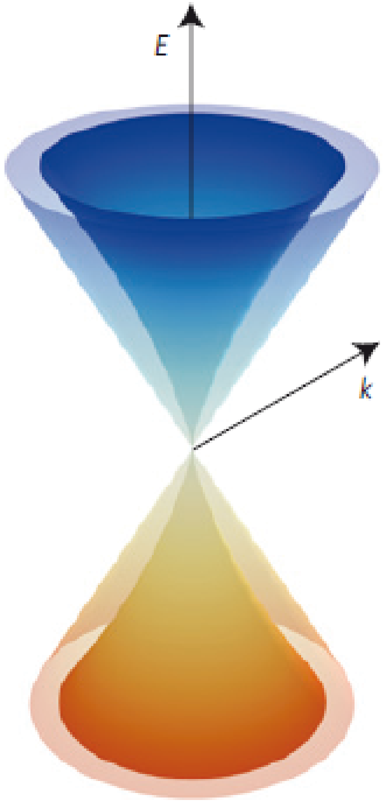
@ B = 18 T



D.M. Basko et al., 2D Materials **3**, 015004, (2016) Interaction effects II :

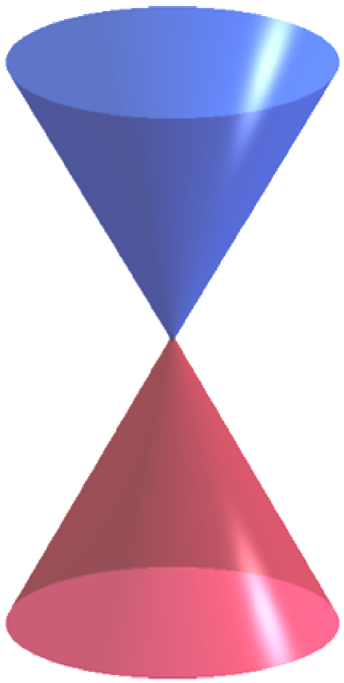
Electron-electron interaction

renormalization of the band velocity

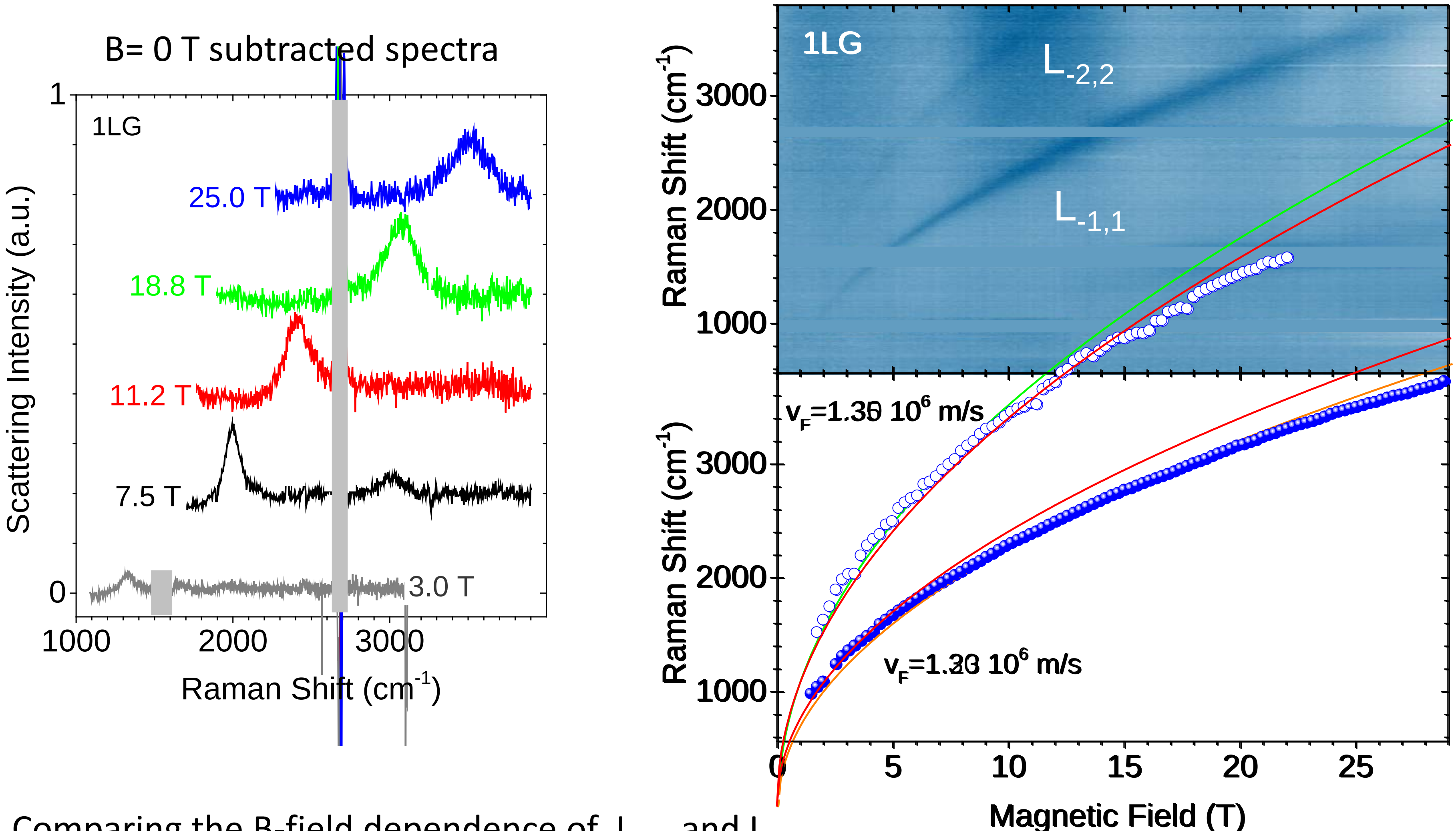


VS

$$\alpha_g = (c/v)(\alpha/\varepsilon)$$



D.C. Elias *et al.* Nat. Phys. **7**, 701 (2011)

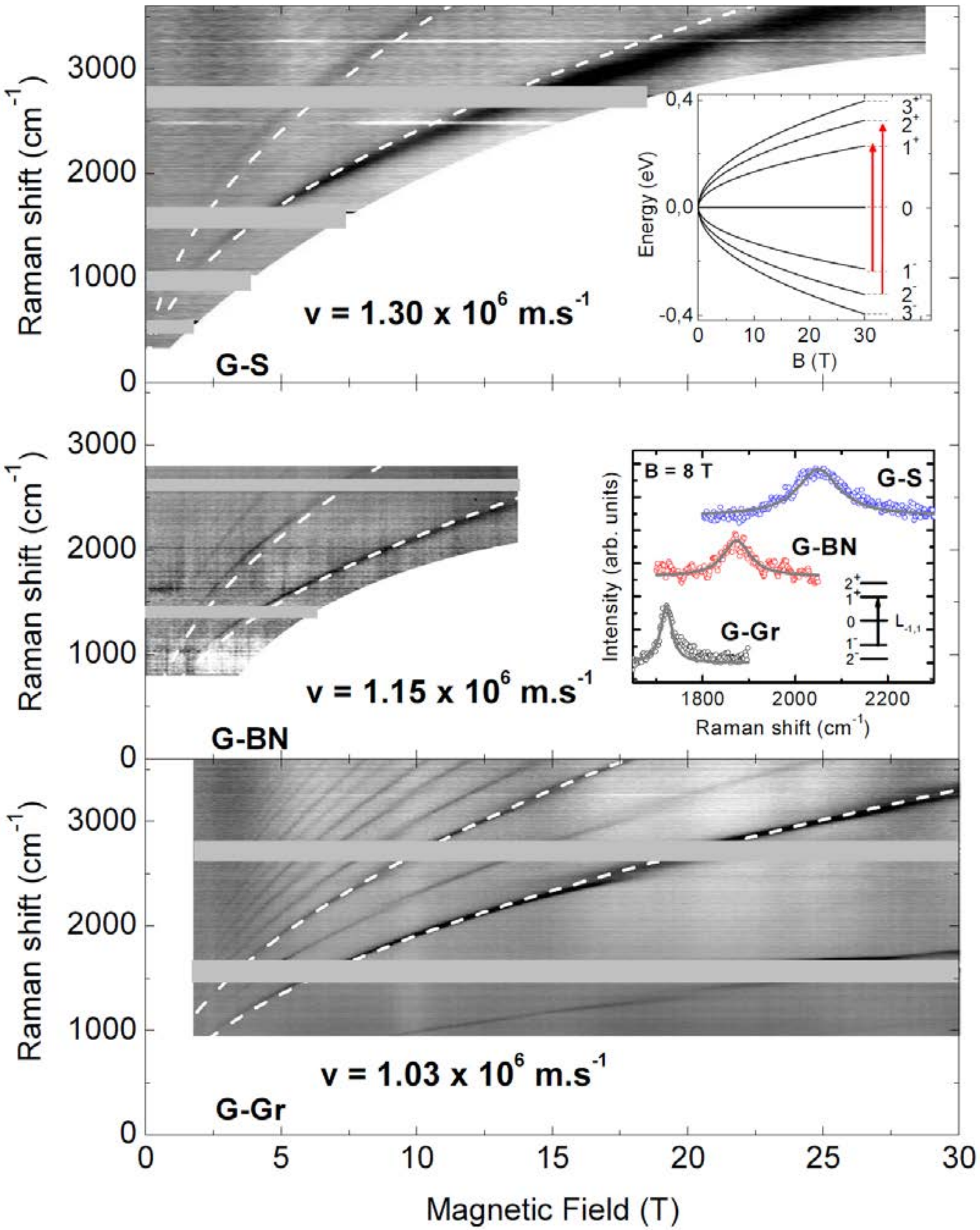


Comparing the B-field dependence of $L_{-1,1}$ and $L_{-2,2}$

→ **clear deviation from the $\sqrt{|n|B}$ scaling**

$$\hbar\omega_n = 2v\sqrt{2e\hbar}\sqrt{B\,n}$$
$$= 2\sqrt{2n}\,\hbar v / l_B$$

$$v_n^{exp} = \omega_{-n,n}^{exp} l_B / \sqrt{8n}$$

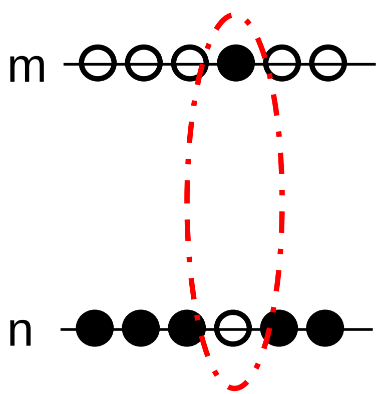


$$\frac{v_F}{v_F^0} = 1 - \frac{\alpha_\varepsilon}{4} ln\left(\frac{E}{W}\right)$$

