XIIth International GeoRaman Conference

VIIIth International Siberian Early Career GeoScientists Conference

June 14–15, 2016, Novosibirsk, Russia

RAMAN STUDY OF MECHANICAL STRESSES IN CRYSTALS

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NANOFER

Ural Federal University named after the first President of Russia B.N.Yeltsin

Institute of Natural Sciences

June 14, 2016

Mechanical stresses in crystals

- External forces lead to **crystal strains** – variations of its shape and volume

- The simplest strains
  - Tension and compression
  - Relative elongation

$$\varepsilon = \frac{l - l_0}{l_0}$$

l_0 – length before tension
l – length after tension

- Elastic forces
  - **Mechanical stress**
  - Proportional to strain
  - Elastic constants
  - Compliance constants

$$\sigma = \frac{F}{S} = C\varepsilon$$

F – elastic force
S – area of section

$$\varepsilon = S\sigma$$

Mechanical stresses in crystals

- Second rank tensors

$$\boldsymbol{\varepsilon} = \begin{bmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} \end{bmatrix} \qquad \boldsymbol{\sigma} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix}$$

- 6 independent components

$$\begin{aligned} &\varepsilon_{21} = \varepsilon_{12} \\ &\varepsilon_{31} = \varepsilon_{13} \Rightarrow \varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}, \varepsilon_{12}, \varepsilon_{13}, \varepsilon_{23} \\ &\varepsilon_{32} = \varepsilon_{23} \end{aligned}$$

$$\begin{aligned} &\sigma_{21} = \sigma_{12} \\ &\sigma_{31} = \sigma_{13} \Rightarrow \sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{12}, \sigma_{13}, \sigma_{23} \\ &\sigma_{32} = \sigma_{23} \end{aligned}$$

Mechanical stresses in crystals

Uniaxial stress

$$\boldsymbol{\sigma} = \begin{bmatrix} \sigma & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Biaxial stress

$$\boldsymbol{\sigma} = \begin{bmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Shear stress

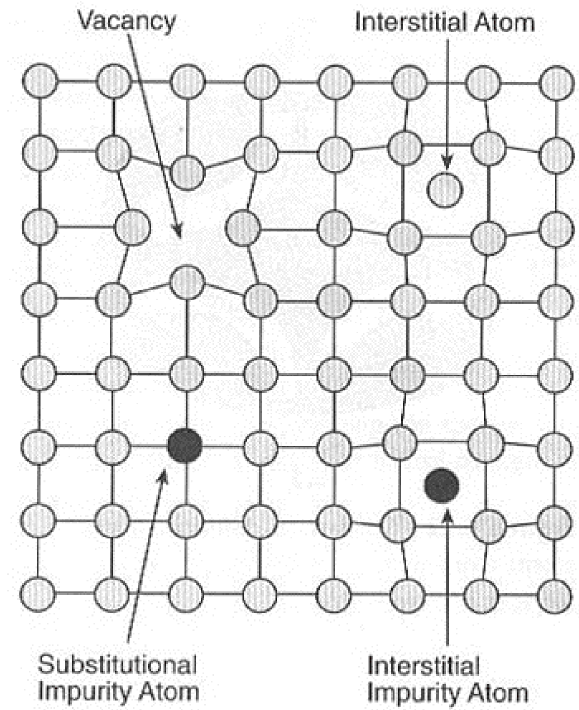
$$\boldsymbol{\sigma} = \begin{bmatrix} 0 & \sigma & 0 \\ \sigma & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Hydrostatic pressure

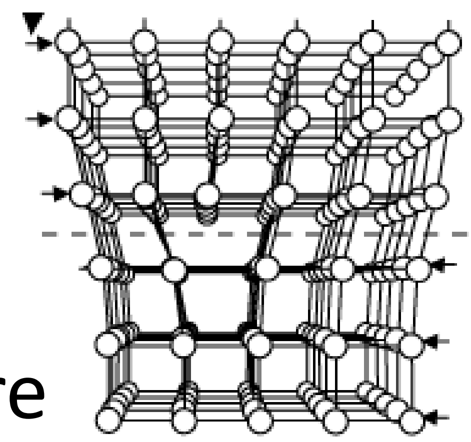
$$\boldsymbol{\sigma} = \begin{bmatrix} -p & 0 & 0 \\ 0 & -p & 0 \\ 0 & 0 & -p \end{bmatrix}$$

Mechanical stresses in crystals

- Crystal lattice defects
  - Inclusions
  - Dislocations
  - Twin and domain walls



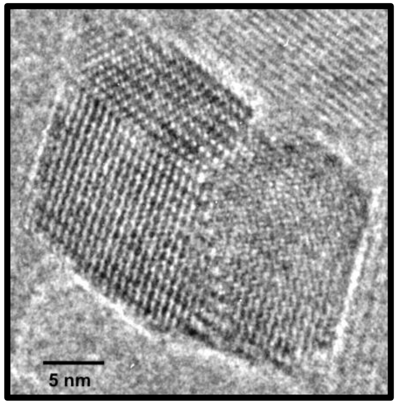
- External pressure/temperature
  - Pressure-induced phase transitions
  - Residual mechanical stresses

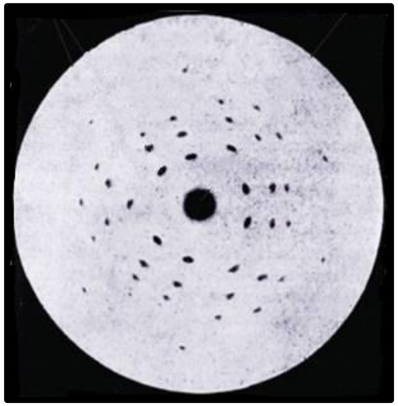
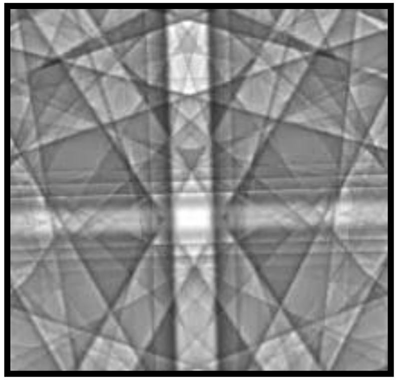


- Indicator of local lattice distortions and/or preceding pressure exposure

Experimental methods

- High-Resolution Transmission Electron Microscopy
  - Spatial resolution 0.1-0.2 nm
  - Samples thickness below 50 nm
- X-Ray Diffraction
  - Spatial resolution 10 µm
  - Strain accuracy 10^{-5}
- Electron Backscatter Diffraction
  - Spatial resolution 100 nm
  - Strain accuracy 10^{-4}
- **Raman Spectroscopy**
  - Spatial resolution 250 nm – 1 µm
  - Strain accuracy 10^{-3}-10^{-4}



Outline

- Stress effect on Raman spectrum
  - Qualitative approach
    - Group-theoretical analysis
    - Example. Rutile
  - Quantitative approach
    - Secular equation
    - Example. Silicon
- Examples
  - Quartz particles in porcelain ceramic
  - Graphene at the silicon grating

STRESS EFFECT ON RAMAN SPECTRUM

QUALITATIVE APPROACH

Qualitative approach

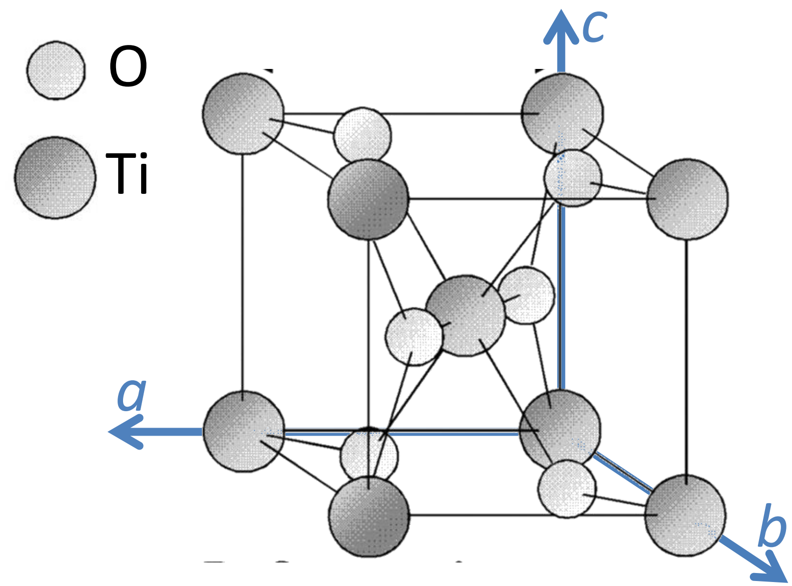
- Raman spectrum – strong correlation with structure and symmetry of the crystal
- Group-theoretical analysis
  - Number of vibrations
  - Symmetry of vibrations
  - Polarization activity
- Input data
  - Initial crystal symmetry
  - Symmetry of the stress
  - Correlation tables

