### **RAMAN-SPEKTROSZKÓPIA**

### SZÉN NANOSZERKEZETEKBEN

### GRAFÉN TÉLI ISKOLA

2011. február 3.

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# VÁZLAT

- Bevezetés a Raman-spektroszkópiáról
- G sáv grafitban (grafénban)
- D sáv grafitban (grafénban)
- **D**\* (= **G**'= 2D) sáv grafitban (grafénban)



#### Sir Chandrasekhara Venkata Raman

(7 November 1888 – 21 November 1970)

#### The Nobel Prize in Physics 1930

"for his work on the scattering of light and for the discovery of the effect named after him". JOURNAL OF RAMAN SPECTROSCOPY J. Raman Spectrosc. 2008; **39**: 316–321 Published online in Wiley InterScience (www.interscience.wiley.com) DOI: 10.1002/jrs.1948

Preface

#### 80<sup>TH</sup> Anniversary of the discovery of the Raman Effect: a celebration

#### DISCOVERY

Eighty years ago on 31 March 1928, a letter dated 16 February was published in Nature by C. V. Raman (Fig. 1) and K. S. Krishnan with the title 'A New Type of Secondary Radiation'. This letter, which is reproduced in Fig. 2, was the first account in the scientific literature of what soon became known as the Raman Effect. The experiments reported in this letter were based on the use of complementary light filters to detect the presence of modified scattered radiation using focused sunlight as an excitation source and the eye as a detector. Raman and his co-workers soon improved on this rather basic experimental procedure by using a spectroscope to examine the scattered radiation. The first Raman spectrum was reportedly obtained on 28 February 1928. On 29 February the Associated Press of India gave the first newspaper report under the heading 'New Theory of Radiation - Prof. Raman's Discovery'; and on 1 March 1928, The Statesman, an English language daily of Calcutta, carried an article with the title 'Scattering of Light by Atoms - New Phenomenon - Calcutta Professor's Discovery' which is reproduced in Fig. 3. The paragraph heading 'Two colours from one' is attractive and accurate journalism, but there are several palpable scientific errors in the text. It has to be recognised that Raman's earliest papers were couched in rather general terms and it was only in a letter submitted to Nature on 22 March and published on 5 May that a spectrum was presented, although spectra were included in a lecture by Raman in Bangalore on 16 March.

Shortly after the publication of Raman and Krishnan's letter in *Nature*, Landsberg and Mandelstam in Russia reported the observation of light scattering with change of frequency in quartz in a paper in *Die Naturwissenschaften* published on 13 July 1928 and reproduced here in Fig. 4. This paper was submitted on 6 May, one day after the official publication date of Raman and Krishnan's definitive paper. Landsberg and Mandelstam could not have had any information in Moscow about this paper but they did refer to Raman's earlier publications saying that they were unable to decide whether there was any connection with their work because Raman's description was too brief and lacking in detail. The two discoveries must be regarded as quite independent.

Although quantum theory was still in its infancy in the nineteen twenties, the Raman Effect had been predicted by quantum mechanics in two classic papers, one by Smekal<sup>1</sup> published in 1923 and one by Kramers and Heisenberg<sup>2</sup> in 1925.



JRS

Figure 1. C. V. Raman

#### DEVELOPMENT

Raman's discovery attracted immediate international interest and was followed up very quickly in many countries. In France Y. Rocard,<sup>3</sup> and separately J. Cabannes<sup>4</sup> published papers in *Comptes Rendus* on the Raman Effect in April 1928. In the United States R. W. Wood<sup>3</sup> quickly followed up Raman's experiments and sent a letter to *Nature* by cable saying that he had verified Raman's work in every particular and describing it as a very beautiful discovery. The wording of Wood's letter is rather awkward because in his cable prepositions and articles were omitted to save money!

In Germany the journal *Die Naturwissenschaften* for 3 August 1928 contained the first review article on the new phenomenon. The author was P. Pringsheim,<sup>6</sup> who proposed that the new effect should be called the Raman Effect.

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#### A New Type of Secondary Radiation.

IF we assume that the X-ray scattering of the 'unmodified ' type observed by Prof. Compton corresponds to the normal or average state of the atoms and molecules, while the 'modified' scattering of altered wave-length corresponds to their fluctuations from that state, it would follow that we should expect also in the case of ordinary light two types of scattering, one determined by the normal optical properties of the atoms or molecules, and another representing the effect of their fluctuations from their normal state. It accordingly becomes necessary to test whether this is actually the case. The experiments we have made have confirmed this anticipation, and shown that in every case in which light is scattered by the molecules in dust-free liquids or gases, the diffuse radiation of the ordinary kind, having the same wave-length as the incident beam, is accompanied by a modified scattered radiation of degraded frequency.