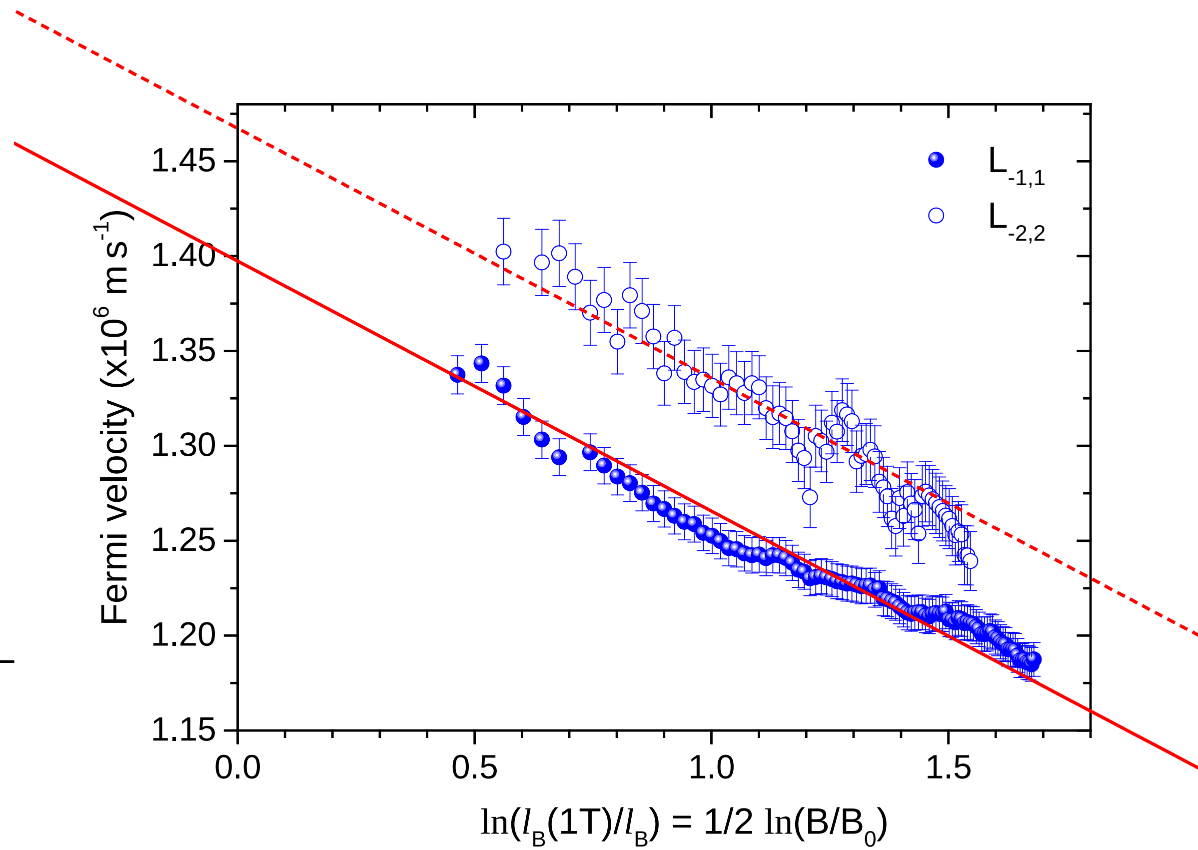
Incomplete picture

→ Predicts $v^{n=1} > v^{n=2}$

(magneto-) excitonic effects are missing !



$$E = E_m - E_n + E_{exciton} + E_{exchange}$$



Gonzalez *et al.* PRB(R) **59**, 2474 (1999)
K. Shizuya, PRB **81**, 075407 (2010)
J. Hoffman *et al.* PRL **113,** 105502 (2014)

K. Shizuya, Phys. Rev. B **81**, 075407 (2010).

B > 0 **Denis Basko**

First order perturbation theory with respect to $\alpha_\varepsilon = (c/v)(\alpha/\varepsilon)$

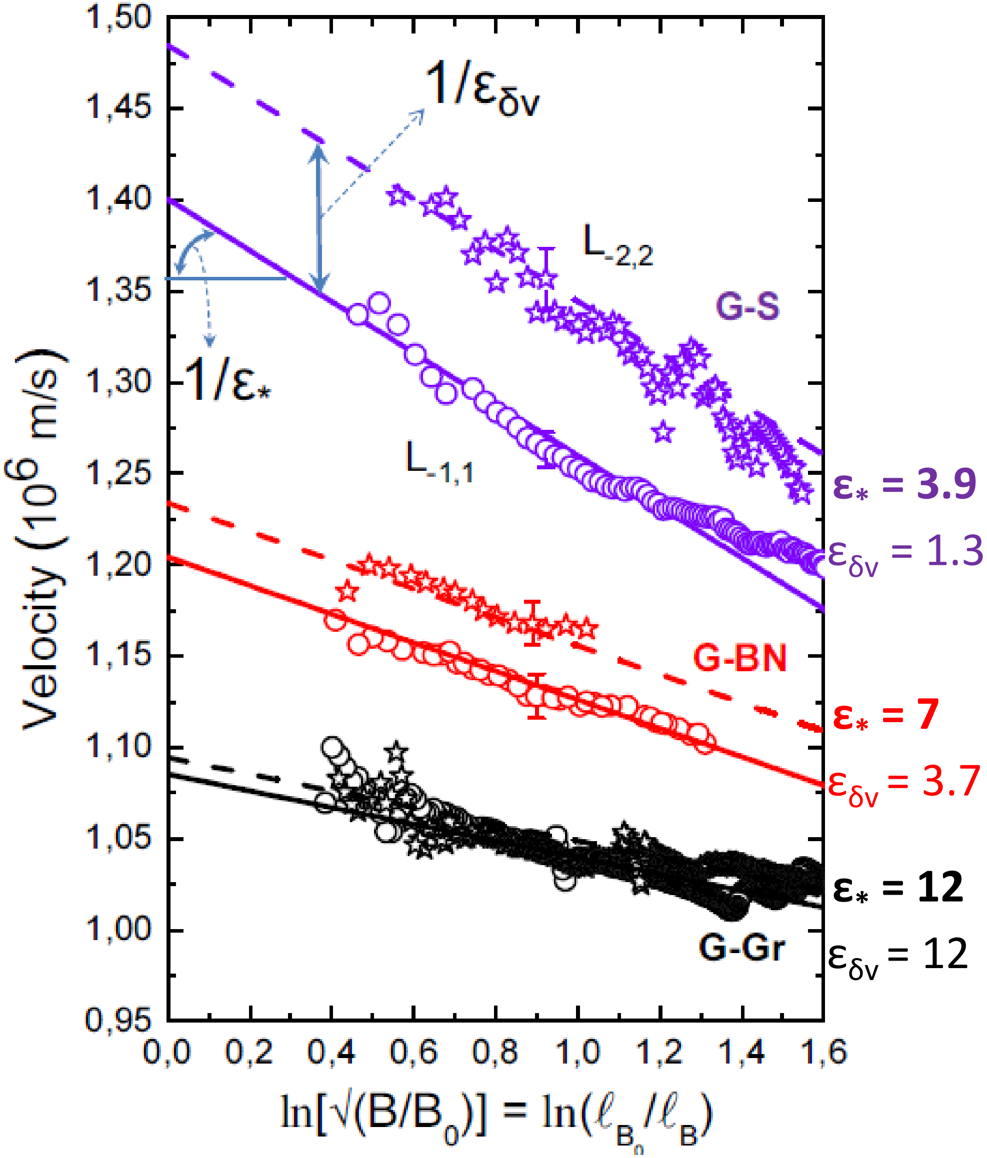
$$v_n \equiv \frac{\omega_{-n,n} l_B}{\sqrt{8n}} = v_0 + \frac{\alpha c}{4\varepsilon}(\mathcal{L} - \ln\frac{l_{B_0}}{l_B}) + \frac{\alpha c}{4\varepsilon} C_n$$

$C_1 = -0.4$, $C_2 = -0.2$

↓

$$v_2 > v_1$$

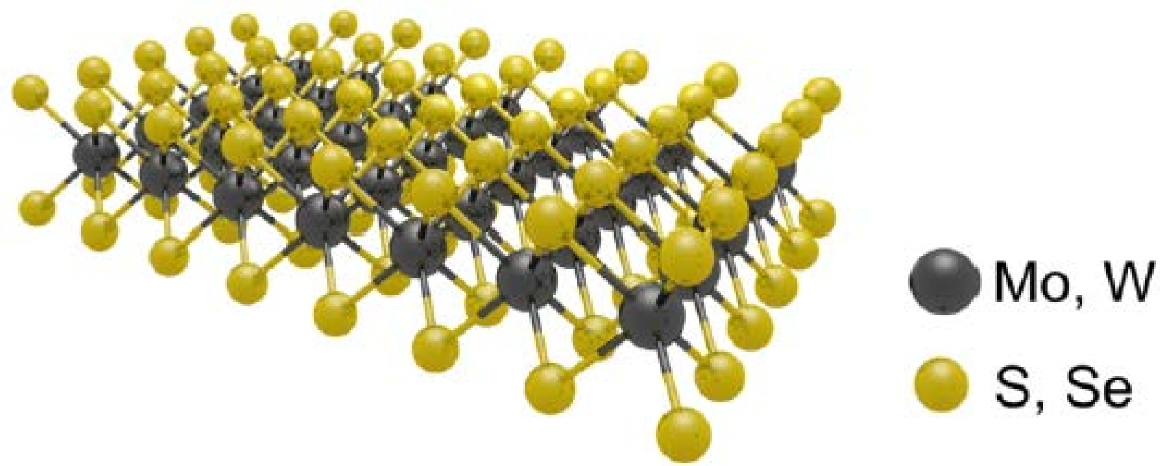
$$v_n = v_0 + \frac{\alpha c}{4\varepsilon_*}(\mathcal{L} - \ln\frac{l_{B_0}}{l_B}) + \frac{\alpha c}{4\varepsilon_{\delta v}} C_n$$



Outline:

- Why combining optical spectroscopy with magnetic fields ?
- Experimental techniques
- Dirac fermions in graphene:
  - Cyclotron motion/resonance & Landau levels
  - Magneto-Raman scattering
  - Interaction effects (electron-phonon and electron-electron)
- Semiconducting transition metal dichalcogenides
  - Excitonic properties
  - Zeeman spectroscopy
  - Magnetic brightening
- Summary

Monolayers of semiconducting transition metal dichalcogenides (TMD)



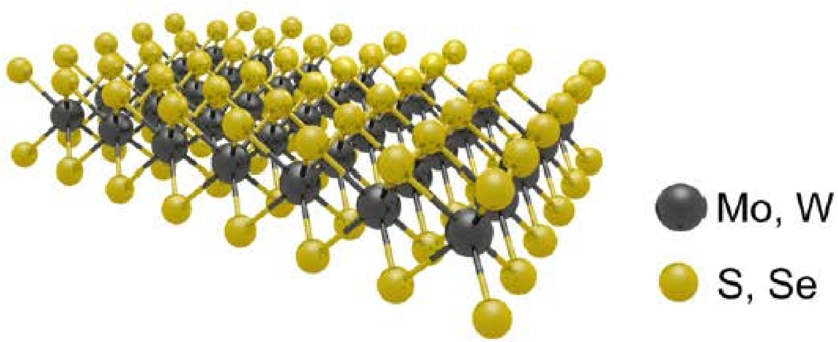
Bulk s-TMD

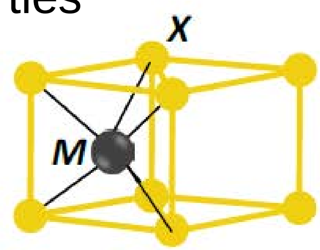
MX_2 where M = Mo or W and X = S, Se, or Te