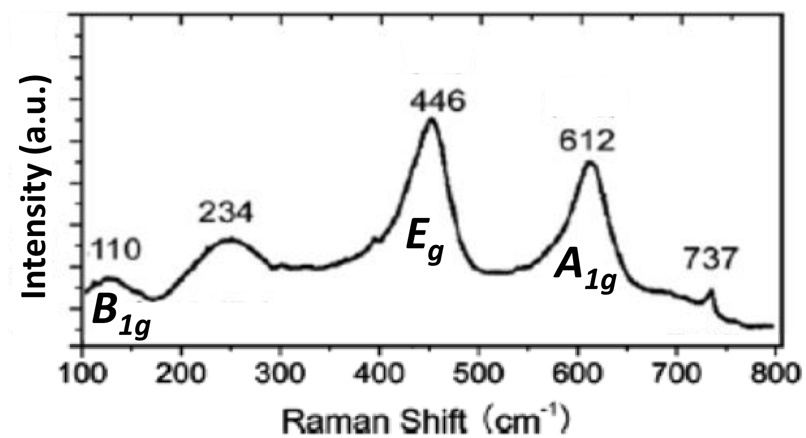
Qualitative approach

- Uniaxial mechanical stress $D_{\infty h}$
- Initial point group of the crystal G_0
- Symmetry reduction G_1
- Compatibility relations → Possible variation of vibration spectrum
- Curie Principle
  - G_1 group contains symmetry elements that are common for group G_0 and for group of the stress
  - compare symmetry elements of G_0 and $D_{\infty h}$

Qualitative approach. Example

- Rutile TiO_2
- Unstressed crystal
  - Tetragonal structure
  - D_{4h} *(P4/mmm)*
  - 15 optical modes
  - $\Gamma = A_{1g} + B_{1g} + B_{2g} + E_g$
    $+ A_{2u} + 3E_u + A_{2g} + 2B_{1u}$
  - **Raman active:** $\boldsymbol{A_{1g}}$, $\boldsymbol{B_{1g}}$, $\boldsymbol{B_{2g}}$ **and** $\boldsymbol{E_g}$
  - IR active: A_{2u} and $3E_u$
  - Forbidden: A_{2g} and $2B_{1u}$





J. Phys. Chem. B **103**, 3308 (1999); J. Phys. Chem. C **117**, 24015 (2013)

Qualitative approach. Example

- Stress along *a*-axis
- Common symmetry elements for D_{4h} and $D_{\infty h}$
  - $E, C_2^z, 2C'_2, i, \sigma_h, 2\sigma_v$
  - Point group D_{2h}
- Correlation table (Bilbao Crystallographic Server)

D_{4h}	A_{1g}	A_{1u}	A_{2g}	A_{2u}	B_{1g}	B_{1u}	B_{2g}	B_{2u}	E_g	E_u
D_{2h}	A_g	A_u	B_{1g}	B_{1u}	B_{1g}	B_{1u}	A_g	A_u	$B_{2g}+B_{3g}$	$B_{2u}+B_{3u}$

- Stressed crystal
  - $\Gamma = 2A_g + 2B_{1g} + B_{2g} + B_{3g} + 2A_u + B_{1u} + 3B_{2u} + 3B_{3u}$
  - **Raman active: $2A_g, 2B_{1g}, B_{2g}, B_{3g}$**
  - IR active: $B_{1u}, 3B_{2u}, 3B_{3u}$
  - Forbidden: $2A_u$

STRESS EFFECT ON RAMAN SPECTRUM

QUANTITATIVE APPROACH

Quantitative approach

- Dynamic equation

$$\left[\mathbf{K}-\omega_r^2\mathbf{M}\right]\vec{u}_r = 0$$

$\mathbf{K}$ – force constant matrix
$\mathbf{M}$ – mass matrix
ω_r - frequency of r^{th} vibrational mode
$\vec{u}_r$ – relative atomic displacement during r^{th} mode

- Matrix $\mathbf{K}$
  – depends on average atomic distances
  – sensitive to stress/strain state of the crystal

- For strained crystal

$$\left[\mathbf{K}^{(\varepsilon)}-\omega_r^2\mathbf{M}\right]\vec{u}_r = 0$$

Quantitative approach

- For low strains

$$K_{ij}^{(\varepsilon)} = K_{ij}^{0} + \sum_{k,l} \left(\frac{\partial K_{ij}}{\partial \varepsilon_{kl}} \right) \varepsilon_{kl} = K_{ij}^{0} + \sum_{k,l} K_{ijkl}^{(\varepsilon)} \varepsilon_{kl}$$

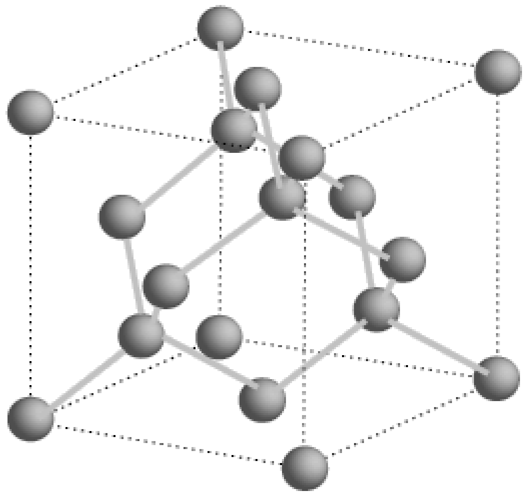
  – $K_{ij}^{0} = \omega_0^2 \delta_{ij}$
  – ω_0 - mode frequency without stress/strain

- $K_{ijkl}^{(\varepsilon)}$ - phonon deformation potentials
  – 4th rank tensor
  – structure and number of independent components is determined by the crystal symmetry

Quantitative approach. Example

- **Crystals with diamond structure (Si)**

  Tensor $K_{ijkl}^{(\varepsilon)}$ has only three independent components: *p, q, r*



- Secular equation

$$\begin{vmatrix} p\varepsilon_{11}+q(\varepsilon_{22}+\varepsilon_{33})-\lambda & 2r\varepsilon_{12} & 2r\varepsilon_{13} \\ 2r\varepsilon_{12} & p\varepsilon_{22}+q(\varepsilon_{33}+\varepsilon_{11})-\lambda & 2r\varepsilon_{23} \\ 2r\varepsilon_{13} & 2r\varepsilon_{23} & p\varepsilon_{33}+q(\varepsilon_{11}+\varepsilon_{22})-\lambda \end{vmatrix} = 0$$

- Eigenvalues: $\lambda_j = \omega_j^2 - \omega_0^2$
- Frequency shift: $\Delta\omega_j \approx \dfrac{\lambda_j}{2\omega_{j0}}$

Quantitative approach. Example

- Unstressed Si crystal
  - $\lambda_1 = \lambda_2 = \lambda_3$
  - 3-fold degeneracy mode
  - ω_0 = 520 cm^{-1}

- For uniaxial stress σ along [100] direction

$$\varepsilon_{11} = S_{11}\sigma \qquad \varepsilon_{22} = S_{12}\sigma \qquad \varepsilon_{33} = S_{12}\sigma$$

- Therefore frequency shift

$$\Delta\omega_1 = \frac{\lambda_1}{2\omega_0} = \frac{1}{2\omega_0}\left[pS_{11} + 2qS_{12}\right]\sigma$$

