

The basics of graphene and its Raman spectroscopy

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Outline:

- 1. Structure and electronic properties
- 2. Optical properties: infrared absorption
- 3. Optical properties: Raman scattering

"Mother of all graphitic forms"



A. K. Geim and K. S. Novoselov, Nature Materials 6, 183 (2007)

σ - and π -bonds



Bloch states in a periodic potential

$$-\frac{\nabla^2}{2m} + V(\mathbf{r}) \int \psi(\mathbf{r}) = \epsilon \,\psi(\mathbf{r})$$

 $V(\mathbf{r} + \mathbf{a}_i) = V(\mathbf{r})$

 $\mathbf{a}_1, \mathbf{a}_2$ - lattice vectors



Bloch theorem: $\psi(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{b\mathbf{k}}(\mathbf{r})$

quantum $\begin{cases} k \text{ in the first Brillouin zone} \\ b \text{ band index} \end{cases}$

 $u_{b\mathbf{k}}(\mathbf{r} + \mathbf{a}_i) = u_{b\mathbf{k}}(\mathbf{r})$ periodic Bloch function, found from the Schrödinger equation in a single unit cell

 $\epsilon = \epsilon_{bk}$ band structure



Crystal symmetry

$$\left[-\frac{\nabla^2}{2m} - \frac{i\mathbf{k}}{m} \cdot \nabla + V(\mathbf{r})\right] u(\mathbf{r}) = \left(\epsilon - \frac{k^2}{2m}\right) u(\mathbf{r})$$

at K point: \hat{C}_{3v} - rotation by $2\pi/3$

- mirror reflection

C_{6v}
rotation by π/3
mirror reflection

C_{3v} character table:

 C_{3v} E $2C_3$ $\sigma'_{a,b,c}$ symmetry
operations A_1 1111 A_2 11-1E2-10irreducible2-dimensional
representationsrepresentationDoubly degenerate states at the K point

are allowed by the symmetry



Tight-binding model



Schrödinger equation:



P. R. Wallace, Phys. Rev. 71, 622 (1947)

$$\psi(\mathbf{r}) = \sum_{j} \left[C_{A\mathbf{k}} \phi(\mathbf{r} - \mathbf{r}_{Aj}) e^{i\mathbf{k}\mathbf{r}_{Aj}} + C_{B\mathbf{k}} \phi(\mathbf{r} - \mathbf{r}_{Bj}) e^{i\mathbf{k}\mathbf{r}_{Bj}} \right]$$

sum over unit cells

diagonal matrix element:

atomic level:

 $\gamma_0 \approx 3 \, \mathrm{eV}$

$$\int \phi(\mathbf{r} - \mathbf{r}_A) \left(-\frac{\nabla^2}{2m} + V \right) \phi(\mathbf{r} - \mathbf{r}_A) d^3 \mathbf{r} = \epsilon_{\pi} \to 0 \quad \text{choose as} \\ \text{the origin}$$

nearest-neighbor matrix element:

$$\int \phi(\mathbf{r} - \mathbf{r}_B) \left(-\frac{\nabla^2}{2m} + V \right) \phi(\mathbf{r} - \mathbf{r}_A) d^3 \mathbf{r} = -\gamma_0$$

nearest-neighbor overlap:

 $\int \phi(\mathbf{r} - \mathbf{r}_B) \, \phi(\mathbf{r} - \mathbf{r}_A) \, d^3 \mathbf{r} = s_0$

often neglected

two bands touch at the corners of the hexagon

Pristine graphene: half-filled bands

2D Dirac electrons



ARPES measurements



Angle-Resolved Photo-Emission Spectroscopy: X-ray photon absorbed, electron emitted energy-momentum conservation

measure electronic disperson





Electric Field Effect in Atomically Thin Carbon Films



Klein tunneling



Transmission over a potential barrier (for two heights):