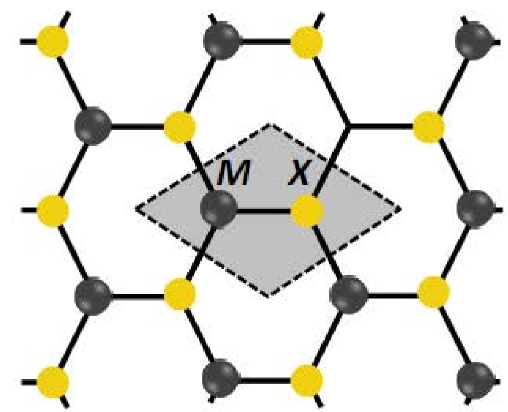
van der Waals stacks of 2 hexagonal planes of X atoms and 1 plane of M atoms

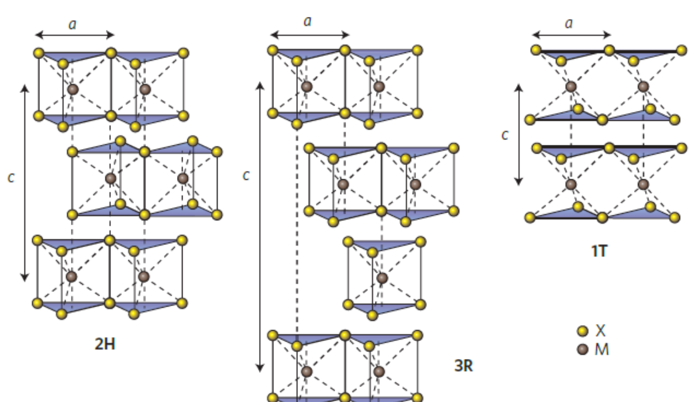
Trigonal prismatic arrangement

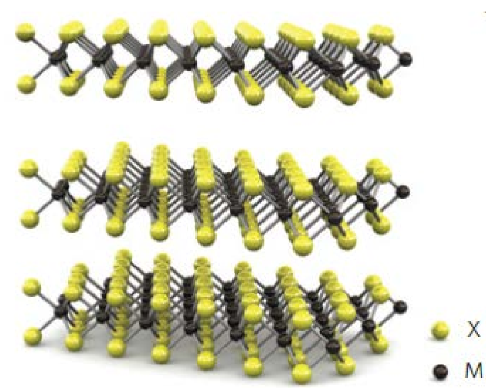
3 phases (2H, 3R, 1T) with different properties









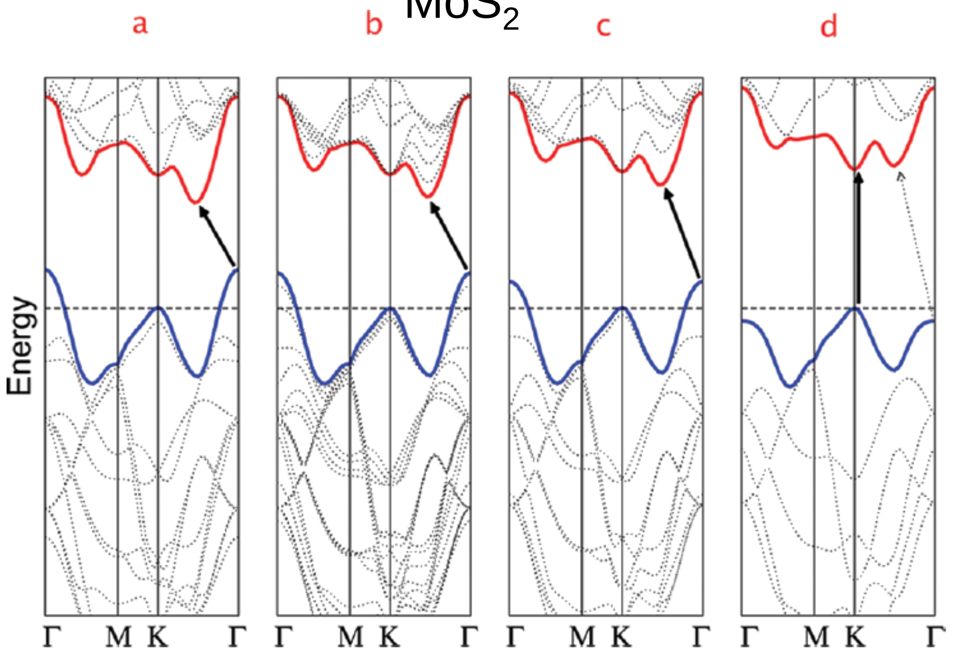


Band structure

Bulk and multilayers are indirect band gap semiconductors

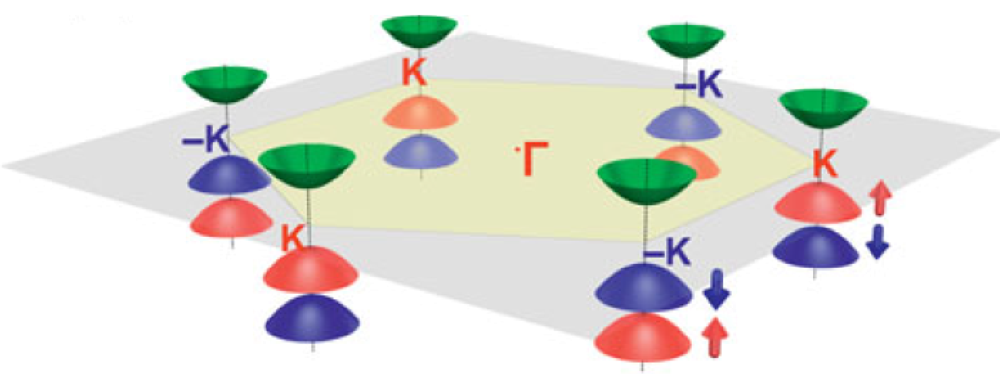
Monolayers are direct band gap semiconductors

MoS_2



bulk 4L 2L 1L

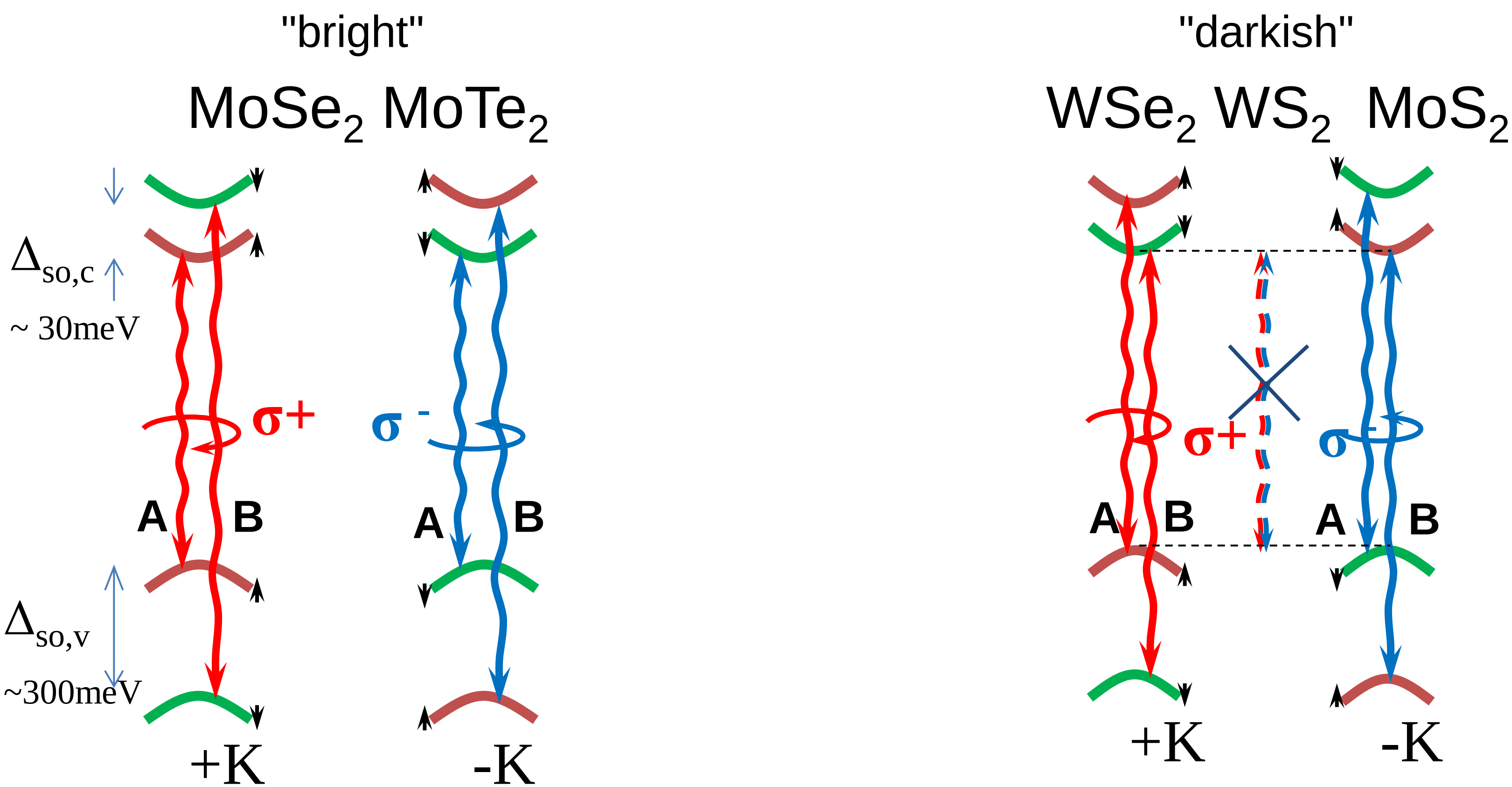
Splendiani et al., NanoLett. 2010
DFT calculations



