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Raman scattering in graphene: what can we learn from the peak intensities?

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Collaboration: I. L. Aleiner (*Columbia*)

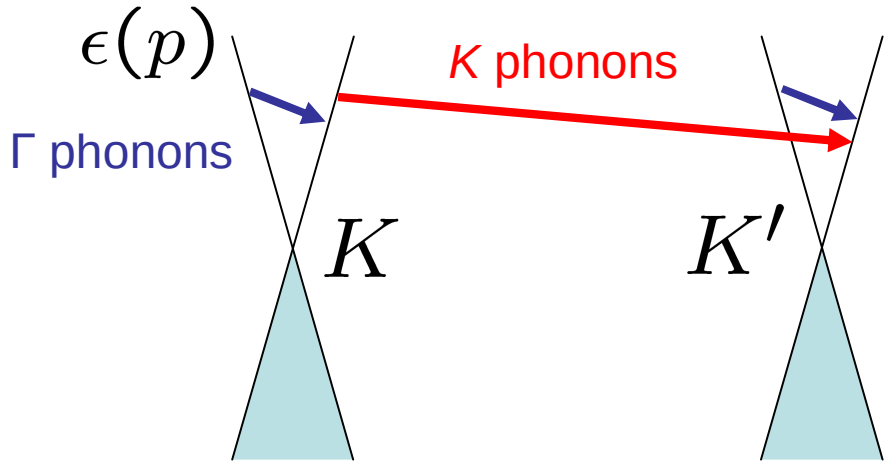
S. Piscanec, A. Ferrari (*Cambridge*)

Discussions: F. Mauri (*Paris 6*), J. Yan (*Columbia*)

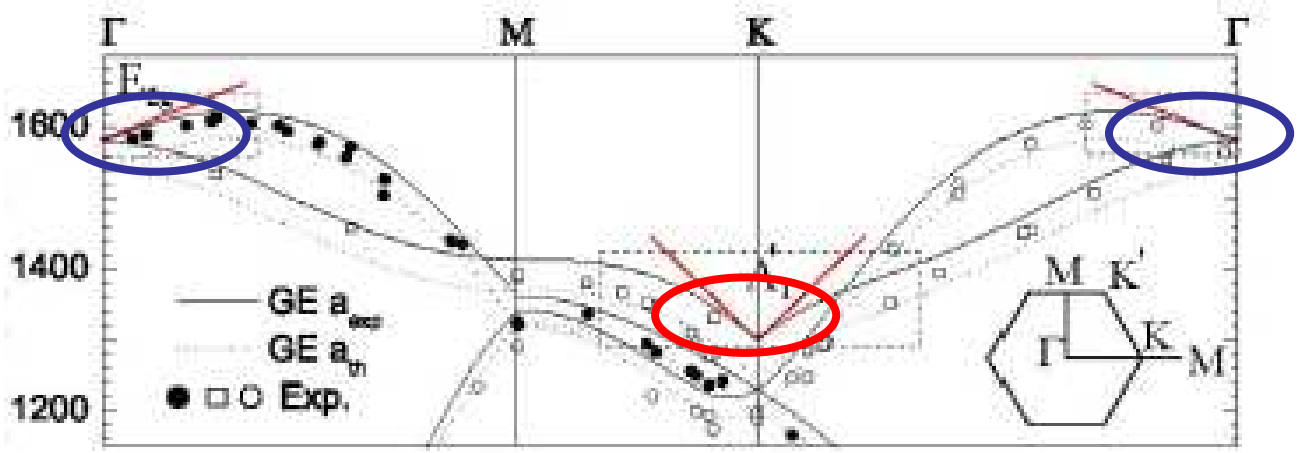
Raman scattering: photons ↔ electrons ↔ phonons