M. I. Katsnelson,

K. S. Novoselov,

A. K. Geim. Nature Phys. 2, 620 (2006)



 $\int \psi_{-\mathbf{p},s}^{\dagger}(\mathbf{r}) \begin{pmatrix} V(\mathbf{r}) & 0\\ 0 & V(\mathbf{r}) \end{pmatrix} \psi_{\mathbf{p},s}(\mathbf{r}) d^{2}\mathbf{r} = 0$

unit transmission at normal incidence

The same potential on A and B sublattices

No backscattering by a smooth potential No electrostatic confinement



Universal optical absorption



no intrinsic energy scale for the Dirac spectrum \rightarrow

$$a(\omega) = (\text{const} \sim 1) \cdot \alpha$$

Universal optical absorption



no intrinsic energy scale for the Dirac spectrum \rightarrow

$$a(\omega) = (\text{const} \sim 1) \cdot \alpha$$

R.R. Nair et al., Science 320, 1308 (2008)

$$const = \pi$$

Gate voltage dependence





Residual conductivity: broken momentum conservation

- Coulomb impurities [T. Stauber et al., PRB 78, 085418 (2008);

P. Yuan et al., PRB 84, 195418 (2011)]

- electron-electron scattering [A. G. Grushin et al., PRB 80, 155417 (2009)]

Landau level spectroscopy



$$\epsilon_n = \pm \sqrt{2ev^2 B|n|}$$

to the Dirac velocity

Landau level spectroscopy



experimental access to the Dirac velocity



M. Orlita et al., PRL 101, 267601 (2008)

Raman scattering

L. I. Mandelshtam and G. S. Landsberg, Zeitschrift für Physik **50**, 169 (1928) C. V. Raman and K. S. Krishnan, Nature **121**, 501 (1928)



Some excitation is left in the system

Phonons in graphene



Raman scattering: photons ↔ electrons ↔ phonons intermediate states



Raman scattering: photons ↔ electrons ↔ phonons



Phonons in graphene



real linear combinations of A_1 phonons @ K and K'







Raman spectrum of graphene



no *D* peak (1 phonon @ *K*): momentum conservation, no impurities

Raman scattering probability

$$\sum_{\vec{q_1}+\ldots+\vec{q_n}=0} |\mathcal{M}(\vec{q_1},\ldots,\vec{q_n})|^2 2\pi \delta(\omega+\omega_{\vec{q_1}}+\ldots+\omega_{\vec{q_n}}-\omega_{in})$$

information about the final states (the phonon spectrum)

most suitable: G peak

Measure the shift of the G peak as a function of

- gate voltage
- magnetic field
- strain
- impurity concentration
- •

Effect of charging on the phonon frequency, probed by Raman scattering



J. Yan *et al.*, PRL **98**, 166802 (2007) see also S. Pisana *et al.*, Nature Materials **6**, 198 (2007)

Effect of strain on the G peak





G peak shift and splitting





Polarization dependence of the two components: $I_{G^-} \propto \sin^2(\theta_{in} + \theta_{out} + 3\varphi_s), \quad I_{G^+} \propto \cos^2(\theta_{in} + \theta_{out} + 3\varphi_s)$ possibility to determine the absolute crystal orientation! T. M. G. Mohiuddin *et al.*, PRB **79**, 205433 (2009)

Effect of a magnetic field on the phonon frequency, probed by Raman scattering

C. Faugeras et al., PRL 103, 186803 (2009)



Effect of a magnetic field on the phonon frequency, probed by Raman scattering

C. Faugeras et al., PRL 103, 186803 (2009)





Note: the splitting depends on the electronic occupations! avoided crossing between the phonon and an electronic inter-Landau-level excitation

T. Ando, J. Phys. Soc. Jpn. **76**, 024712 (2007) M. O. Görbig *et al.*, PRL **99**, 087402 (2007)

Raman scattering probability

$$\sum_{\vec{q_1}+\ldots+\vec{q_n}=0} |\mathcal{M}(\vec{q_1},\ldots,\vec{q_n})|^2 2\pi \delta(\omega + \omega_{\vec{q_1}} + \ldots + \omega_{\vec{q_n}} - \omega_{in})$$

information about
the intermediate states
(electrons and holes)
most suitable: 2D peak