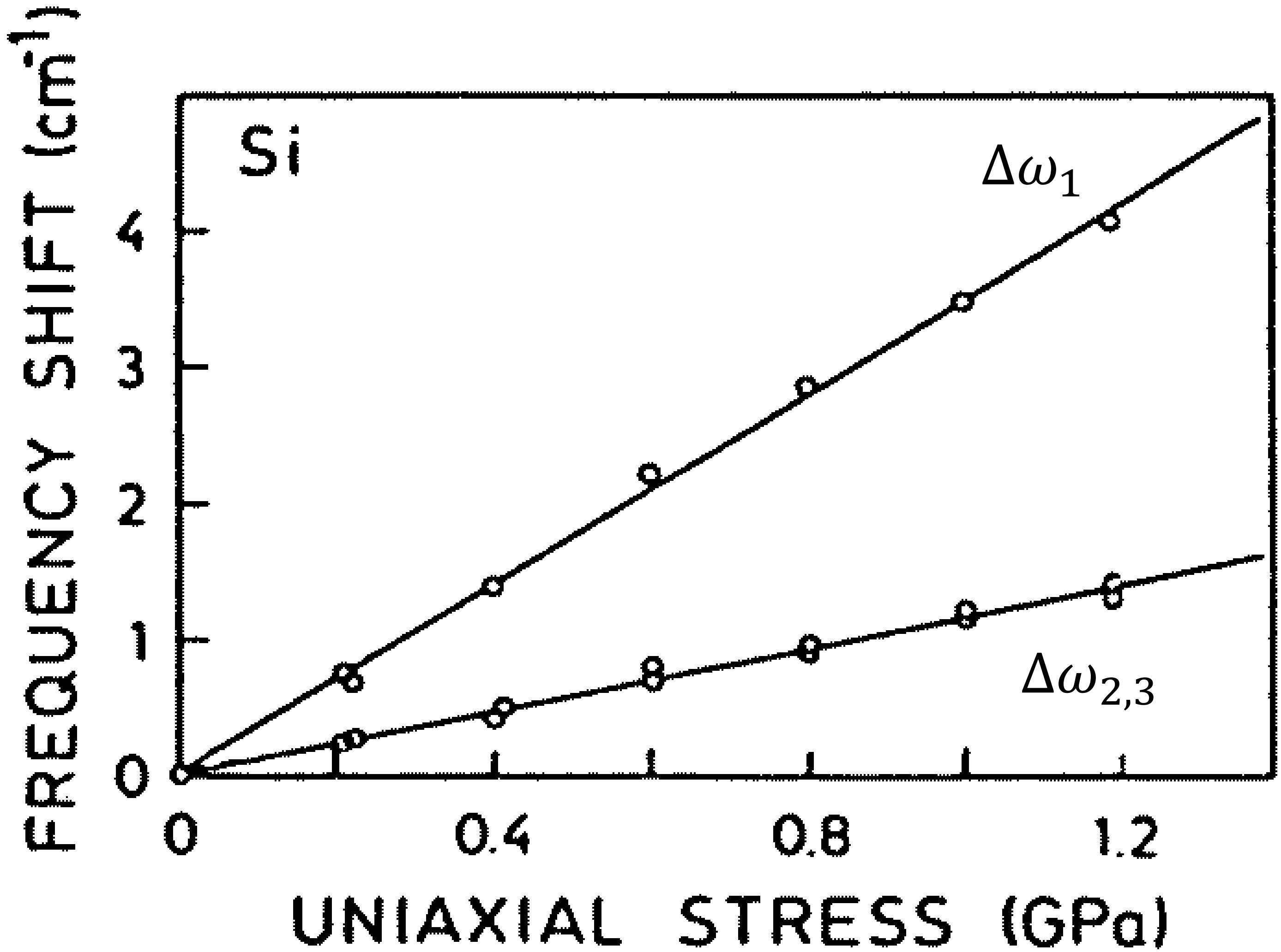
1-fold degeneracy mode

$$\Delta\omega_2 = \frac{\lambda_2}{2\omega_0} = \frac{1}{2\omega_0}\left[pS_{12} + q(S_{11} + S_{12})\right]\sigma$$

$$\Delta\omega_3 = \frac{\lambda_3}{2\omega_0} = \frac{1}{2\omega_0}\left[pS_{12} + q(S_{11} + S_{12})\right]\sigma$$

2-fold degeneracy mode

Quantitative approach. Example



Quantitative approach. Example

- For biaxial stress in (110) plane with stress components σ_{11} and σ_{22}

$$\Delta\omega_3 = \frac{\sigma_{11} + \sigma_{22}}{2\omega_0}\left[pS_{12} + q(S_{11} + S_{12})\right]$$

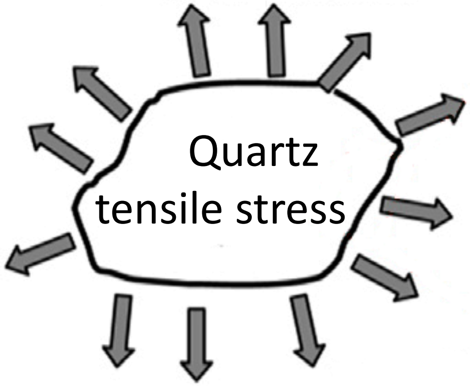
- For Si crystal
  - Compressive stress → increase of Raman frequency
  - Tensile stress → decrease of Raman frequency

EXAMPLES

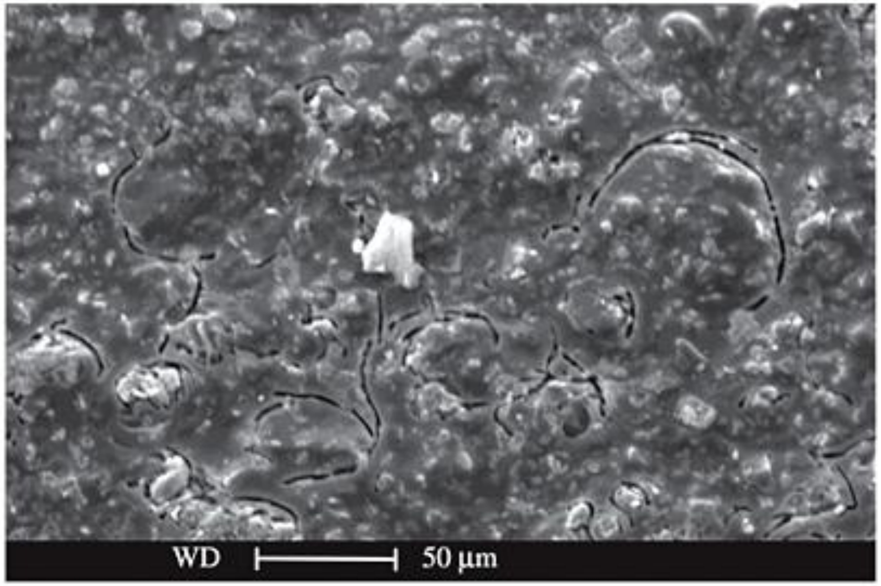
QUARTZ PARTICLES IN PORCELAIN CERAMIC

Quartz particles in porcelain ceramic

- Porcelain ceramic = glass matrix + crystalline phases
- Quartz is the most abundant crystalline phase
- Quartz particles reinforce the ceramic
  - Higher coefficient of thermal expansion
  - Strong compressive stresses on matrix
  - Strength improvements of the ceramic



- Very high stresses can lead to cracks

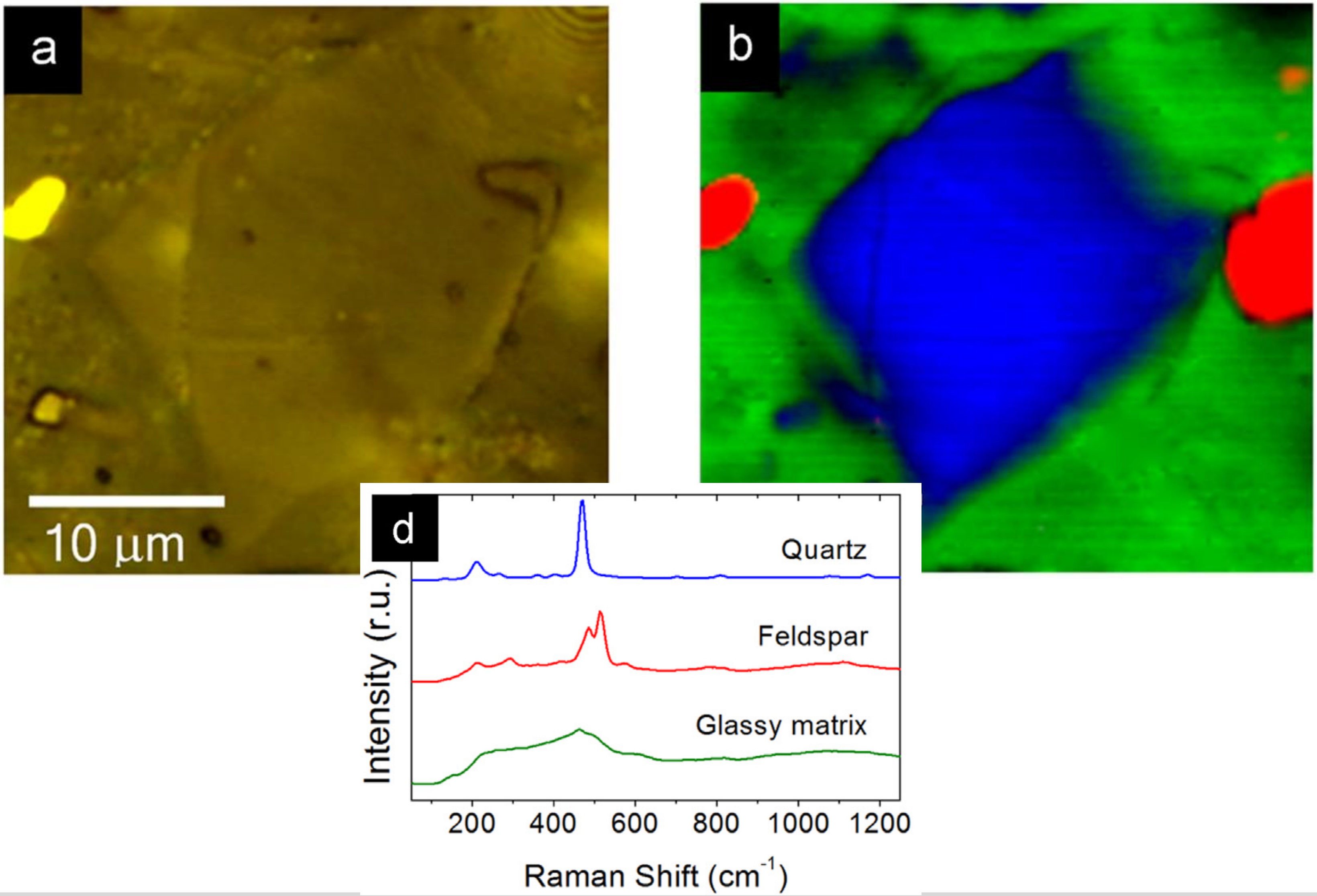


Material Research **8**, 39 (2005)