schematic hexagonal Brillouin zone

Two classes of S-TMD monolayers,

Distinct alignment of spin-orbit split subbands in the conduction band



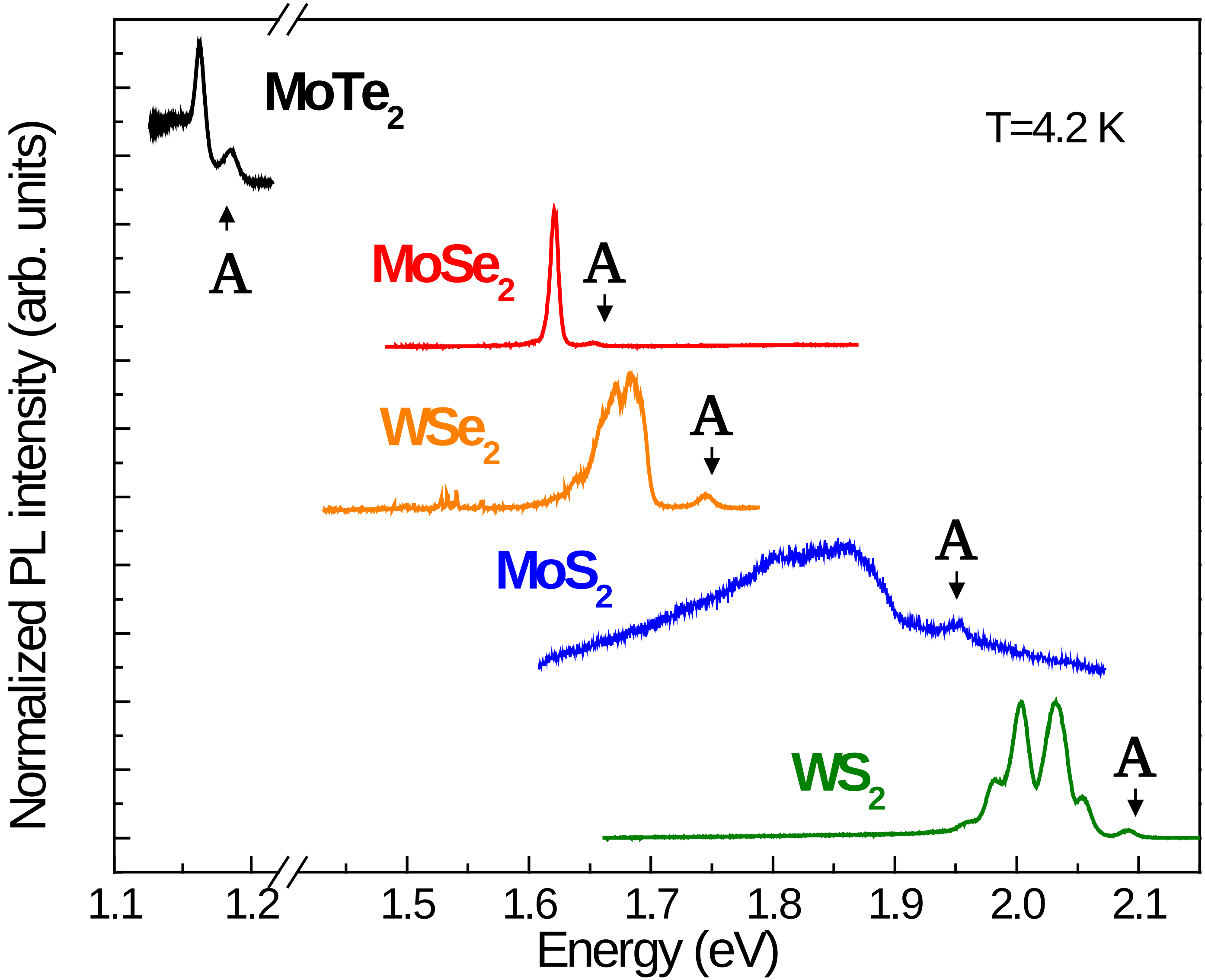
Ground state exciton

optically active

optically inactive

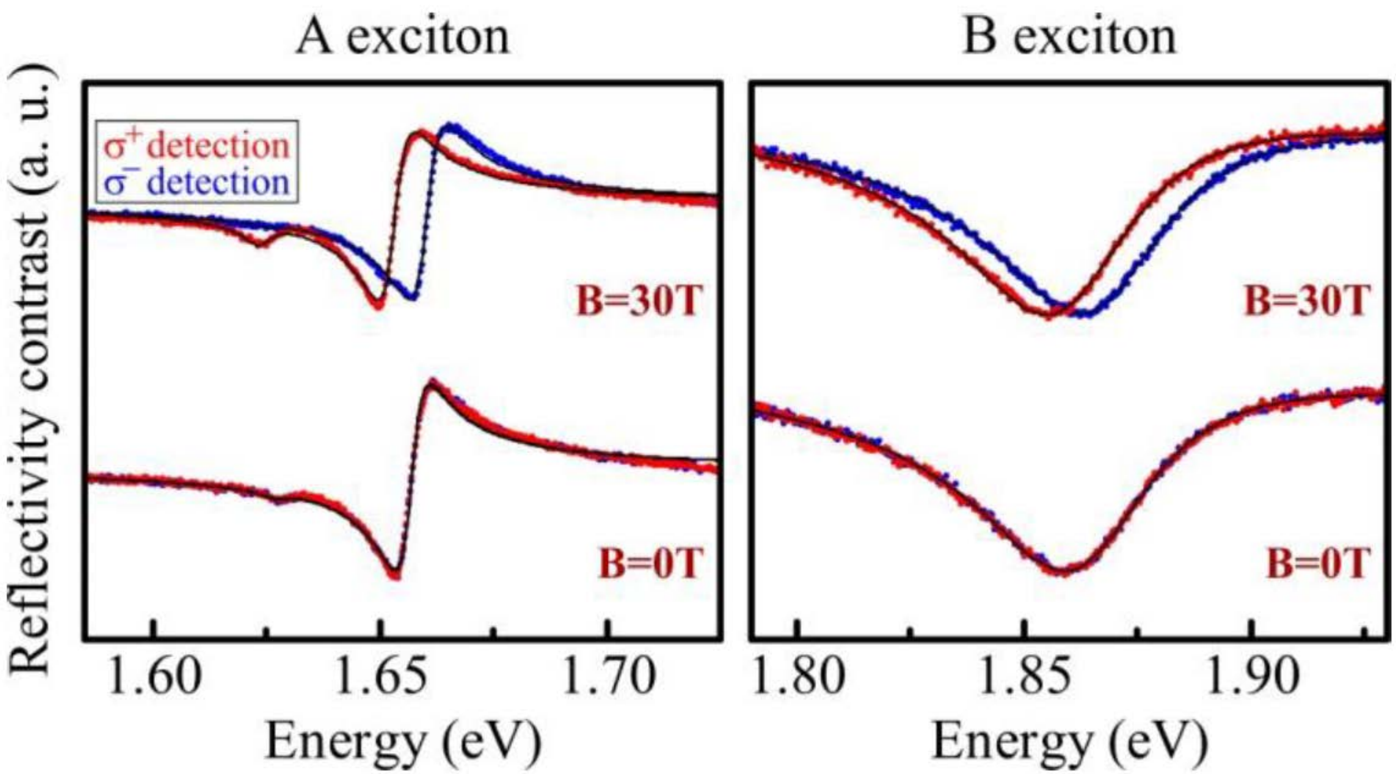
A. Arora el al., Nanoscale (2015), G. Wang et al. arXiv (2015), H. Dery,et al. , Phys. Rev. B (2015)
X-X. Zhang et al, PRL (2015), ……..

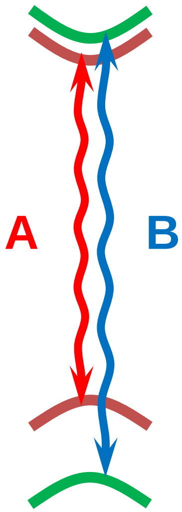
2 distinct types of emission spectra



M.R. Molas et al, in preparation (2017)

Zeeman spectroscopy of excitons in sTMD





$MoSe_2$ monolayer

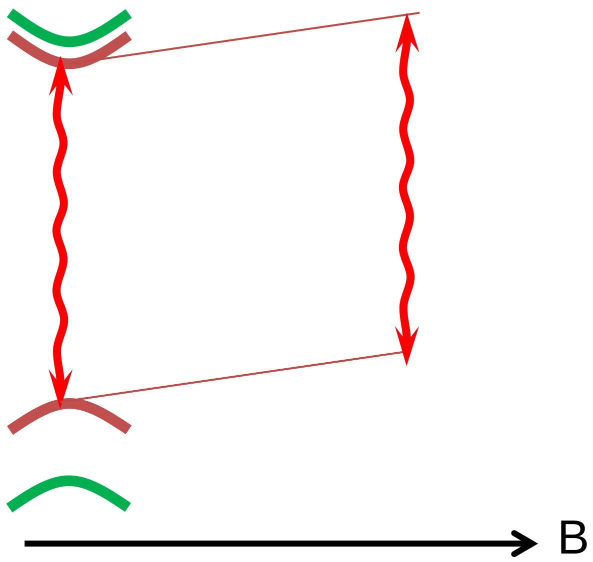
$E(\sigma +) - E(\sigma -) = g\,\mu_B\,B$

$\mu_B \approx 0.058$ meV / T

Koperski et al., Nanophotonics in press (2017)

B field couples to

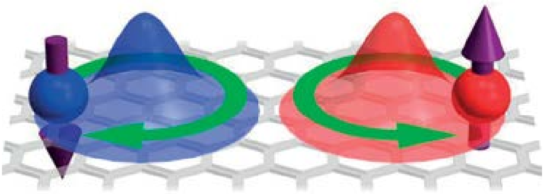
Real spin +



Not relevant when measuring interband excitations that conserve spin

B field couples to

Real spin + orbital contributions



Two contributions equal in both valleys but opposite in sign :

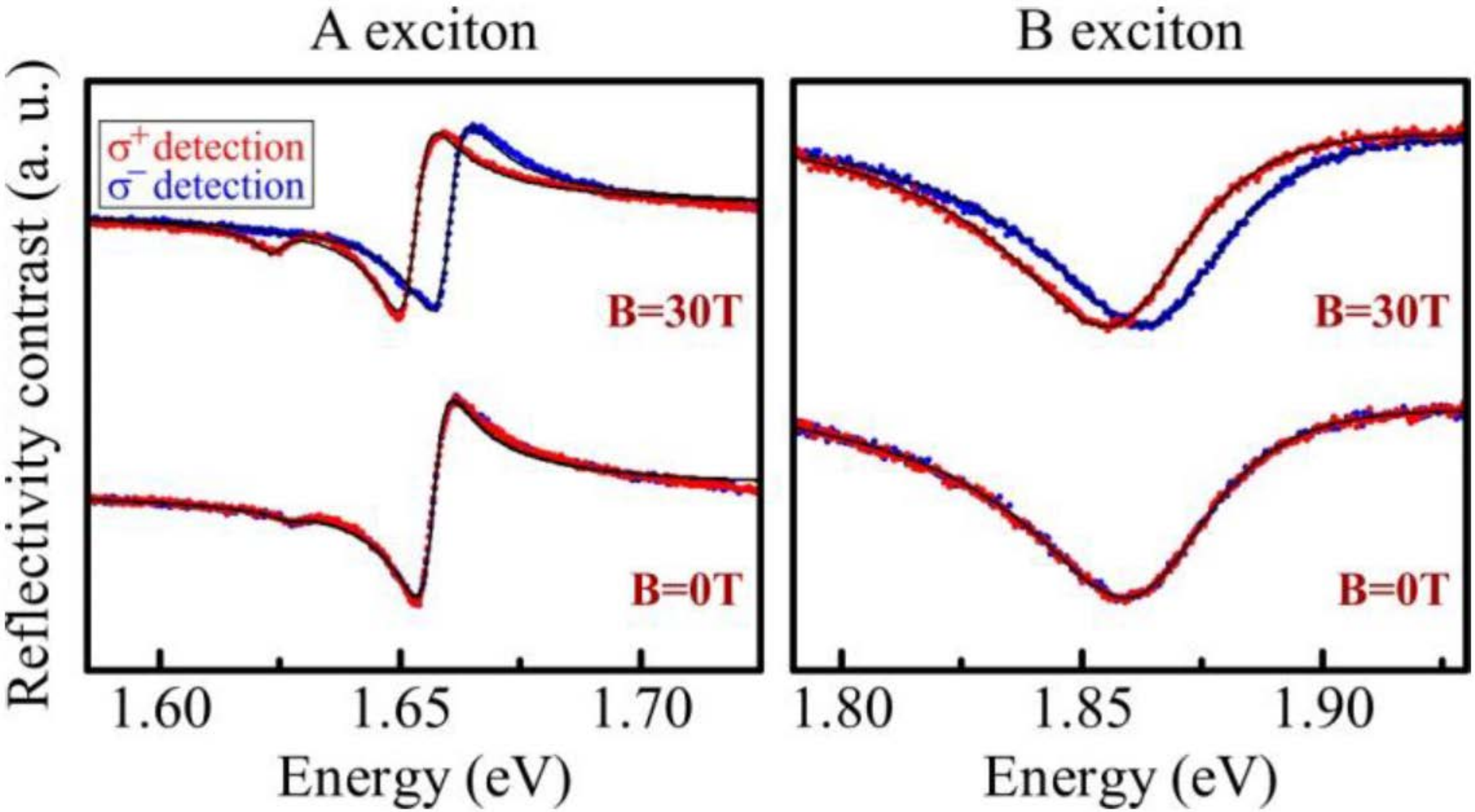
from d_2 atomic orbitals (acts only on valence band electrons)