The new type of light scattering discovered by us naturally requires very powerful illumination for its observation. In our experiments, a beam of sunlight was converged successively by a telescope objective of 18 cm. aperture and 230 cm. focal length, and by a second lens of 5 cm. focal length. At the focus of the second lens was placed the scattering material, which is either a liquid (carefully purified by repeated distillation in vacuo) or its dust-free vapour. To detect the presence of a modified scattered radiation, the method of complementary light-filters was used. A blue-violet filter, when coupled with a yellow-green filter and placed in the incident light, completely extinguished the track of the light through the liquid or vapour. The reappearance of the track when the yellow filter is transferred to a place between it and the observer's eye is proof of the existence of a modified scattered radiation. Spectroscopic confirmation is also available.

Some sixty different common liquids have been examined in this way, and every one of them showed the effect in greater or less degree. That the effect is a true scattering and not a fluorescence is indicated in the first place by its feebleness in comparison with the ordinary scattering, and secondly by its polarisation, which is in many cases quite strong and comparable with the polarisation of the ordinary scattering. The investigation is naturally much more difficult in the case of gases and vapours, owing to the excessive feebleness of the effect. Nevertheless, when the vapour is of sufficient density, for example with ether or amylene, the modified scattering is readily demonstrable.

C. V. RAMAN. K. S. KRISHNAN.

210 Bowbazar Street, Calcutta, India, Feb. 16.

Fig. 1.1 (a) Facsimile of paper by Raman and Krishnan (published 31 March 1928 in *Nature*, vol. 121, page 501)

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**Figure 2.** Spectra of scattered light in quartz (double magnification): 1 -reference spectrum, 2, 3 - scattered light spectra obtained at 20 °C and 220 °C (105 h exposure);  $\alpha$  - red satellites;  $\beta$  - violet satellites.





D.A. Long: Raman spectroscopy

$$\frac{Raman - vz ords}{Varribus kep}$$

$$P(\omega) = \left[ d_{0} + d_{n} \cdot \cos(\Omega t) \right] \cdot E_{0} \cos(\omega t)$$

$$\stackrel{\uparrow}{=} \frac{d_{0}}{da} \frac{ugelmatten resid}{ugelmatten resid}$$

$$\Rightarrow P = d_{0} E_{0} \cos(\omega t) + d_{n} \frac{E_{0}}{2} \cdot \left\{ \cos((\omega + \Omega)t) + \cos((\omega - \Omega)t) \right\}$$

$$ugelmas residen 
$$kventum mechanikai kep$$

$$tw \rightarrow \frac{1}{2} \rightarrow t(\omega - \Omega) \qquad tw \rightarrow \frac{1}{2} + h(\omega + \Omega)$$

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$$tw \rightarrow \frac{1}{2} \rightarrow t = \frac{1}{2} + \frac{1}{2}$$$$



Fig. 1.4 Diagrammatic representation of Raman spectra for different states of matter: (a) gas under high resolution showing resolved Stokes and anti-Stokes rotation and vibration-rotation lines; (b) gas under low resolution showing unresolved Stokes and anti-Stokes rotation and vibration-rotation bands; (c) liquid, showing Stokes and anti-Stokes vibration bands; and (d) crystal, showing splitting of Stokes and anti-Stokes vibration bands and Stokes and anti-Stokes libration bands S t o k e s

D.A. Long: Raman spectroscopy

a

n

S

0

k

e

S



**Stokes:**  $\omega_2 = \omega_1 - \omega$ 

(Anti-Stokes:  $\omega_2 = \omega_1 + \omega$ )

$$K_{2f,10} = \sum_{a,b} \frac{\langle \omega_2, \omega, 0 | H_{eR,\rho} | 0, \omega, b \rangle \langle 0, \omega, b | H_{ep} | 0, 0, a \rangle \langle 0, 0, a | H_{eR,\sigma} | \omega_1, 0, 0 \rangle}{(E_1 - E_{ai}^e - i\gamma)(E_1 - \hbar\omega - E_{bi}^e - i\gamma)}$$









Comparison of Raman spectra at 514 nm for bulk graphite and graphene. They are scaled to have similar height of the D\* peak at 2700 cm<sup>-1</sup>.



