

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

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

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

 a_1, a_2 - lattice vectors

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

quantum \int k in the first Brillouin zone $\begin{bmatrix} b & \text{band index} \end{bmatrix}$ numbers

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

 $\epsilon = \epsilon_{b\mathbf{k}}$ band structure

Crystal 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:

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

nearest-neighbor matrix element:

atomic level:

choose as

the origin

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

 $\gamma_0 \approx 3 \text{ eV}$

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)

unit transmission at normal incidence

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

 $\int \psi_{\mathbf{p},s}(\mathbf{r}) d^2\mathbf{r} = 0$

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 →

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

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$$
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$$

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

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

experimental access 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 \leftrightarrow electrons \leftrightarrow phonons intermediate states

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Phonons in graphene

real linear combinations of $A_{\overline{j}}$ 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
- \bullet ...

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 sin²(θ_{in} + θ_{out} + 3 φ_s), I_{G} \propto cos²(θ_{in} + θ_{out} + 3 φ_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

$$
\sum_{\vec{q}_1 + \dots + \vec{q}_n = 0} |\mathcal{M}(\vec{q}_1, \dots, \vec{q}_n)|^2 2\pi \delta(\omega + \omega_{\vec{q}_1} + \dots + \omega_{\vec{q}_n} - \omega_{in})
$$

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

$$
\frac{\partial in}{\partial c} \to 0
$$

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 ~ *ωph*

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 $\pm 1 \implies \mathcal{M} = 0$ 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:

$$
I_{2D} = \frac{\alpha^2 \lambda_K^2}{48} \frac{\omega_{in}^2}{c^2} \frac{v^2}{\gamma^2} \begin{bmatrix} I_{2D'} = \frac{\alpha^2 \lambda_\Gamma^2}{24} \frac{\omega_{in}^2}{c^2} \frac{v^2}{\gamma^2} \end{bmatrix} \lambda_\mu = \frac{F_\mu^2}{\rho v^2 \omega_\mu} \begin{array}{c} \text{dimensionless} \\ \text{e-ph coupling} \\ \text{strength} \end{array}
$$

mass density of the crystal D. M. Basko, PRB **78**, 125418 (2008)

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 $|\varphi - \pi| \sim \sqrt{\gamma/\omega_{in}}$

The phonon momentum is fixed: The two-phonon peak

,,,,,,,,,,,,,,,,,

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

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

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

Two-phonon process: polarization dependence

Two-phonon process: polarization dependence

Strong dependence on the **relative** 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:

 $|\vec{q}| \approx 2|\vec{p}| \cos \varphi$ instead of $|\vec{q}| \approx 2|\vec{p}|$

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

Two-phonon process: magnetic field dependence

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magnetic field (T)

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

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

Edge-assisted one-phonon Raman scattering

Energy mismatch $\sim \omega_{ph}$ = 0.17 eV

uncertainty principle

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

Electron energy $\epsilon \sim 1$ 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): $I_D \propto \cos^2 \theta$

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: $I_D(\theta) = I_{\text{max}} \cos^2(\theta - \theta_{\text{max}}) + I_{\text{min}} \cos^2(\theta - \theta_{\text{min}})$

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

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

Basko, PRB **79**, 205428 (2009)

Dependence on the polarization

3. A single armchair segment *d* >> *v/ω*_{in}

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

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

 $\theta_{\rm max}$ along the segment,

$$
\frac{I_{\rm min}}{I_{\rm max}}\sim \frac{v/\omega_{\rm in}}{d}
$$

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

Basko, PRB **79**, 205428 (2009)

d

Small *I min I max* good quality of the edge

Raman scattering on electronic excitations

Without magnetic field With magnetic field

discrete peaks from inter-LL transitions

spectrum

Selection rules in a magnetic field

co-circular polarization: $n \to n$ no angular momentum transfer

cross-circular polarization: $n \to n \pm 2$ 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

see also Garcia-Flores *et al.*, PRB **79**, 113105 (2009) Faugeras *et al*., PRL **107**, 036807 (2011) Kim *et al.*, PRB **85**, 121403(R) (2012)

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