Quartz particles in porcelain ceramic

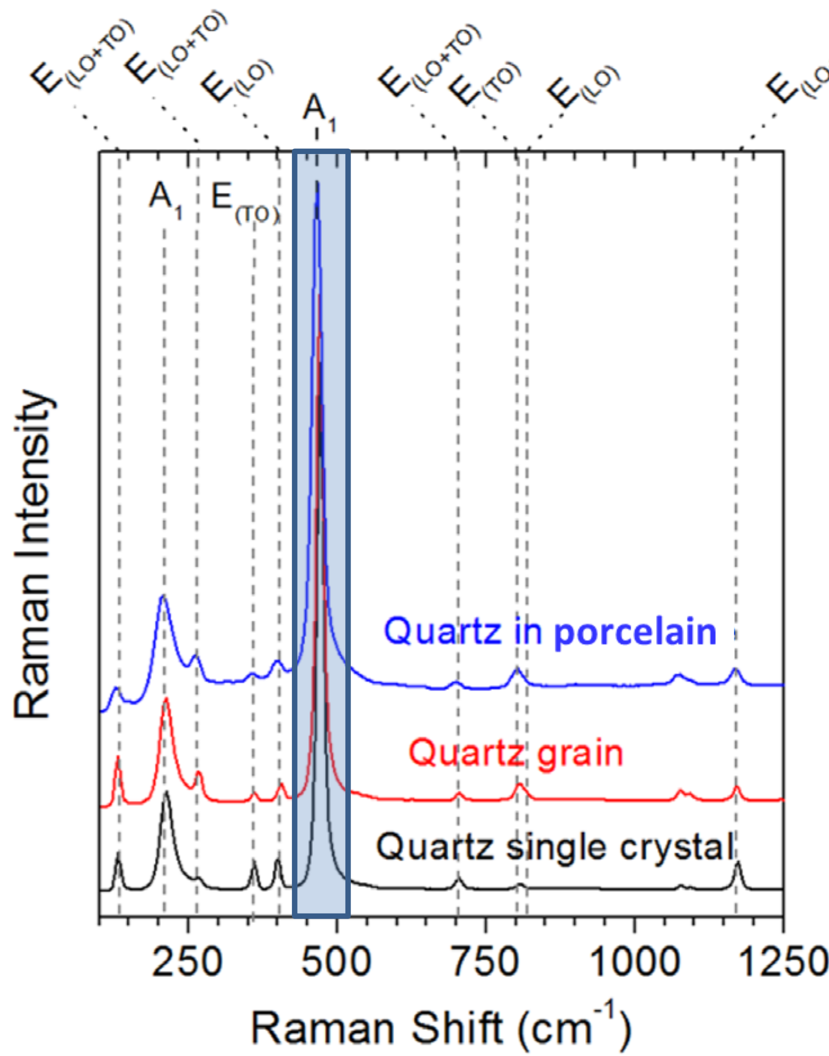
Optical Microscopy

Raman Phase Map

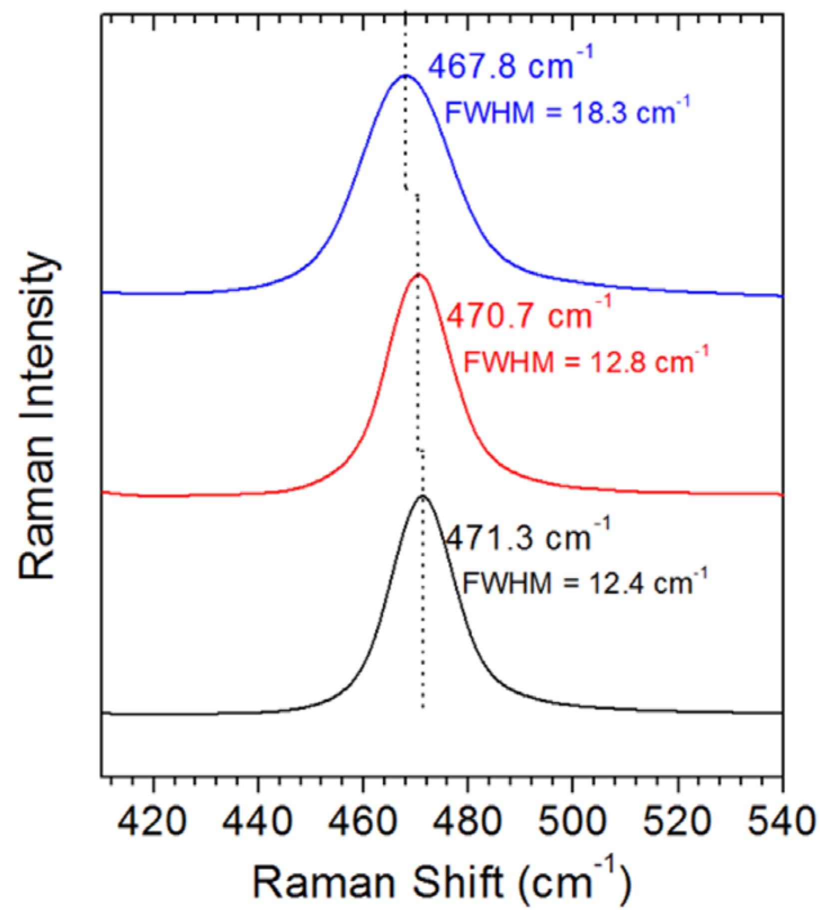


Ceramics International **41**, 13598 (2015)