### Egyfalú szén nanocsövek keverékének Raman-spektruma





# G-band (graphene)

## pressure dependence



Mohiuddin et al, Physical Review B 79, 205433 (2009)







(a) G and (b) 2D peaks as a function of uniaxial strain. The spectra are measured with incident light polarized along the strain direction, collecting the scattered light with no analyzer. Note that the doubly degenerate G peak splits in two subbands  $G^+$  and  $G^-$ , while this does not happen for the 2D peak. The strains, ranging from 0 to 0.8%, are indicated on the right side of the spectra.

### NANOLETTERS

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### Probing Strain-Induced Electronic Structure Change in Graphene by Raman Spectroscopy

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**ABSTRACT** Two-phonon Raman scattering in graphitic materials provides a distinctive approach to probing the material's electronic structure through the spectroscopy of phonons. Here we report studies of Raman scattering of the two-dimensional mode of single-layer graphene under uniaxial stress and which implicates two types of modification of the low-energy electronic structure of graphene: a deformation of the Dirac cone and its displacement away from the K point.

KEYWORDS Graphene, Raman spectroscopy, strain, electronic structure

DOI: 10.1021/nl102123c | Nano Lett. 2010, 10, 4074-4079





$$I_{G-} \propto \sin^2(\theta_{in} + \theta_{out} + 3\phi_s), \quad I_{G+} \propto \cos^2(\theta_{in} + \theta_{out} + 3\phi_s)$$

Mohiuddin et al, Physical Review B 79, 205433 (2009)



Mohiuddin et al, Physical Review B 79, 205433 (2009)



# D-band , D\*-band in graphite (graphene)

### **DOUBLE RESONANCE**



### **D** band in graphite

• graphite single crystal

• stress-annealed pyrolite graphite

• commercial graphite

• activated charcoal

F.Tuinstra and J.L.Koenig, J. of Chem. Phys. 53, 1126 (1970)

### A grafit D-sávjának diszperziója E<sub>laser</sub> függvényében



 $\partial \omega_{\rm D} / \partial E_{\rm laser} \approx 50 \ {\rm cm}^{-1}/{\rm eV}$ 

I. Pócsik, M. Hundhausen, M. Koós and L. Ley, J. of Non-Crystalline Solids 227-230B, 1083 (1998)





Valence force field MO/8

C.Mapelli et al. PRB 60 12710 (1999)





J.Maultzsch et al, PRL 92, 075501, (2004)

### **Disorder induced resonant Raman scattering**



### **Raman amplitudes for the Feynman diagrams**

$$K = \sum_{a,b,c} \frac{M}{(E_{las,in}^{S,AS} - E_{el}^{a} - i\gamma)(E_{las,in}^{S,AS} - E_{el}^{b} - i\gamma)(E_{las,in}^{S,AS} - E_{el}^{c} \mp \hbar \omega_{q} - i\gamma)}$$
  
anti Stokes  
$$E_{a,l}^{a} = \varepsilon^{\text{conduction}}(k) - \varepsilon^{\text{valence}}(k)$$
$$E_{a,l}^{b} = \varepsilon^{\text{conduction}}(k') - \varepsilon^{\text{valence}}(k)$$

**Double resonance**: <u>two</u> of the denominators are zero at the same time

(C.Thomsen and S.Reich, PRL 85, 5214, 2000 : for graphite)







### Relevant 4<sup>th</sup> order Feynman diagrams for Stokes and antiStokes processes



phonon scattering

### **Raman amplitudes for the Feynman diagrams**

$$K^{I,III} = \sum_{a,b,c} \frac{M}{(E_{las,in}^{S,AS} - E_{el}^{a} - i\gamma)(E_{las,in}^{S,AS} - E_{el}^{b} - i\gamma)(E_{las,in}^{S,AS} - E_{el}^{c} + \hbar\omega_{q} - i\gamma)}$$

$$K^{II,IV} = \sum_{a,b,c} \frac{M}{(E_{las,in}^{S,AS} - E_{el}^{a} - i\gamma)(E_{las,in}^{S,AS} - E_{el}^{b} + \hbar\omega_{q} - i\gamma)(E_{las,in}^{S,AS} - E_{el}^{c} + \hbar\omega_{q} - i\gamma)}$$

$$E^{a}_{el} = \varepsilon^{\text{conduction}}(\mathbf{k}) - \varepsilon^{\text{valence}}(\mathbf{k}), \qquad E^{b}_{el} = \varepsilon^{\text{conduction}}(\mathbf{k}') - \varepsilon^{\text{valence}}(\mathbf{k}), \quad \text{etc}$$

**Double resonance**: <u>two</u> of the denominators are zero at the same time

(C.Thomsen and S.Reich, PRL 85, 5214, 2000 : for graphite)







#### **Calculated D band of graphene**



#### Simple qualitative interpretation of the maxima 1, 2 and 3







(A) Optical micrograph of the flake used to study a single edge, indicated by the arrow;

(B) (B) flake containing two edges at 90°;

(C,D) optical and AFM images of a flake with two edges at an angle of 150°.