intermediate states

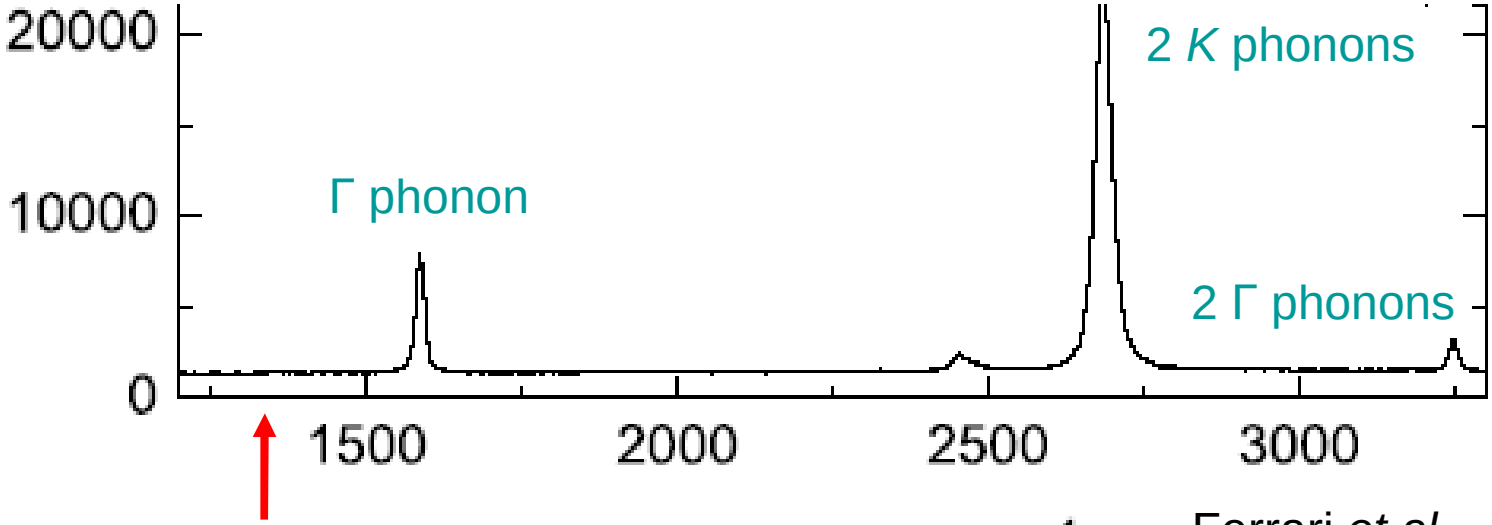
Electron spectrum:
two Dirac cones



phonon
spectrum

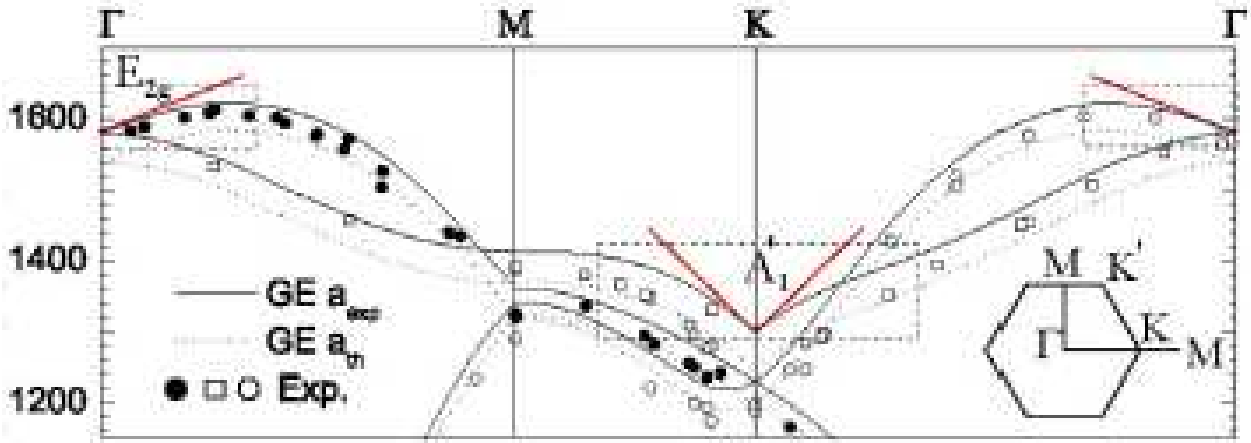


DFT calculation: Piscanec *et al.,* PRL **93**, 185503 (2004)
Inelastic X-ray scatt.: Maultzsch *et al*., PRL **92**, 075501 (2004)