Quartz particles in porcelain ceramic

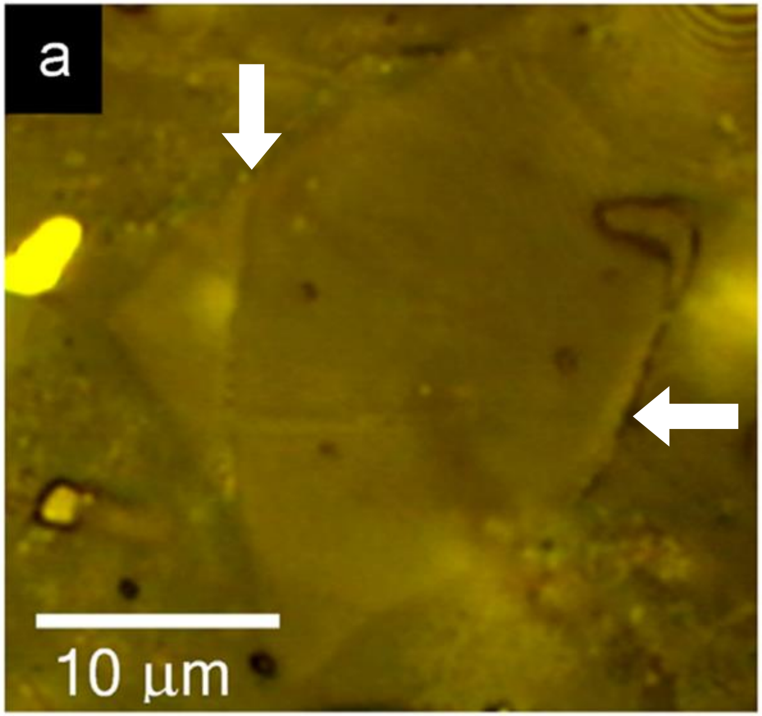


A_1 - bending vibration of SiO_4

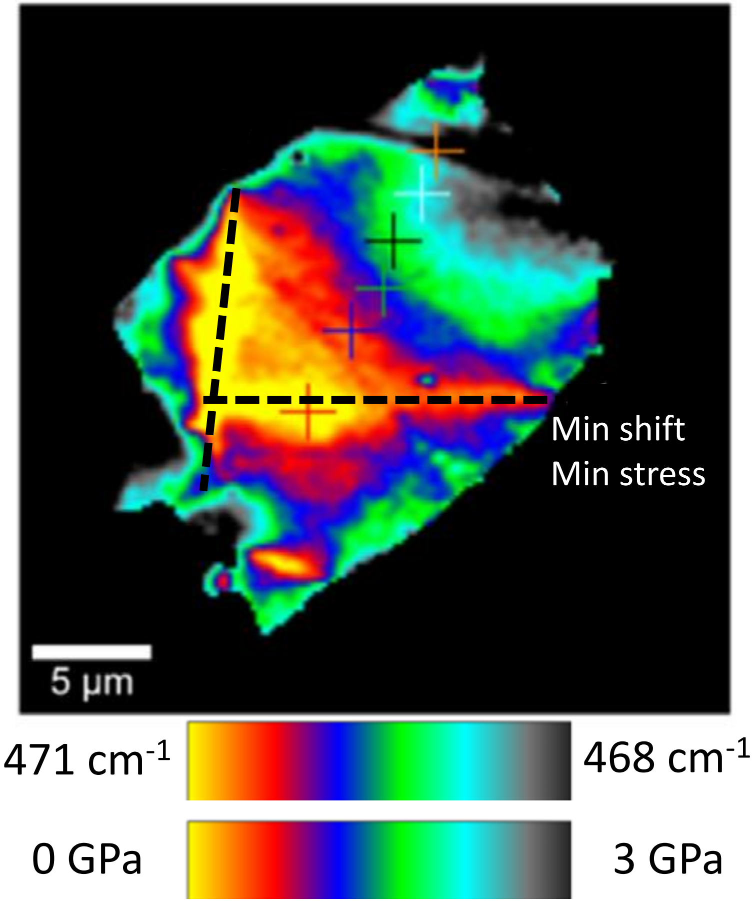


Quartz particles in porcelain ceramic

Optical Microscopy



Position of A_1 line

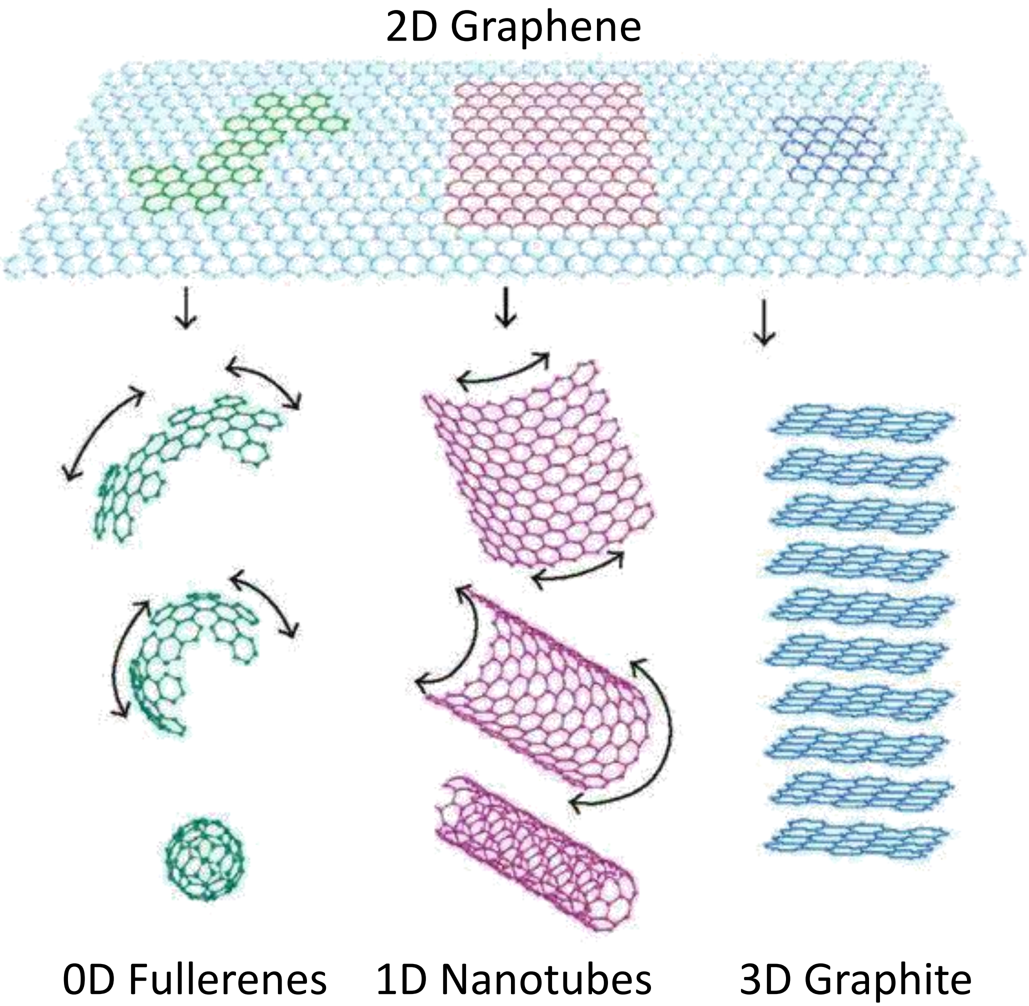


1 cm^{-1} ≈ 1 GPa

EXAMPLES

GRAPHENE
AT THE SILICON GRATING

Graphene

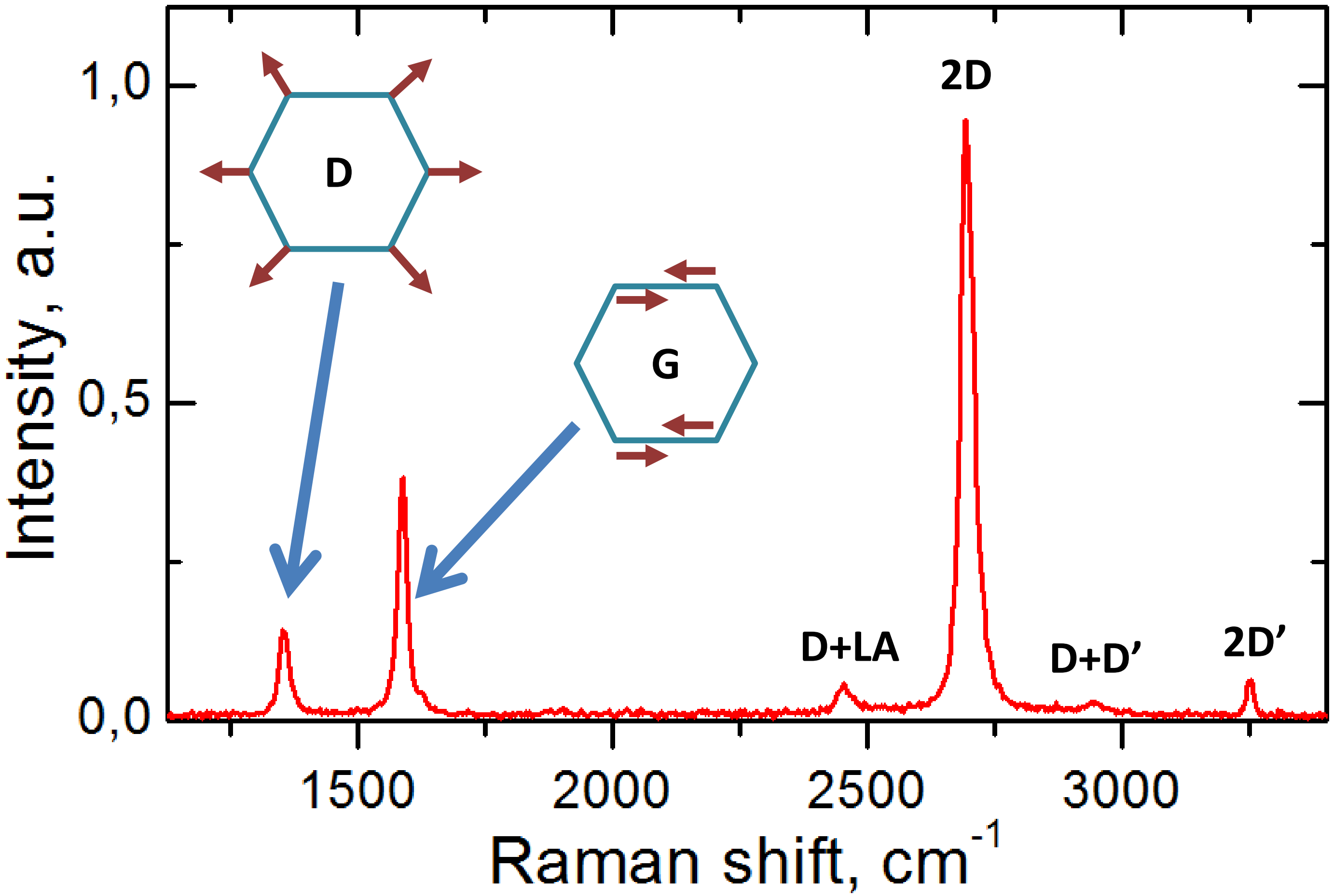


- Single layer of *sp*^{2} bonded carbon atoms
- Basic structure for fullerenes, nanotubes and graphite
- Unique electrical, mechanical, optical and thermal properties

Raman Spectrum of Graphene

Main Raman lines:

- G-line (1580 cm^{-1}): in-plane vibrations of C-atoms
- D-line (1350 cm^{-1}): defect-activated breathing mode
- 2D-line (2692 cm^{-1}): 2^{nd}-order scattering of D-line