Theory for semiconductors:

1960-70-ies



Dirac spectrum: *e-h* symmetry

additional symmetry brings additional physics

But: $m_e = m_h$ in InBr, InI

I. G. Lang et al., Sov. Phys. Solid State 32, 2000 (1990)

One-phonon Raman scattering

Photon wave vector

$$\frac{\omega_{in}}{c} \rightarrow 0$$

No disorder \rightarrow momentum conservation emit phonon with q = 0

$$\mathcal{M} = \sum_{1,2} \frac{\langle f | \hat{H}_{e-light} | 2 \rangle \langle 2 | \hat{H}_{e-ph} | 1 \rangle \langle 1 | \hat{H}_{e-light} | i \rangle}{(\omega_{in} - E_1 + 2i\gamma)(\omega_{in} - E_2 + 2i\gamma)}$$

At least one virtual state: energy denominator ~ ω_{ph}

Numerator in the Dirac approximation: $\hat{H}_{e-light} \propto \sigma_x, \sigma_y, \ \hat{H}_{e-ph} \propto \sigma_x, \sigma_y$ angular momentum ±1 $\longrightarrow \mathcal{M} = 0$ Trigonal warping must be included

+1 + 1 + 1 = +3 = 0 - cross-circular polarization



Two-phonon Raman scattering: $\vec{q}, -\vec{q}$



$$\mathcal{M} = \sum_{1,2,3} \frac{\langle f | \hat{H}_{e-light} | 3 \rangle \langle 3 | \hat{H}_{e-ph} | 2 \rangle \langle 2 | \hat{H}_{e-ph} | 1 \rangle \langle 1 | \hat{H}_{e-light} | i \rangle}{(\omega_{in} - E_1 + 2i\gamma)(\omega_{in} - E_2 + 2i\gamma)(\omega_{in} - E_3 + 2i\gamma)}$$

Dimensionless quantum efficiency of the 2D and 2D' peaks:

D. M. Basko, PRB 78, 125418 (2008)

mass density of the crystal

Three-phonon Raman scattering: $\vec{q_1} + \vec{q_2} + \vec{q_3} = 0$



1. Odd number of phonons: at least one virtual state

2. Even number of phonons: all denominators can vanish simultaneously

These are the consequences of the electron-hole symmetry

I. G. Lang et al., Sov. Phys. Solid State 32, 2000 (1990)

Raman matrix element in the real space



Green's functions admit a quasiclassical representation



The quasiclassical picture works both for real and virtual processes

Two-phonon process: backscattering

.....



The process looks allowed by momentum conservation but the electron and the hole cannot meet in space!

the angular spread is limited by the quantum uncertainty $|arphi-\pi|\sim \sqrt{\gamma/\omega_{in}}$

The phonon momentum is fixed:

.....

$$|\vec{q}| = |\vec{p}_0| + |\vec{p}_1| = \frac{\omega_{in} + \omega_{out}}{2v}$$

The two-phonon peak

(a) is narrow ($\omega_{\vec{q}} + \omega_{-\vec{q}}$ is not arbitrary) (b) depends on the excitation frequency $\frac{d\omega_{2D}}{d\omega_{\rm in}} = \frac{2v_{\rm ph}}{v} \approx 100 \frac{{\rm cm}^{-1}}{{\rm eV}}$

Vidano et al., Solid State. Comm. 39, 341 (1981)

Two-phonon process: polarization dependence



Two-phonon process: polarization dependence





Strong dependence on the **<u>relative</u>** angle between the polarizer and the analyzer

The scattered photon remembers about the polarization of the incident photon

Two-phonon process: magnetic field dependence



Electronic trajectories are circles:

 $ert ec q ert pprox 2 ert ec p ert \cos arphi$ instead of ert ec q ert pprox 2 ert ec p ert

 $\frac{d\omega_{\vec{q}}}{dq} > 0 \rightarrow \text{red shift of the peak}$ random length $\sim v/\gamma \rightarrow$ broadening