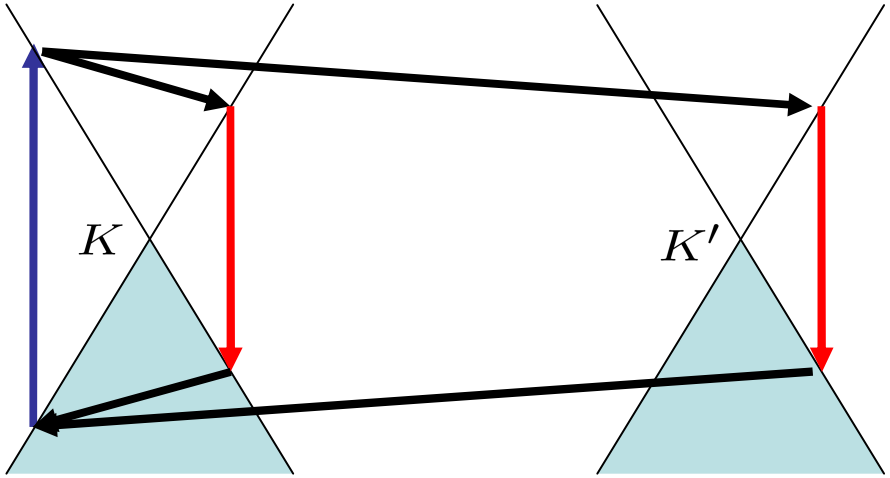


no *K* phonon
momentum conservation
no impurities

Ferrari *et al.*
PRL **97,** 187401 (2006)

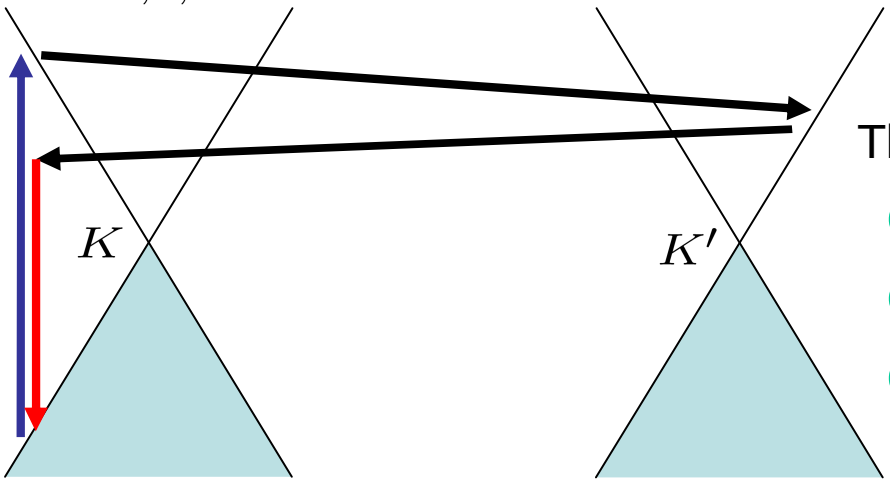


Two-phonon Raman scattering: $\vec{q}, -\vec{q}$



Full resonance: all intermediate states are real →
the amplitude is determined by $i\gamma$

$$A \sim \sum_{1,2,3} \frac{\langle 0|\hat{H}_{e-light}|1\rangle\langle 1|\hat{H}_{e-phonon}|2\rangle\langle 2|\hat{H}_{e-phonon}|3\rangle\langle 3|\hat{H}_{e-light}|0\rangle}{(\omega_{exc} - E_1 + i\gamma)(\omega_{exc} - E_2 + i\gamma)(\omega_{exc} - E_3 + i\gamma)}$$



Double resonance

Thomsen & Reich, PRL 85, 5214 (2000)