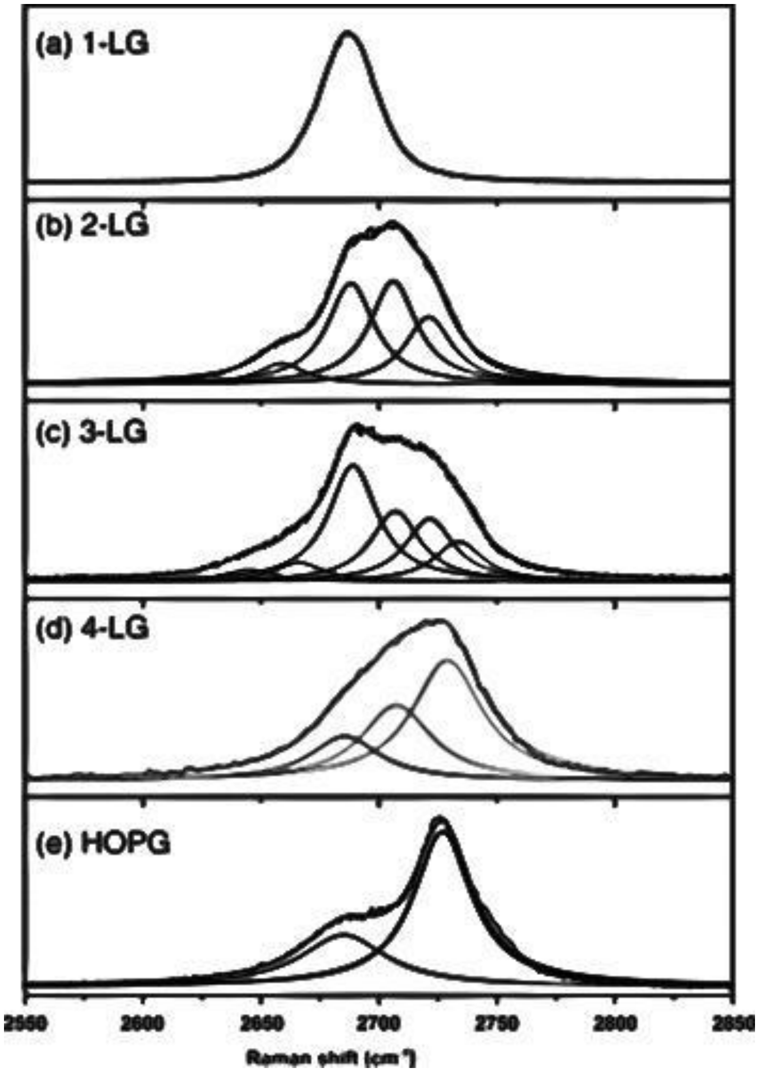
Raman Characterization of Graphene

- **Number of layers**
- Orientation of layers
- **Defects**
- **Mechanical stresses**
- Doping and functionalization
- Electrical transport
- Heat transport
- Magnetic properties

For details: publications of **Andrea C. Ferrari** and **Mildred S. Dresselhaus**

Raman Characterization of Graphene

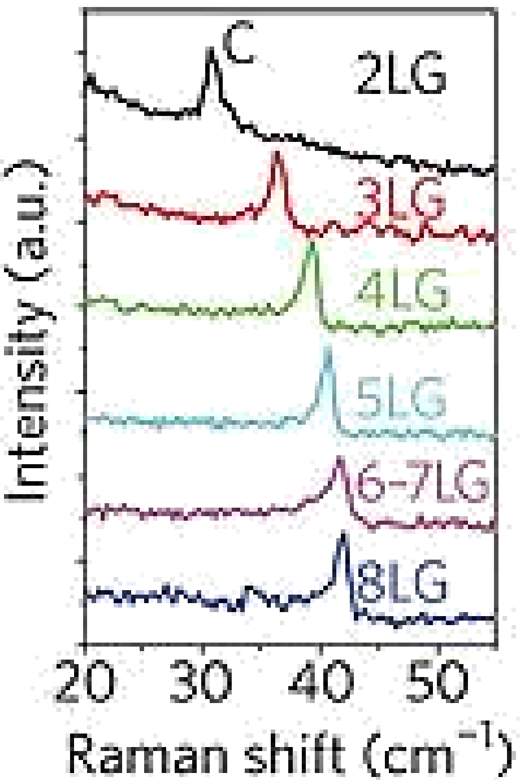
- **Number of layers (2D-line)**
  - Shape changes:
    - SLG - Single line
    - BLG - 4 lines
    - Graphite - 2 lines
  - Weak difference in shape for graphene with more than 5 layers

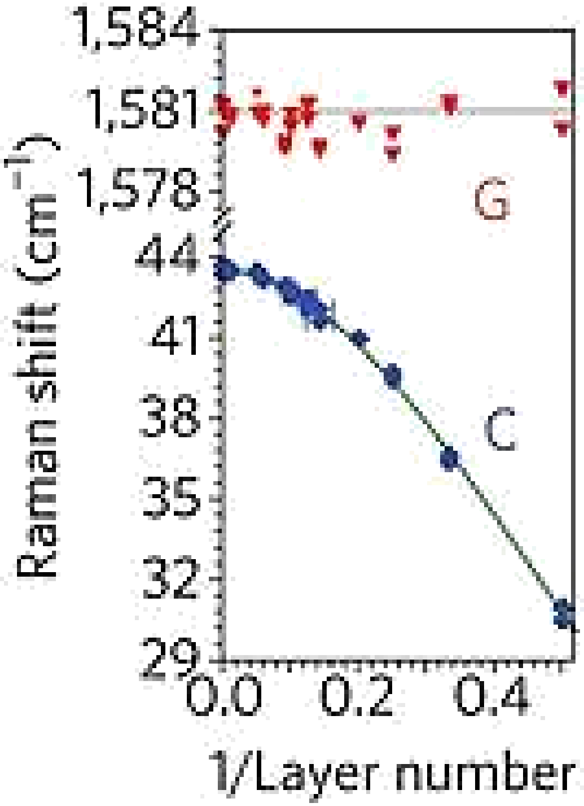


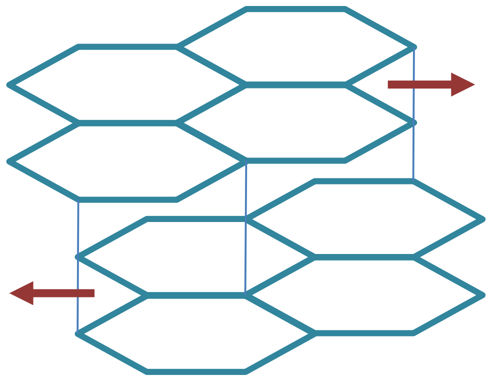
L.M. Malard, M.A. Pimenta et al. Phys. Rep. **473**, 51 (2009)

Raman Characterization of Graphene

- **Number of layers (C-line)**
  - New line corresponding to shear vibrations of layers
  - Position depends on number of layers







$$Pos(C) \propto \sqrt{1+\cos\left(\frac{\pi}{N}\right)}$$

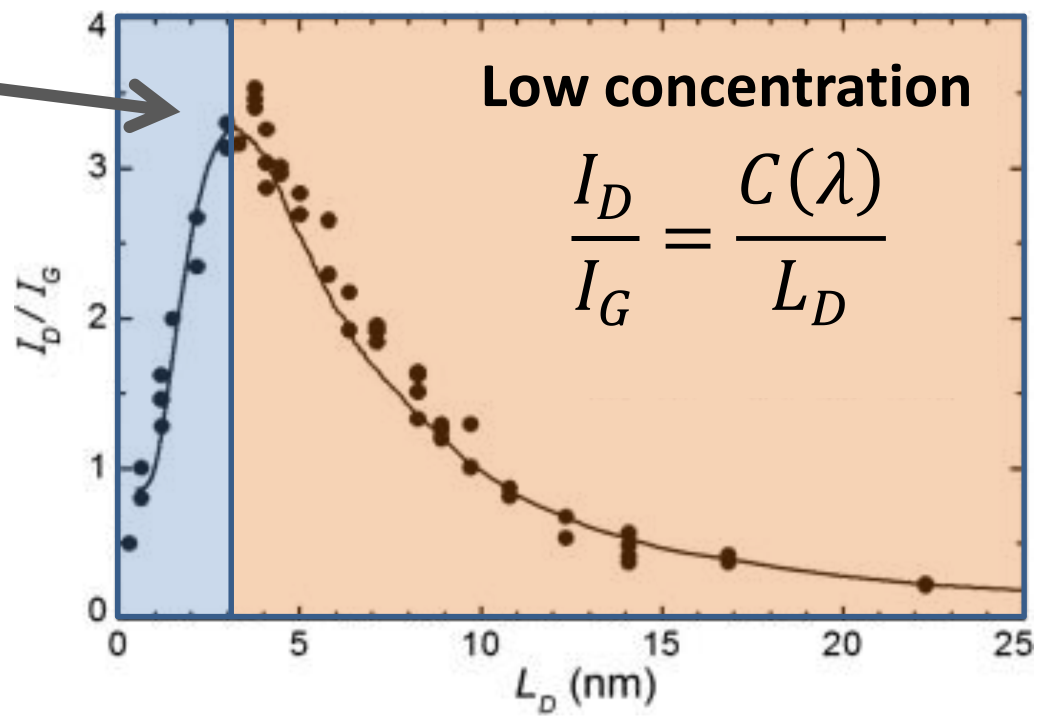
Raman Characterization of Graphene

- **Defects**
  - Defect-activated D-line
  - Satisfy momentum conservation law
  - Defect characterization by ratio I_D/I_G
  - L_D – average distance between defects