a crystal structure contribution, the “valley magnetic moment”, Berry curvature, self rotating wave packet

$$E(\sigma +) - E(\sigma -) = g\, \mu_B\, B$$

$$\mu_B \approx 0.058 \text{ meV / T}$$

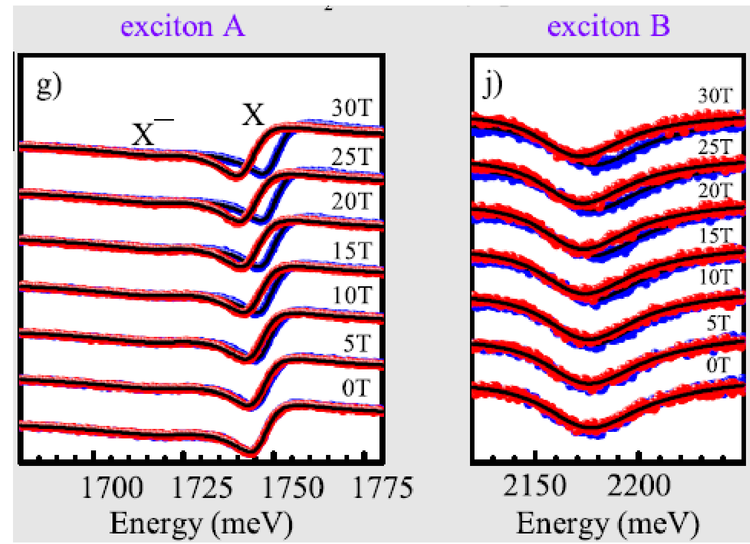
$MoSe_2$ monolayer



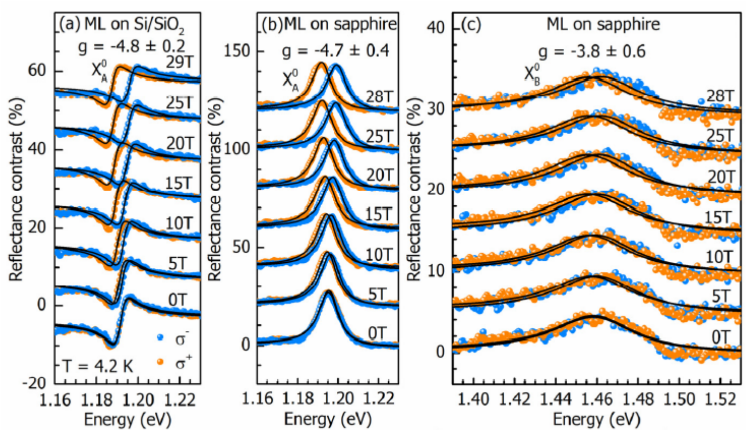
Koperski et al., Nanophotonics in press (2017)

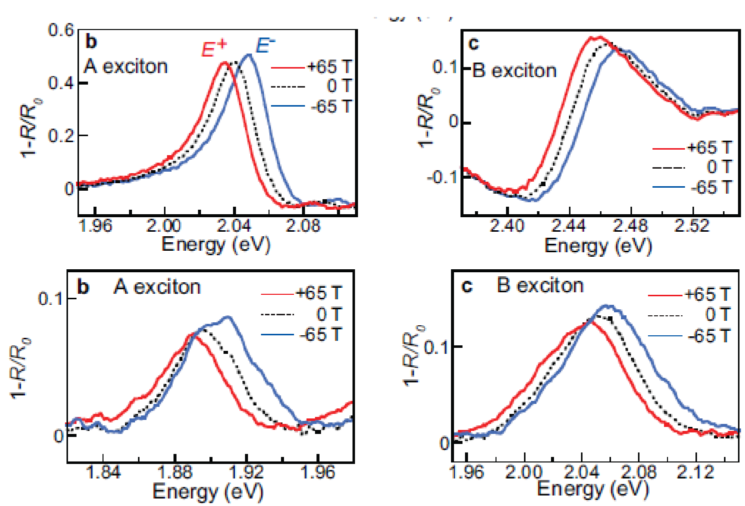
Zeeman spectroscopy of various S-TMD monolayers

WSe_2 , Grenoble, to be published



$MoTe_2$, Arora et al., Nano Lett. (2016)





WSe_2

MoS_2

A.V. Stier et al., Nature Comm. (2016)

Zeeman spectroscopy of various S-TMD monolayers

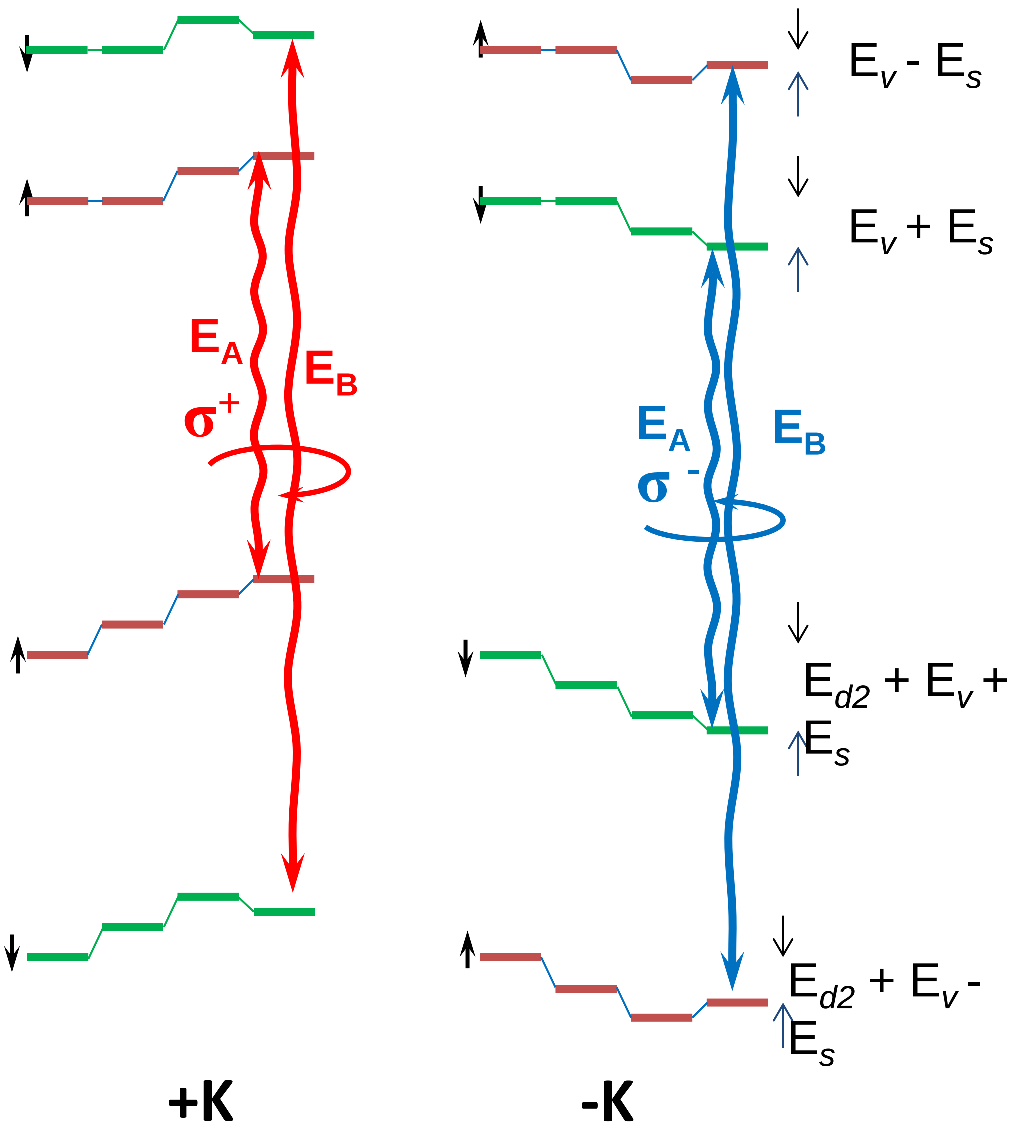
material	neutral exciton A g-factor	neutral exciton B g-factor
MoS_2	-4.0±0.2* *(reflectance)*	-4.2±0.2* *(reflectance)*
$MoSe_2$	-4.2±0.2 *(reflectance)*	-4.2±0.2 *(reflectance)*
$MoTe_2$	-4.8±0.2** *(reflectance)*	-3.8±0.2** *(reflectance)*
WS_2	-4.3±0.2 *(transmission)* -3.9±0.2* *(reflectance)*	-4.3±0.2 *(transmission)* -4.0±0.2* *(reflectance)*
WSe_2	-3.8±0.2 *(reflectance)*	-3.9±0.2 *(reflectance)*

$$g_A \sim g_B \sim -4$$

measure of relative Zeeman splitting in the conduction and valence band

Koperski et al., Nanophotonics in press (2017)