Raman spectra inside the sample (black) and at the edge (red) at 514 nm.

A strong D peak is visible at the edge. Note the log scale for the intensity and that the peak at  $\sim$ 1450 cm<sup>-1</sup> is the third order of the silicon substrate.

### Micro-Raman spectra from graphite edges



D band is strong for armchair edge and weak for zigzag edge





Real space representation of the scattering process for the D peak in the vicinity of an edge. The wavy lines represent the incident photon generating an electronhole pair, and the scattered photon produced from the pair recombination. The solid black arrows are the quasi-classical trajectories of electron and hole. The dashed arrow is the emitted phonon.

(a) Backscattering off an ordered edge is possible only at normal incidence (up to the quantum diffraction correction to the quasiclassical approximation, of order  $(hv_{ph}/\varepsilon)^{1/2} \ll 1$ ).

(b) For oblique incidence on an ordered edge, reflection is specular, so the electron and hole will not meet at the same point and will not recombine radiatively. (c) For a disordered edge backscattering is possible even at oblique incidence. The typical distance *x* from the edge is determined by the lifetime of the virtual electron-hole pair,  $\sim v/v_{ph}$ .



Casiraghi et al, Nano Lett 9, 1433 (2009)

The wavevector direction of electrons back-scattered by a zigzag, or armchair edge  $(d_Z, d_A)$  is perpendicular to the edge.



Raman can tell us if the edge has an armchair or zigzag structure















(a) G and (b) 2D peaks as a function of uniaxial strain. The spectra are measured with incident light polarized along the strain direction, collecting the scattered light with no analyzer. Note that the doubly degenerate G peak splits in two subbands  $G^+$  and  $G^-$ , while this does not happen for the 2D peak. The strains, ranging from 0 to 0.8%, are indicated on the right side of the spectra.





Mohr et al, Physical Review B 80, 2054310(2009)



(a) electronic band structure

### and

(b) phonon dispersion curves of unstrained and  $\epsilon$ =0.02 strained graphene along the  $\theta$ =0°-direction.

The corresponding paths in the Brillouin zone are indicated. A closeup for the electronic bands along KM is shown in the inset of (a).

Mohr et al, Physical Review B 80, 2054310(2009)

#### Simple qualitative interpretation of the maxima 1, 2 and 3







(a) TEM of suspended graphene. The grid is also visible in optical microscopy.
(b) High-resolution image of a folded edge of a single layer and
(c) a wrinkle within the layer.
(d) Folded edge of a two layer, and
(e) internal foldings of the two layer. The amorphous contrast on the sheets is most likely due to hydrocarbon adsorbates on the samples that were cracked by the electron beam.

(f) Electron diffraction pattern for close to normal incidence from single layer and

(g) from two layers.

Weak diffraction peaks from the supporting metal structure are also present.

(h) Intensity profile plot along the line indicated by the arrows in (f),(g). The relative intensities of the spots in the two layer are consistent only with *A-B* (and not *A-A*) stacking. Scale bars: (a) 500 nm; (b–e) 2 nm.

A.C.Ferrari et al, PRL 97, 187401 (2006)



Comparison of Raman spectra at 514 nm for bulk graphite and graphene. They are scaled to have similar height of the D\* peak at 2700 cm<sup>-1</sup>.



(b) Evolution of the spectra at 514 nm with the number of layers.

(c) Evolution of the Raman spectra at 633 nm with the number of layers.

(d) Comparison of the D band at 514 nm at the edge of bulk graphite and single layer graphene. The fit of the D1 and D2 components of the D band of bulk graphite is shown.

(e) The four components of the 2D band in 2 layer graphene at 514 and 633 nm.

A.C.Ferrari et al, PRL 97, 187401 (2006)



A.C.Ferrari et al, PRL 97, 187401 (2006)

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