High concentration

$$\frac{I_D}{I_G} = C'(\lambda) L_D^2$$

Maximum: No additional contribution from new defects



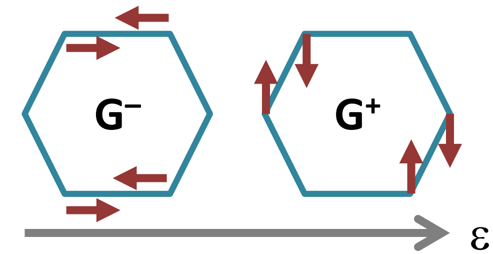
Low concentration

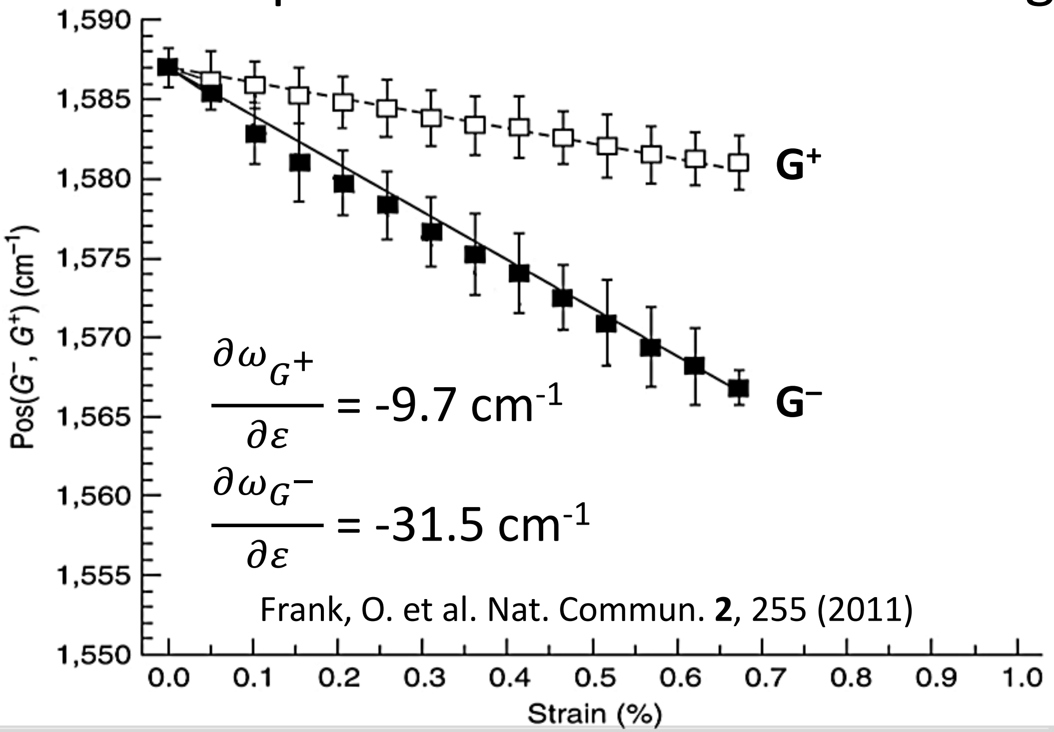
$$\frac{I_D}{I_G} = \frac{C(\lambda)}{L_D}$$

M.M. Lucchese, F. Stavale et al., Carbon **45**, 1592 (2010)

Raman Characterization of Graphene

- **Mechanical strains (G-line)**
  - Splitting into G^- and G^+ under uniaxial strain
  - Linear position shift:
    - Tension → Phonon softening
    - Compression → Phonon hardening

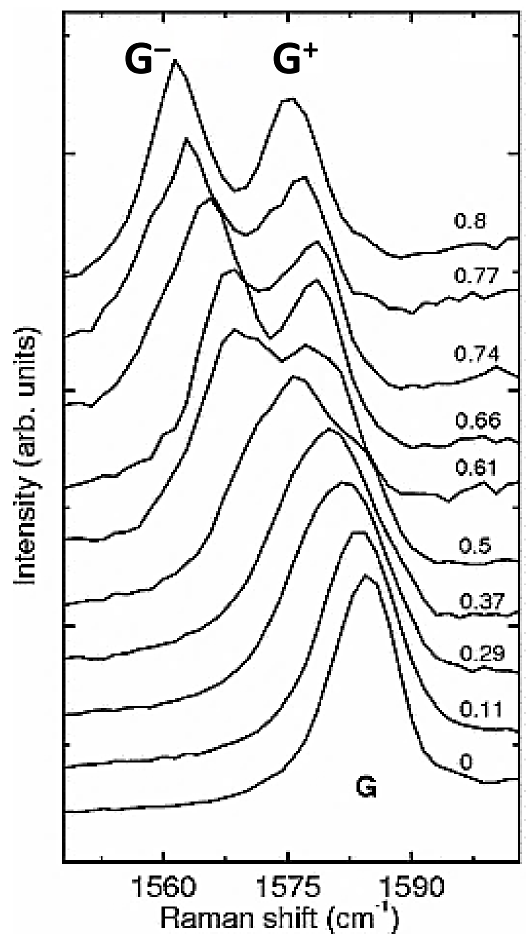




$$\frac{\partial \omega_{G^+}}{\partial \varepsilon} = -9.7 \text{ cm}^{-1}$$

$$\frac{\partial \omega_{G^-}}{\partial \varepsilon} = -31.5 \text{ cm}^{-1}$$

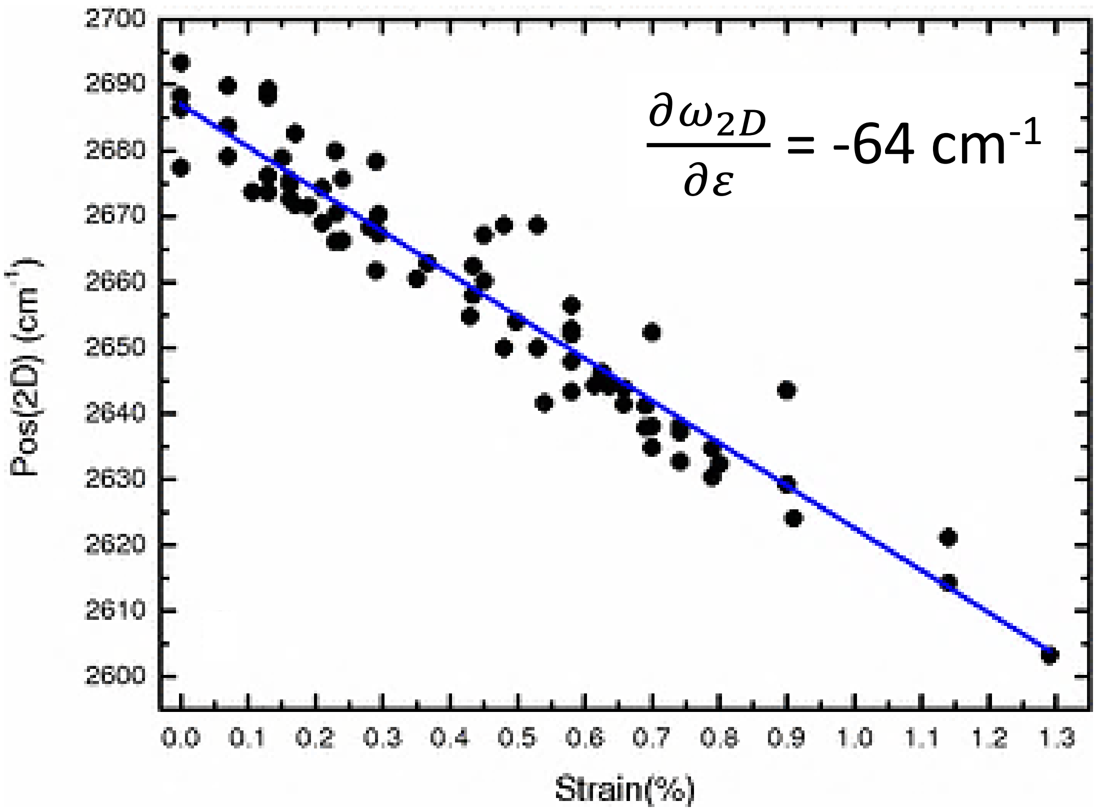
Frank, O. et al. Nat. Commun. **2**, 255 (2011)