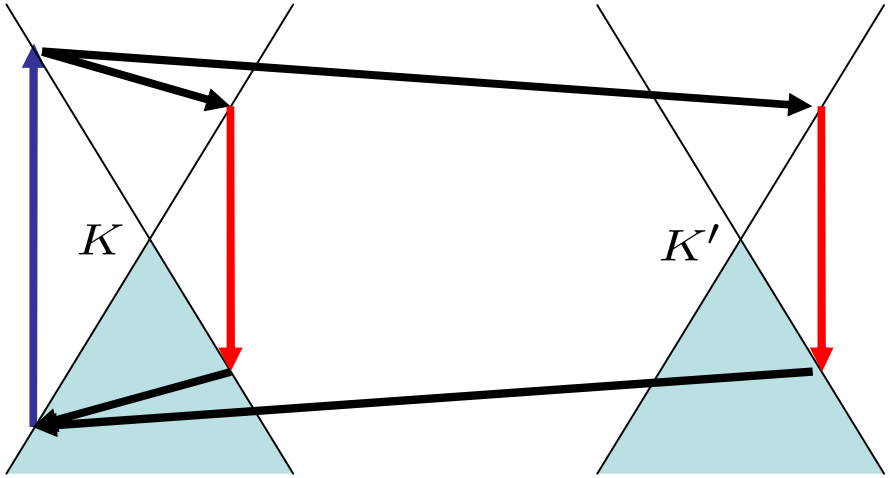
one virtual state

energy mismatch $\sim \omega_{ph}$

contribution smaller by

$\sim (\gamma/\omega_{ph})^2$

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



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$$I_{2\Gamma} = \frac{(e^2/c)^2}{48}\frac{v^2}{c^2}\left(\lambda_\Gamma \frac{\omega_{exc}}{\gamma}\right)^2$$

$$I_{2K} = \frac{(e^2/c)^2}{24}\frac{v^2}{c^2}\left(\lambda_K \frac{\omega_{exc}}{\gamma}\right)^2$$