Expected Zeeman splitting: bright monolayers



G. Aivazian *et al.*, Nat. Phys. 11, 148 (2015)

3 different contributions

$E_{d2} = \pm g_{d2} \mu_B B \quad (g_{d2} \cong 2)$

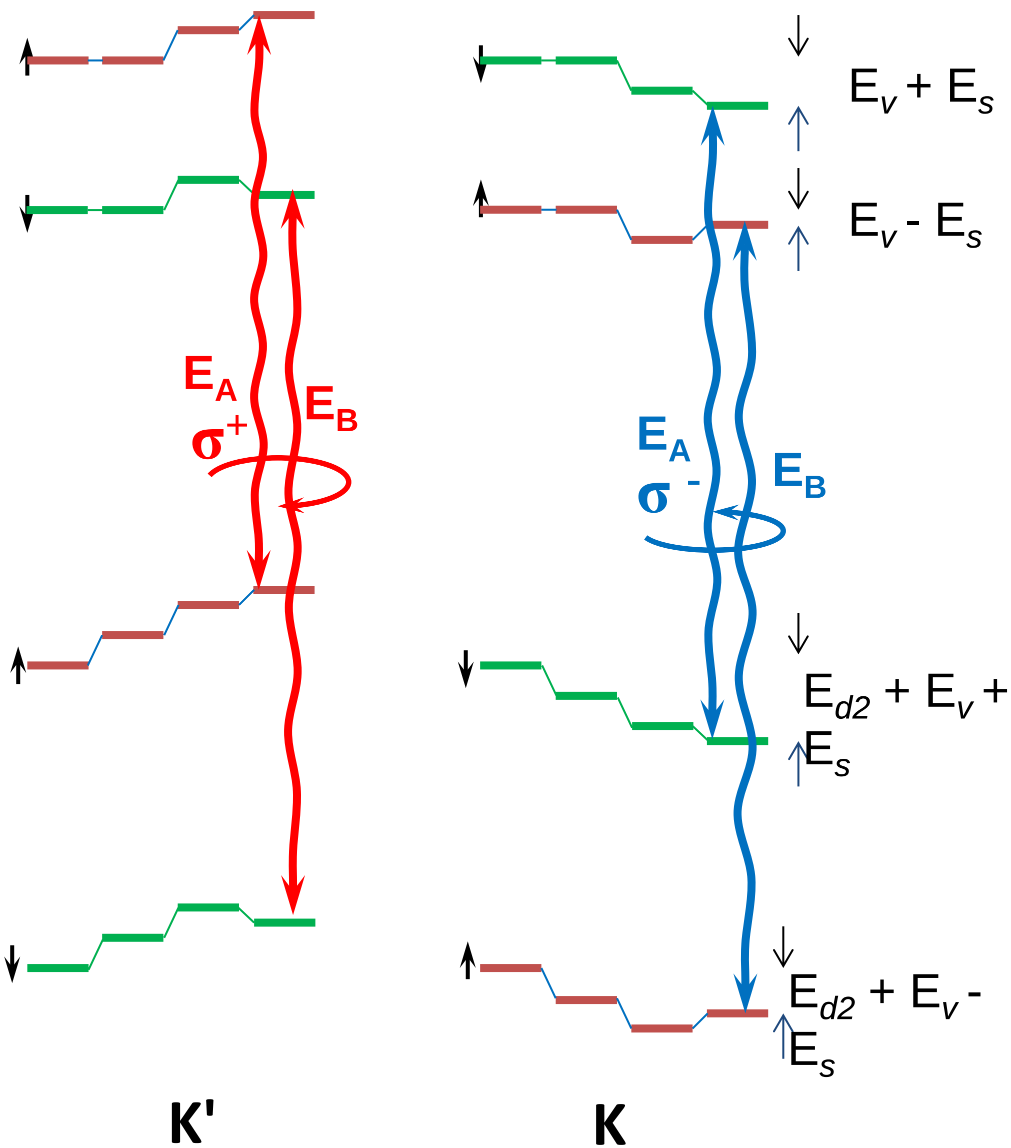
$E_{\text{"valley"}} = \pm g_v \mu_B B \quad (g_v \sim 2)$

$E_s = \pm \left(\frac{1}{2} g_e \right) \mu_B B \quad (1/2\, g_e \cong 1)$

Expected Zeeman splitting of optically active transitions (excitons A, B, X^-)

$E_A - E_A = E_B - E_B = -2 E_{d2} = -2 g_{d2} \mu_B B \cong -4 \mu_B B$

Expected Zeeman splitting: "darkish" monolayers



3 different contributions

$\mathbf{E_{d2} = \pm g_{d2}\, \mu_B\, B}$ $\quad$ $\mathbf{(g_{d2} \cong 2)}$

$\mathbf{E_{\text{"valley"}} = \pm g_v\, \mu_B\, B}$ $\quad$ $\mathbf{(g_v \sim 2)}$

$\mathbf{E_s = \pm \left(\frac{1}{2} g_e\right) \mu_B\, B}$ $\quad$ $\mathbf{(1/2\, g_e \cong 1)}$

Expected Zeeman splitting of optically active transitions (excitons A, B, X^-)

$\mathbf{E_A - E_A = E_B - E_B = -2\, E_{d2} = -2\, g_{d2}\, \mu_B\, B \cong -4\, \mu_B\, B}$

Stier AV, et al.
Exciton diamagnetic shifts and valley Zeeman effects in monolayer WS2 and MoS2 to 65 Tesla.
Nat Commun **2016**;7:10643

Aivazian G, et al.
Magnetic control of valley pseudospin in monolayer WSe2.
Nat Phys **2015**;11:148–152.

Srivastava A,et al.
Valley Zeeman effect in elementary optical excitations of monolayer WSe2. Nat Phys **2015**;11:141–147. WSe2

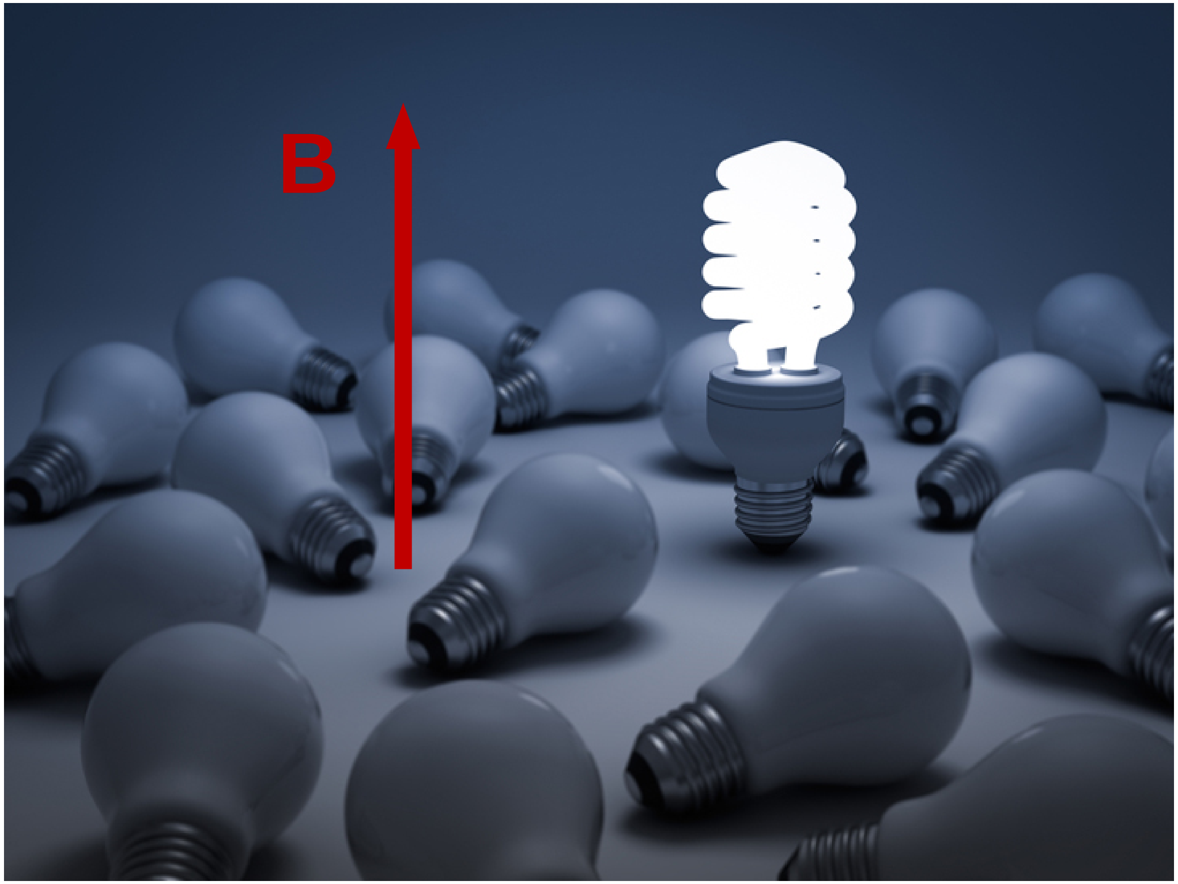
MacNeill D, et al.
Breaking of Valley Degeneracy by Magnetic Field in Monolayer MoSe2.
Phys Rev Lett **2015**;114:37401. MoSe2

Wang G, et al.
Magneto-optics in transition metal diselenide monolayers.
2D Mater **2015**;2:34002.

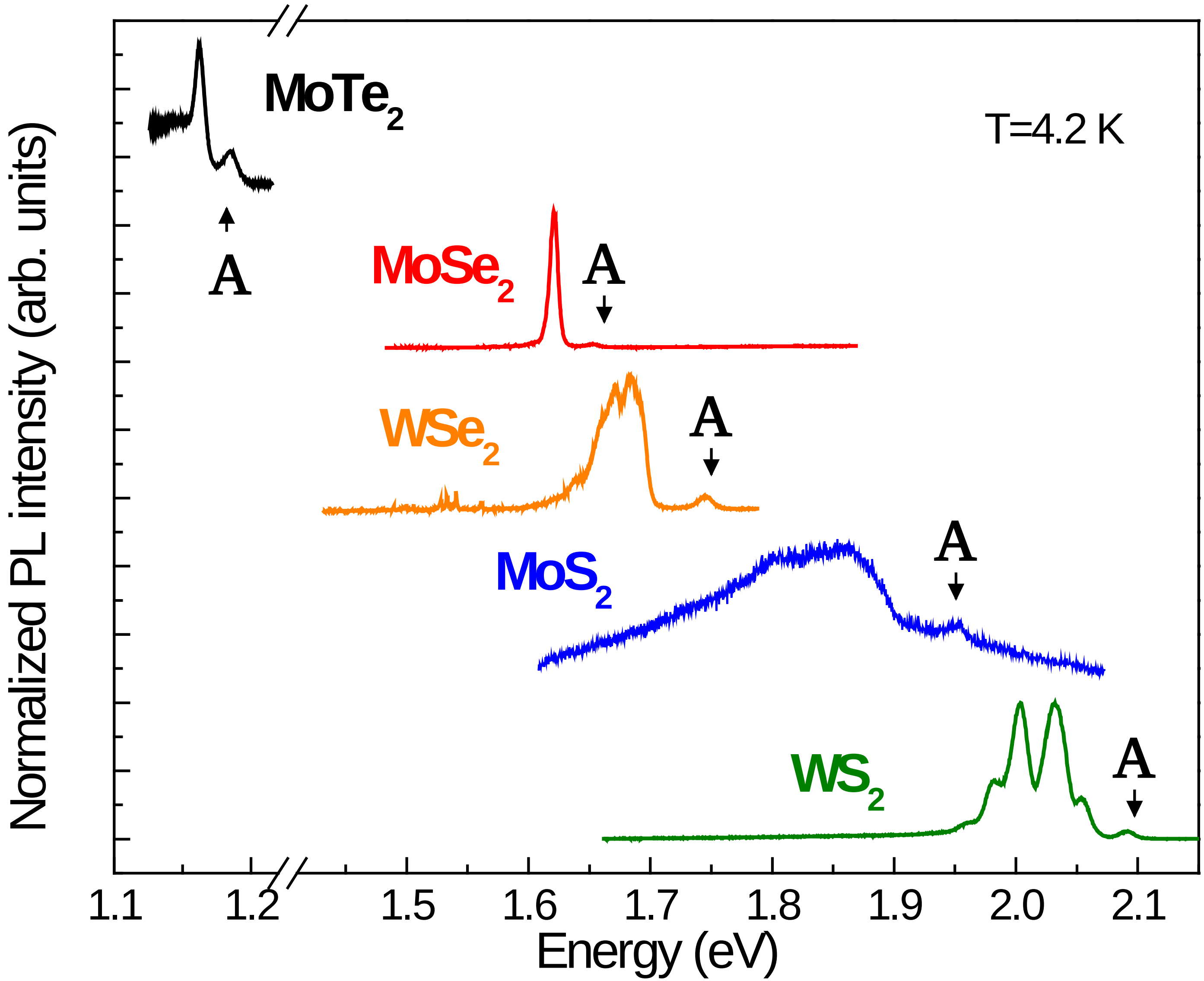
Li Y, et al.
Valley Splitting and Polarization by the Zeeman Effect in Monolayer MoSe2.
Phys Rev Lett **2014**;113:266804.