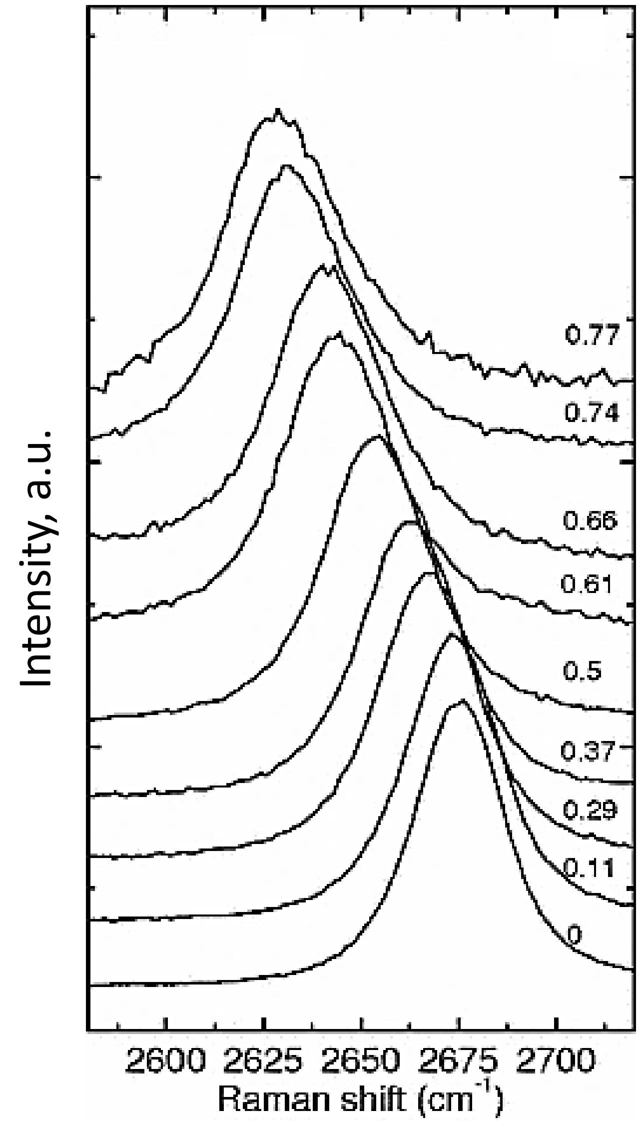
T. M. G. Mohiuddin et al. Phys. Rev. B. **79**, 205433 (2009)

Raman Characterization of Graphene

- **Mechanical strains (2D-line)**
  – Linear position shift
  – No splitting

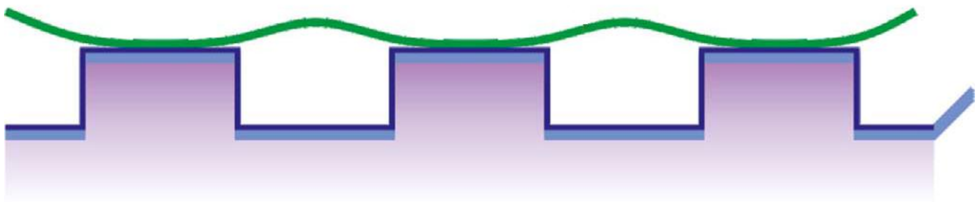


T. M. G. Mohiuddin et al. Phys. Rev. B. **79**, 205433 (2009)

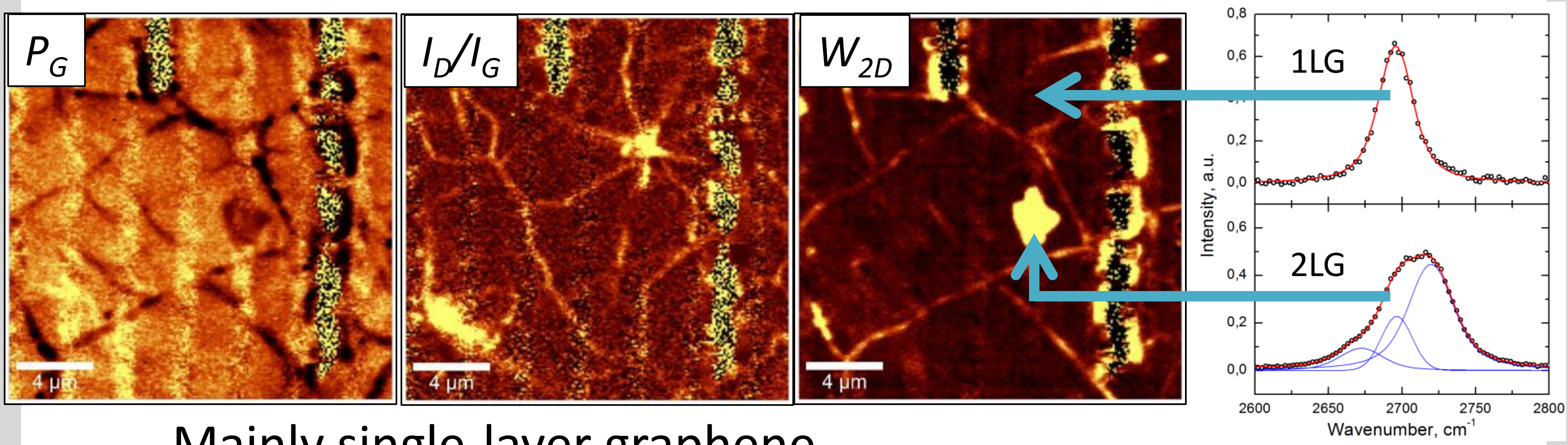


Graphene at the silicon grating

- Scheme of the sample



- Raman mapping (30mm×30mm)



  - Mainly single-layer graphene
  - Graphene flake at the surface
  - Defects' distribution: holes, wrinkles
  - Periodical variations of P_G → Periodical stress

Nat. Comm. **6**, 7572 (2015)

Graphene at the silicon grating

- Position of G-line
  - Linearly proportional to Young modulus $\frac{\partial \omega_G}{\partial \varepsilon} = kE$
- Young modulus *E* is the proportionality coefficient between axial stress *σ* and strain *ε*

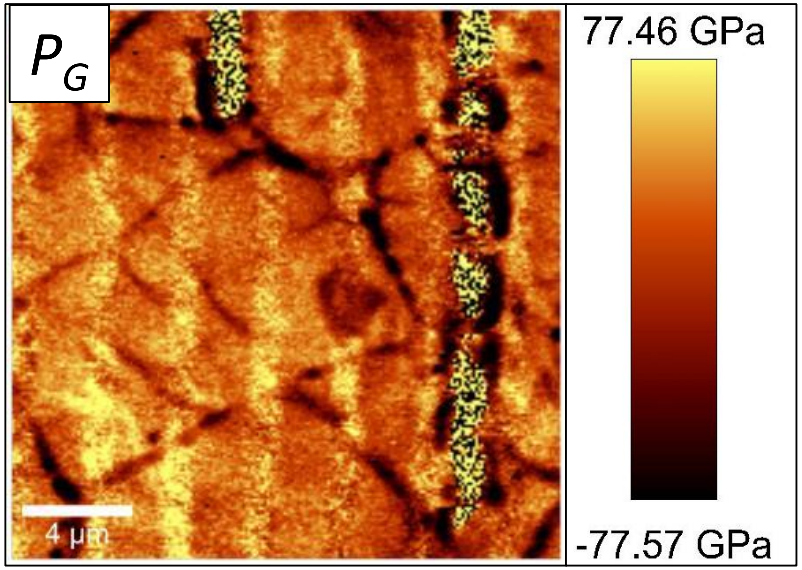
$$\frac{\partial \omega_G}{\partial \varepsilon} = kE \quad \Rightarrow \quad \frac{1}{E}\frac{\partial \omega_G}{\partial \varepsilon} = \frac{\partial \omega_G}{\partial \sigma} = k \quad \Rightarrow \quad \Delta\omega = \omega - \omega_0 = k\sigma$$

- Final expression

$$\sigma = \frac{E(\omega_S - \omega_0)}{\partial \omega / \partial \varepsilon}$$

- For CVD graphene

$$\frac{\partial \omega_G}{\partial \varepsilon} = +41.1\,\mathrm{cm}^{-1}/\%; \quad E = 1.1\,\mathrm{TPa}$$



Summary

- Raman spectroscopy can be used for characterization of mechanical stresses in crystals.
- Powerful tool provide quantitative and qualitative information about stresses.
- The method is based on simple theoretical background.
- We briefly looked the micro-Raman application for characterization of stresses in several systems.

Further reading

- S. Ganesan, A.A. Maradudin, and J. Oitmaa, *A lattice theory of morphic effects in crystals of the diamond structure*, Ann. Phys. **56**, 556 (1970)
- G. Pezzotti, *Raman spectroscopy of piezoelectrics*, J. Appl. Phys. **113**, 211301 (2013)
- M. Hanbucken, P. Muller, and R.B. Wehrspohn, *Mechanical Stress on the Nanoscale* (Wiley-VCH, 2011)
- A.C. Ferrari and D.M. Basko, *Raman spectroscopy as a versatile tool for studying the properties of graphene*, Nature Nanotechnology **8**, 235 (2013)

THANK YOU
FOR YOUR ATTENTION!