$$\lambda_\mu = \frac{F_\mu^2}{\rho v^2 \omega_\mu}$$

dimensionless coupling strength

ρ mass density of the crystal

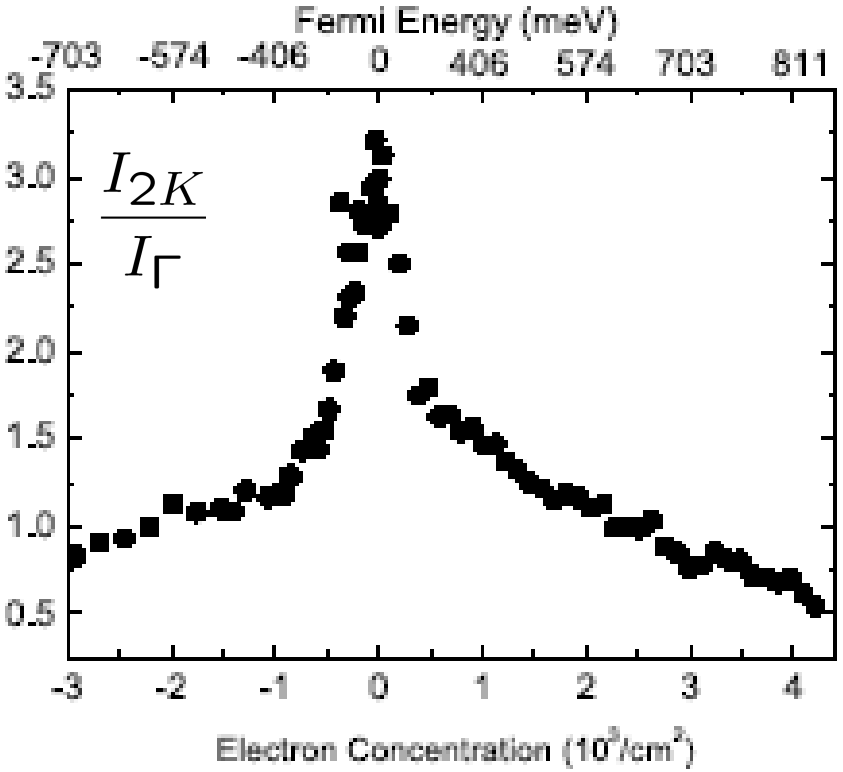
ARPES people prefer

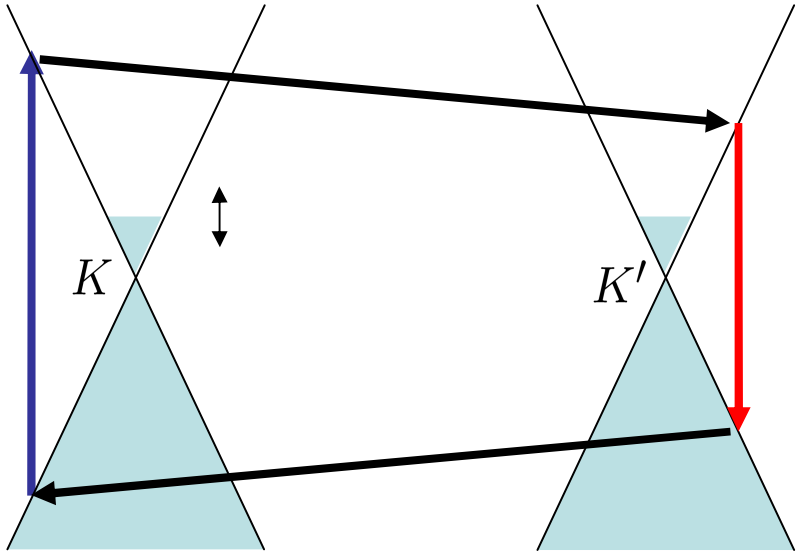
$$\frac{F_\mu^2}{2\pi\rho v^2 \omega_\mu} \ln\frac{W}{\omega_\mu}$$

Basko, PRB **76**, 081405(R) (2007)
PRB (in press), arXiv:0804.3304

Measured intensity of the 2*K* phonon peak (2700 cm^{-1})

Das *et al*., Nature Nanotechnology. **3**, 210 (2008)





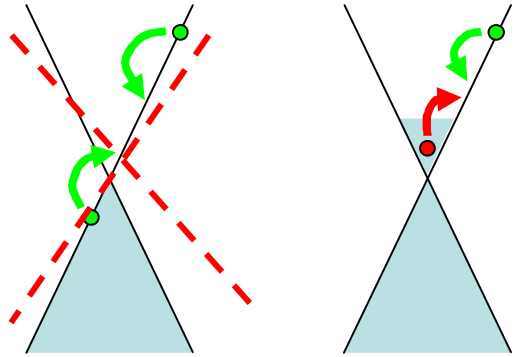
this shows the dependence of 1/γ on doping

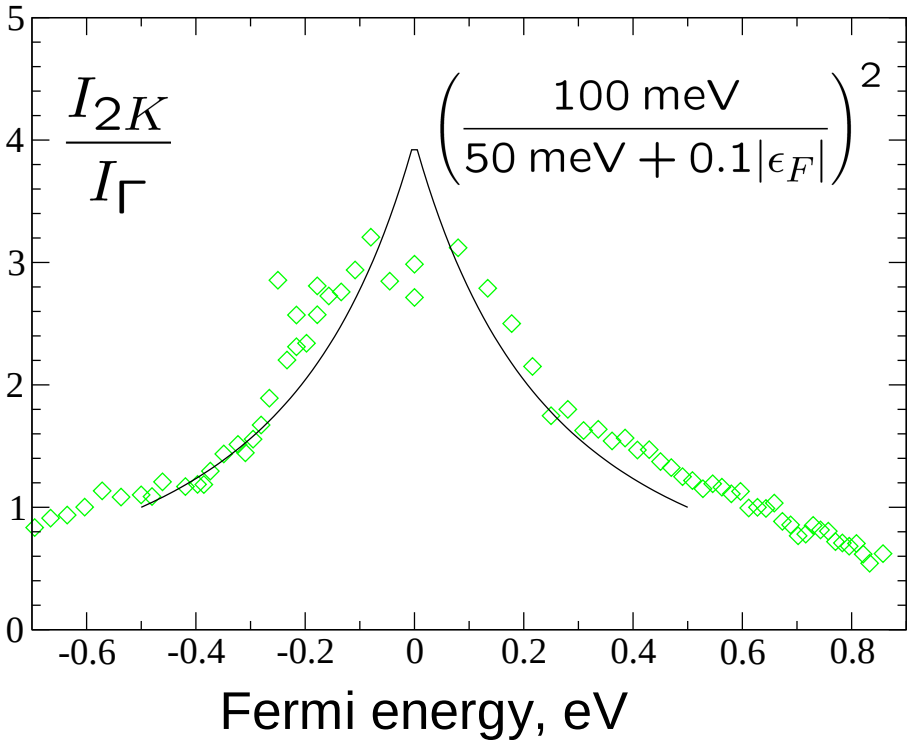
assuming independence of I_Γ (1580 cm^{-1})

Electron-electron scattering

Undoped case: no phase volume to conserve energy and momentum

González, Guinea, and Vozmediano
PRL **77**, 3589 (1996)





Basko, Piscanec and Ferrari (in preparation)

For $\epsilon \gg |\epsilon_F|$

$$\gamma_{e-e} \approx (0.08 - 0.1)|\epsilon_F|$$

calculation analogous to
Hwang, Hu, and Das Sarma,
PRB **76**, 115434 (2007)

$$\gamma_{e-ph} = (\lambda_\Gamma + \lambda_K)\epsilon/4$$

$$\lambda_\Gamma + \lambda_K \approx 0.2$$

What do we know about the coupling constants?