Two-phonon process: magnetic field dependence



Electronic trajectories are circles:

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 $\frac{d\omega_{\vec{q}}}{dq} > 0 \rightarrow \text{red shift of the peak}$ random length $\sim v/\gamma \rightarrow \text{broadening}$





C. Faugeras *et al.*, Phys. Rev. B **81**,155436 (2010)

The fit allows to extract $\gamma = 27 \text{ meV}$ for $\epsilon = 0.85 \text{ eV}$

Edge-assisted one-phonon Raman scattering



Energy mismatch ~ ω_{ph} = 0.17 eV

uncertainty principle

Lifetime of the virtual state ~ $1/\omega_{ph}$

Electron energy $~\epsilon \sim 1~{
m eV} \gg \omega_{ph}$



An ideal zigzag edge cannot scatter an electron from *K* to *K*'



Cançado et al., PRL 93, 247401 (2004)

Backscattering condition



perfect edge, oblique incidence: e and h will never meet



rough edge, oblique incidence: backscattering is possible

Dependence on the polarization



Matrix element for excitation of the *e*-*h* pair: $\mathcal{M} \propto [\vec{E} \times \vec{p}]_z \propto \cos \theta$

D peak intensity (unpolarized detector): $I_D \propto \cos^2 heta$

What happens when $\theta = \pi/2$ ($\vec{E} \perp$ edge)?

In all experiments a finite value is seen

Dependence on the polarization The most general form for unpolarized detection: $I_D(\theta) = I_{\max} \cos^2(\theta - \theta_{\max}) + I_{\min} \cos^2(\theta - \theta_{\min})$

1. Perfect armchair edge: $\theta_{\rm max} = 0$, $I_{\rm min}/I_{\rm max} \sim \omega_{\rm ph}^2/\omega_{\rm in}^2$ symmetry quantum uncertainty

2. Atomically rough edge: $\theta_{max} = 0$, $I_{min}/I_{max} \sim 1$ symmetry diffuse scattering

Basko, PRB 79, 205428 (2009)

Dependence on the polarization

3. A single armchair segment $d >> v/\omega_{in}$

Diffraction from the Huygens-Fresnel principle for the Dirac equation:

$$\psi(\vec{r}) = \int_{\text{boundary}} \vec{n} \cdot [iv \, G(\vec{r} - \vec{r}', \epsilon) \, \vec{\sigma} \, \psi(\vec{r}')] \, d\vec{r}'$$

 $heta_{
m max}$ along the segment,

$$rac{I_{\min}}{I_{\max}} \sim rac{v/\omega_{\mathrm{in}}}{d}$$

STM: Kobayashi *et al.,* PRB **71**, 193406 (2005)



Basko, PRB 79, 205428 (2009)

d ↓

Small $I_{min}/I_{max} \rightarrow$ good quality of the edge

Raman scattering on electronic excitations

Without magnetic field

With magnetic field





discrete peaks from inter-LL transitions

Selection rules in a magnetic field

co-circular polarization: $n \rightarrow n$ no angular momentum transfer cross-circular polarization: $n \rightarrow n \pm 2$ angular momentum transfer ± 2

monolayer: Kashuba and Fal'ko, PRB **80**, 241404 (2009) bilayer: Mucha-Krucziński, Kashuba, and Fal'ko, PRB **82**, 045405 (2010)

Raman scattering on electronic excitations

magneto-Raman spectrum of graphene on graphite from M. Kühne *et al.*, PRB **85**, 195406 (2012)





With magnetic field



discrete peaks from inter-LL transitions

Thank you for your attention!

Two-phonon Raman scattering: $\vec{q}, -\vec{q}$



Phonon momentum selected by the resonance condition:

$$\omega_{\rm ph}(\vec{q}) \approx \omega_{\rm ph}(\vec{K}) + v_{\rm ph} |\vec{q} - \vec{K}|$$

2D peak position depends on the excitation energy phonon group velocity, determined by the Kohn anomaly