Arora A., et al.
Valley Zeeman Splitting and Valley Polarization of Neutral and Charged Excitons in Monolayer $MoTe_2$ at High Magnetic Fields
NanoLett. 16, 3624, (**2016**)

Magnetic brightening



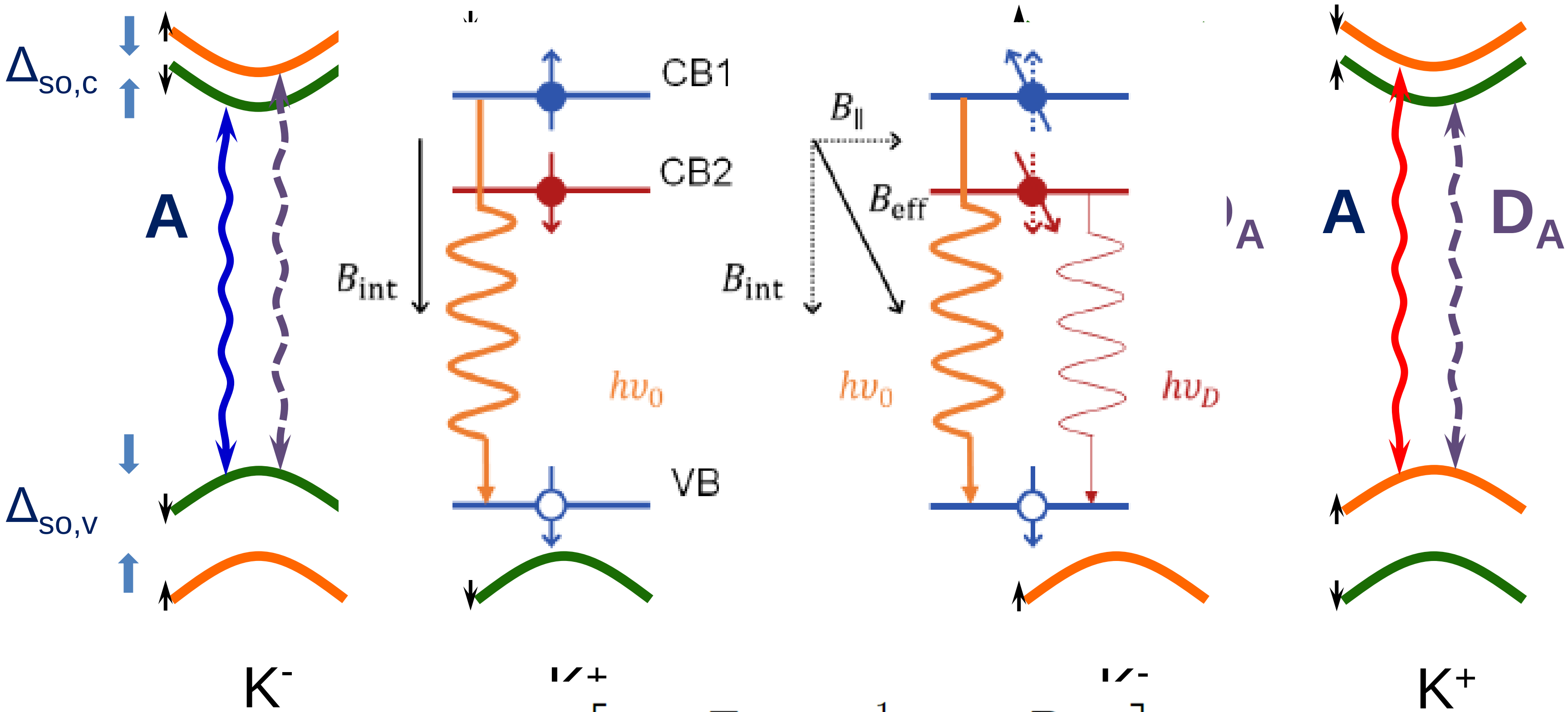
2 distinct types of emission spectra



M.R. Molas et al, in preparation (2016)

DARK EXCITONS – how to „switch them on" ? How to make them bright ?

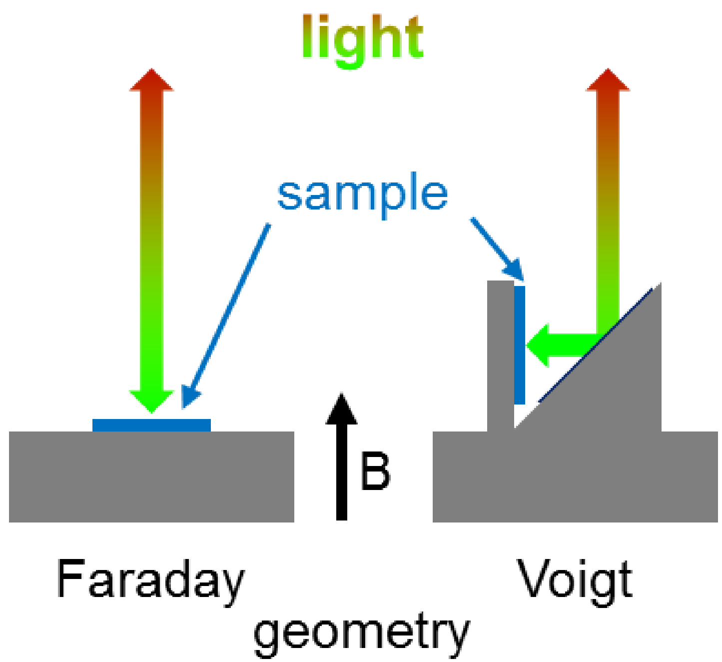
Spin-flip process induced by in-plane magnetic field to induce finite spin projection in the plane



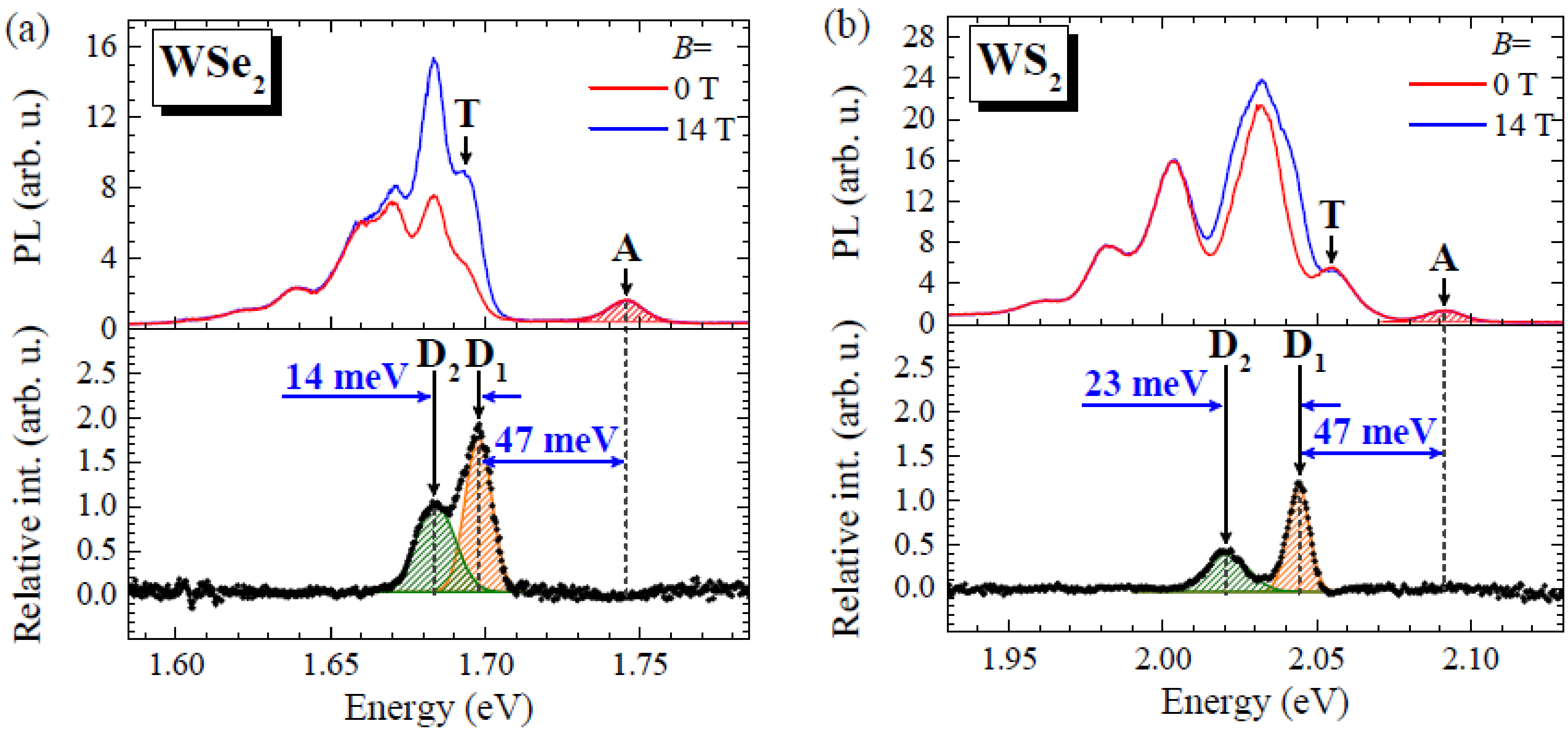
$$H_{ex}^{\tau} = \begin{bmatrix} E_b & \frac{1}{2} g_{cb} \mu_B B_{-\tau} \\ \frac{1}{2} g_{cb} \mu_B B_{\tau} & E_d \end{bmatrix}$$

A. Slobodeniuk and D. M. Basko, 2D Mater. **3**, 035009 (2016)
M.R. Molas et al., 2D Mater. (2017)
X-X. Zhang et al., arXiv:1612.03558

Dark excitons – how to „switch them on” ?
How to make them bright ?