1. Simple tight-binding model: $\lambda_K / \lambda_\Gamma = \omega_\Gamma/\omega_K \approx 1.2$

2. DFT calculation [Piscanec *et al.*, PRL **93**, 185503 (2004)]:
   $\lambda_\Gamma \approx 0.028$, $\lambda_K \approx 0.033$, $\lambda_K/\lambda_\Gamma \approx 1.2$

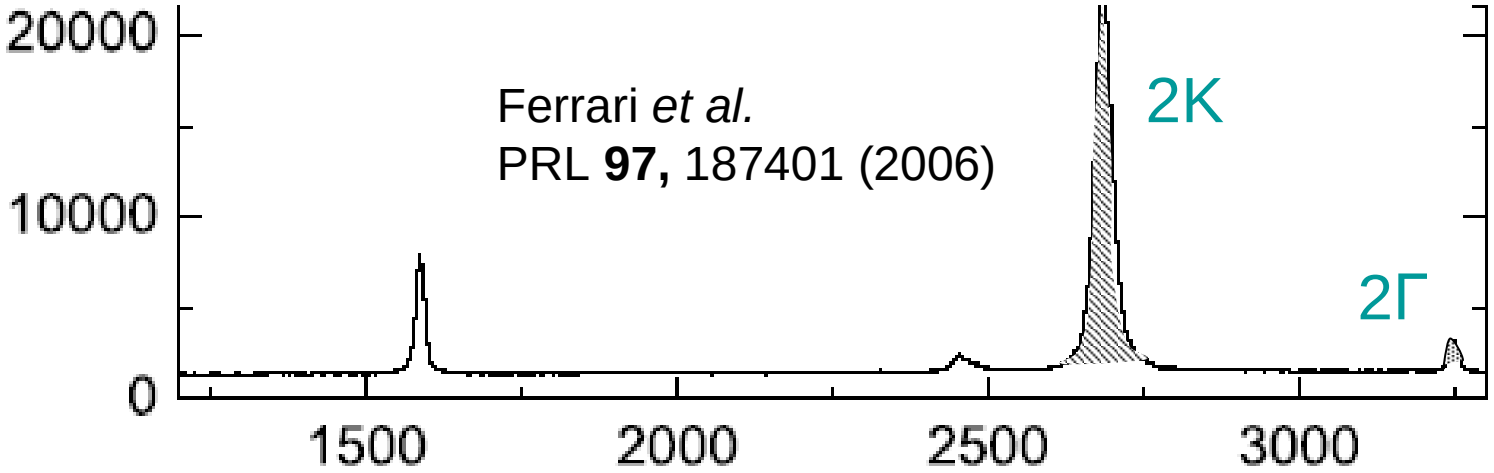
3. Measurements of the phonon dispersion (Kohn anomalies)
   [Maultzsch *et al*., PRL **92**, 075501 (2004)]:
   $\Delta\omega_\Gamma(q)=(\lambda_\Gamma/8)vq \rightarrow \lambda_\Gamma \approx 0.024$

4. Measurements of the doping dependence of the Γ phonon
   frequency [Yan *et al*., PRL **98**, 166802 (2007);
   Pisana *et al*., Nature Materials **6**, 198 (2007)]:
   $\Delta\omega_\Gamma=(\lambda_\Gamma/2\pi)|\varepsilon_F| \rightarrow \lambda_\Gamma \approx 0.034, 0.027$

5. Electron dispersion from ARPES
   [Bostwick *et al*, Nature Physics **3**, 36 (2007)]:
   $\lambda_K+\lambda_\Gamma \approx 0.2–0.3$

λ_K seems to be underestimated

Ratio of integrated intensities



theory: $\frac{I_{2K}}{I_{2\Gamma}} = 2\left(\frac{\lambda_K}{\lambda_\Gamma}\right)^2$ Basko, PRB (in press), arXiv:0804.3304

expt: $\frac{I_{2K}}{I_{2\Gamma}} \approx 20 \quad \Rightarrow \quad \frac{\lambda_K}{\lambda_\Gamma} \approx 3$ DFT: $\frac{\lambda_K}{\lambda_\Gamma} \approx 1.2$

Why such disagreement?

Coulomb interaction in graphene

(recall the talk by I. Aleiner)

$$V_0(\vec{q}) = \frac{2\pi e^2}{\varepsilon |\vec{q}|}$$

dielectric screening by substrate

Perturbation theory → expansion in $g = \frac{\pi}{2\varepsilon}\frac{e^2}{v} \approx \frac{3.4}{\varepsilon}$

no good

$$V(\vec{q},\omega) = \frac{2\pi e^2}{\varepsilon |\vec{q}|} \frac{\sqrt{(vq)^2 - \omega^2}}{gvq + \sqrt{(vq)^2 - \omega^2}}$$

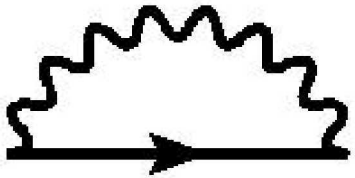
Collecting the RPA series → expansion in $\frac{1}{\mathcal{N}} = \frac{1}{2 \cdot 2}$ ok

spin degeneracy

valley degeneracy

Logarithmic renormalizations

Abrikosov, Beneslavskii, JETP **32**, 699 (1971)
Gonzàlez, Guinea, Vozmediano, Nucl. Phys. B **424**, 595 (1994);
Phys. Rev. B **59**, R2474 (1999)

Exchange self-energy: $\Sigma(\vec{p},\epsilon) =$ 

Correction to the velocity:

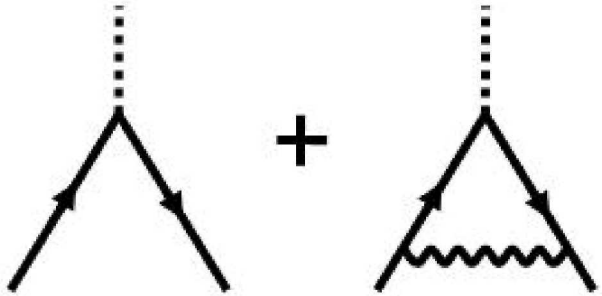
$$\frac{\delta v}{v} = \frac{8}{\pi^2 \mathcal{N}} \left[1 - \frac{\pi}{2g} + \frac{\arccos g}{g\sqrt{1-g^2}} \right] \ln \frac{W}{\epsilon}$$

upper cutoff (bandwidth)

small parameter

The large logarithm
– comes from all length scales
– missed by LDA or GGA

Renormalization of electron-phonon coupling constants:

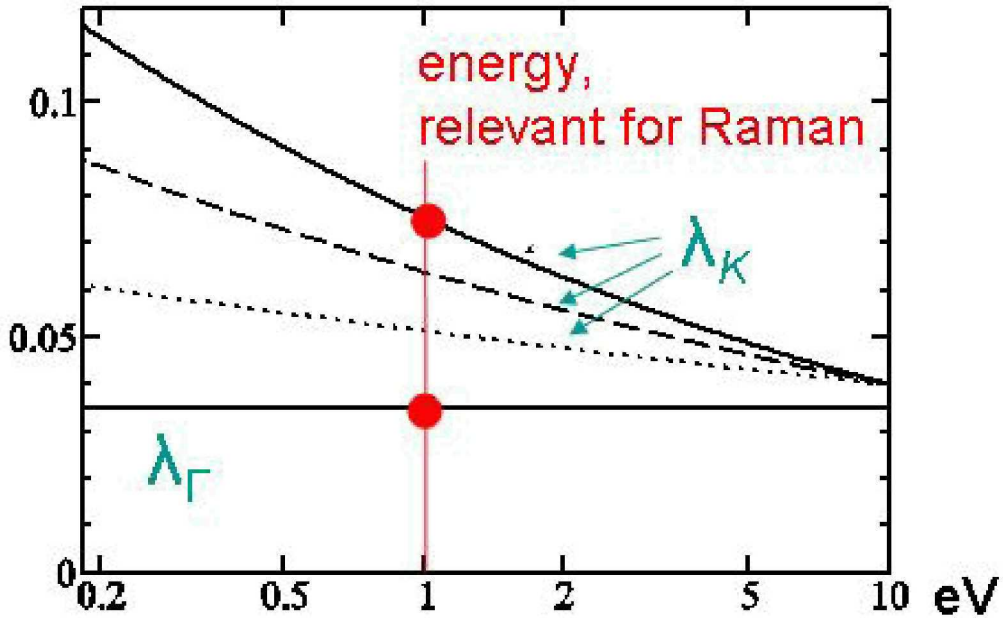


$$\frac{1}{\lambda_K}\frac{d\lambda_K}{d\ln(1/\epsilon)} = \frac{16}{\pi^2\mathcal{N}}\left[1 - \frac{\pi}{2g} + \frac{\arccos g}{g\sqrt{1-g^2}}\right]$$

Basko and Aleiner, PRB **77**, 041409(R) (2008)

$$\frac{1}{\lambda_\Gamma}\frac{d\lambda_\Gamma}{d\ln(1/\epsilon)} = 0$$

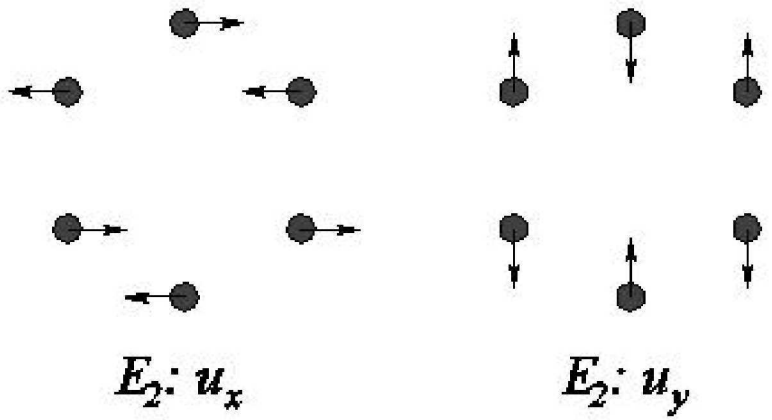
1. $\lambda_\Gamma(0.2\,\text{eV}) \approx 0.035$
   (experiment)
2. $F_\Gamma(10\,\text{eV}) = F_K(10\,\text{eV})$
   (DFT calculation)
3. $g(10\,\text{eV}) = 3.4?\ 1.5?\ 0.5?$
   (uncertainty in the background screening)



$$\frac{\lambda_K(1\,\text{eV})}{\lambda_\Gamma(1\,\text{eV})} \approx \begin{cases} 2.5 & \text{(RG)} \\ 3 & \text{(Raman)} \end{cases}$$

Gauge invariance

$$\frac{d\lambda_\Gamma}{d\ln} = 0$$ is protected by the gauge invariance



Γ-phonon displacements enter the hamiltonian in the same way as a vector potential:

$$H = v\vec{\sigma}\cdot\left(-i\vec{\nabla} - e\vec{A}\right) + F_\Gamma\vec{\sigma}\cdot\vec{u}$$

$$\frac{\tilde{F}_\Gamma}{\tilde{v}} = \frac{F_\Gamma}{v} \quad \Rightarrow \quad \lambda_\Gamma = \frac{F_\Gamma^2}{v^2\rho\omega_\Gamma} = \text{const}$$

Conclusions

- Fully resonant Raman scattering is sensitive to the dynamics of the photo-excited e-h pair [Basko, PRB (2007), PRB (in press)]

- From the ratio of two-phonon peak intensities one can extract the ratio of the electron-phonon coupling constants $\lambda_K / \lambda_\Gamma \approx 3$

- This ratio is explained by renormalization of electron-phonon coupling constants by the Coulomb interaction, missed by local-density DFT calculations [Basko & Aleiner, PRB (2008)]

P.S. Ab initio GW instead of DFT_{LDA} or DFT_{GGA}: λ_Γ unchanged, λ_K twice greater

Lazzeri, Ataccalite, Wirtz & Mauri, arXiv: 0808.2285