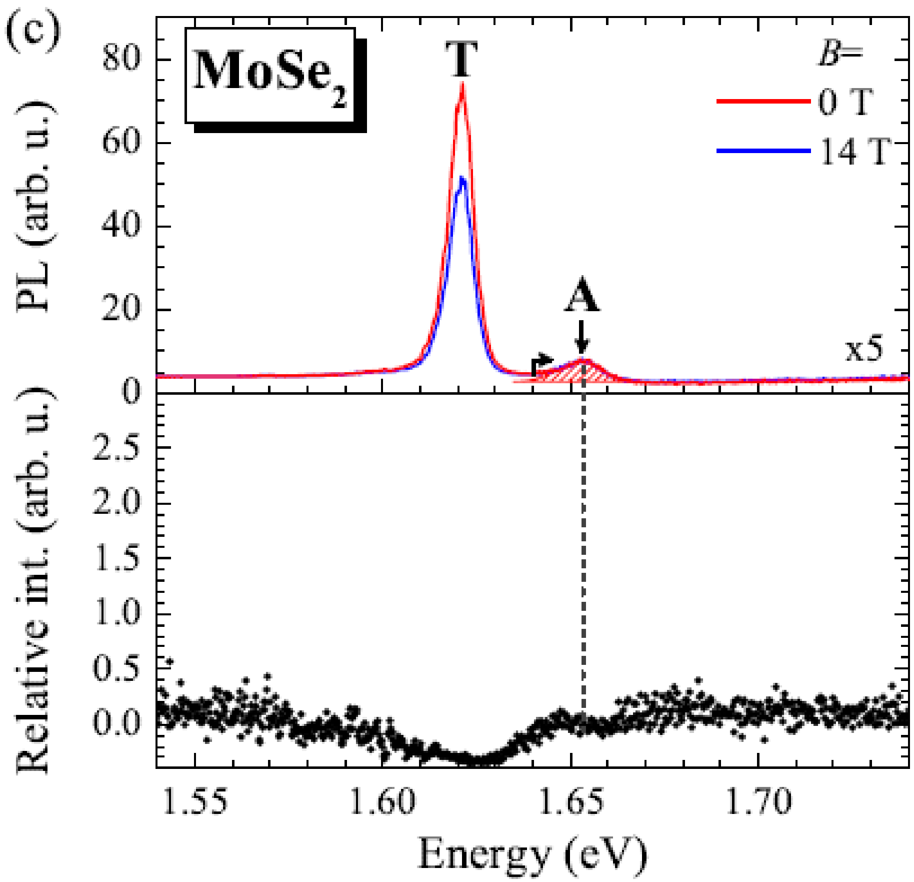
Brightening dark excitons in monolayers of W-based TMDs

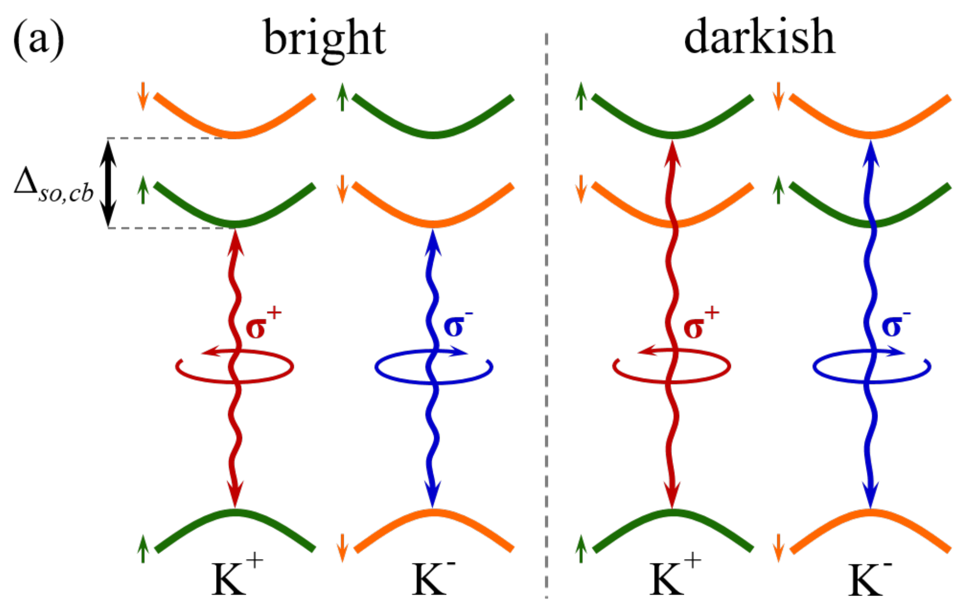


$$PL_{Rel} = \frac{PL(B=14T) - PL(B=0)}{PL(B=0)}$$

M. Molas et al., 2D Materials (2017)
Also Zhang et al, arXiv:1612.03558

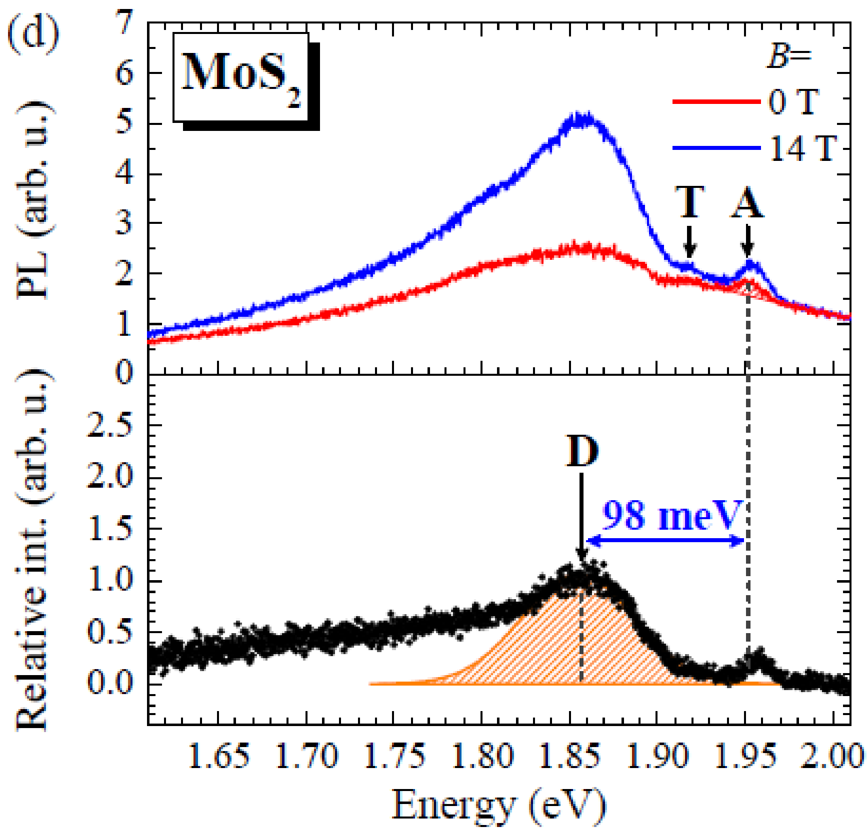
Brightening dark excitons in monolayers of $MoSe_2$?





M. Molas et al., 2D Materials (2017)

Particular case of MoS_2 : a stranger within a well established family



K. Kośminder et al., Phys. Rev. B **87**, 075451 (2013)

G.-B.Liu, et al., Phys. Rev. B **88**, 085433 (2013)

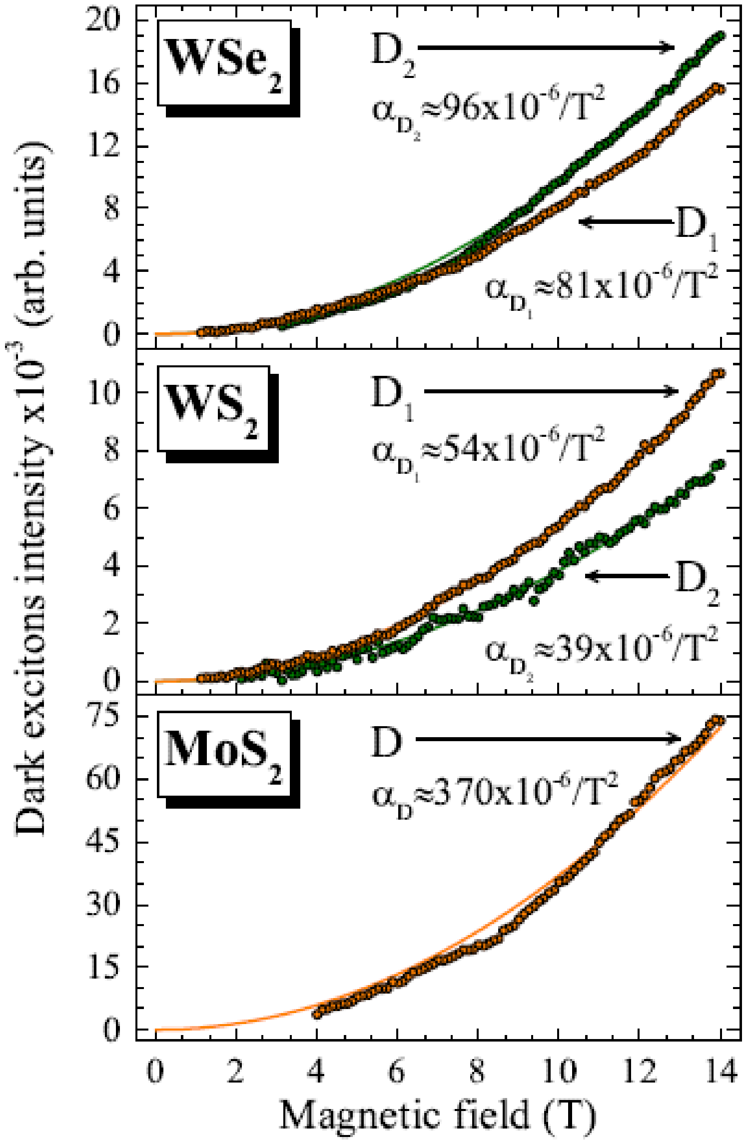
T. Cheiwchanchamnangij et al., Phys. Rev. B **88**, 155404 (2013)

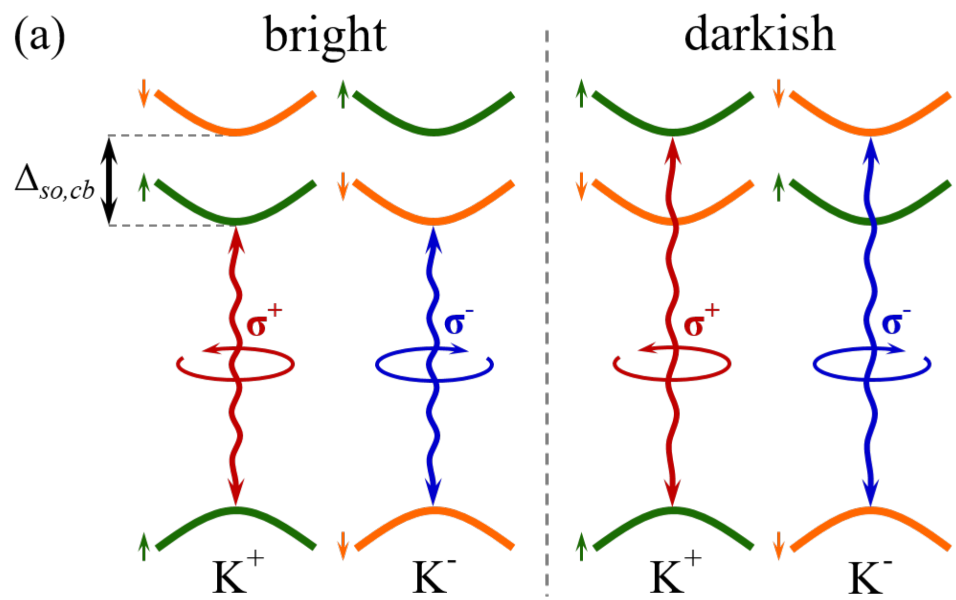
K. Kośmider et al., Phys. Rev. B **88**, 245436 (2013)

A. Kormanyos et al., 2D Mater. **2**, 022001 (2015)

In plane field is a small perturbation

with spectacular effects





M. Molas et al., 2D Materials (2017)

Summary

Magneto-optical spectroscopy is an essential tool to study 2D materials

band structure
scattering efficiency
interaction effects
  electron-phonon interaction
  electron-electron interactions
Zeeman (and valley) spectroscopy
Tuning scattering rates
Magnetic brightening

Thank you for

your attention