

# YFR8010

## Practical Spectroscopy

Jüri Krustok  
Lembit Kurik  
Urmas Nagel (KBFI)

1

## YFR8010 Practical Spectroscopy I

**4** laboratory works:

1. Raman spectroscopy
2. Photoluminescence
3.  $\mu$ -Photoluminescence
4. External quantum efficiency of solar cell

2

## YFR8010

### Practical Spectroscopy

### Raman spectroscopy

Professor Jüri Krustok  
[Juri.Krustok@ttu.ee](mailto:Juri.Krustok@ttu.ee)  
<http://staff.ttu.ee/~krustok>

3

## History

- Discovered in 1928: India (Raman, Krishnan) and Soviet Union (Landsberg, Mandelstam)
- In 1928 Raman and Krishnan published a paper in "Nature", but the explanation of the experiment was not correct.
- Few month later in 1928 Landsberg and Mandelstam published a paper with correct explanation.
- In Soviet Union this effect was called **combination scattering**.

4

## Raman



### The Nobel Prize in Physics 1930

"for his work on the scattering of light and for the discovery of the effect named after him"



### Sir Chandrasekhara Venkata Raman

India

Calcutta University  
Calcutta, India

b. 1888  
d. 1970

5

## Light and matter

- If the light is directed on to matter we observe absorption, reflection and **scattering**.
  - **SCATTERING** can be:
    - Elastic (Rayleigh)  $\rightarrow \lambda_{\text{secondary}} = \lambda_{\text{primary}}$
    - Nonelastic (Raman)  $\rightarrow \lambda_{\text{secondary}} \neq \lambda_{\text{primary}}$ 
      - **The wavelength of light changes with RAMAN scattering**

6

## Elastic (Rayleigh) scattering

$$I = I_o \frac{8\pi^4 N\alpha^2}{\lambda^4 R^2} (1 + \cos^2 \theta)$$

Intensity of scattering depends on the wavelength  $\lambda$  of primary light and on the scattering angle  $\Theta$

Blue light is scattered more than red light

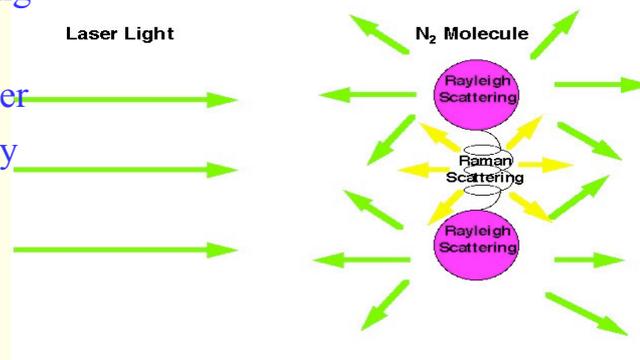
Blue sky- Rayleigh scattering of sunlight on molecules of air!

7

## Raman vs. Rayleigh scattering

Raman scattering intensity is  $10^7$  times weaker than the primary light (laser) intensity

### Raman Scattering



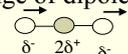
8

## Raman and FTIR (infrared spectroscopy)

### FTIR

i. vibrational modes

ii. change of dipole movement



iii. Excitation of the molecule

to higher vibrational electron state

### Raman

vibrational modes

change in polarizability



Light as an

electromagnetic field:  
disturbing of electron  
cloud near the bond

9

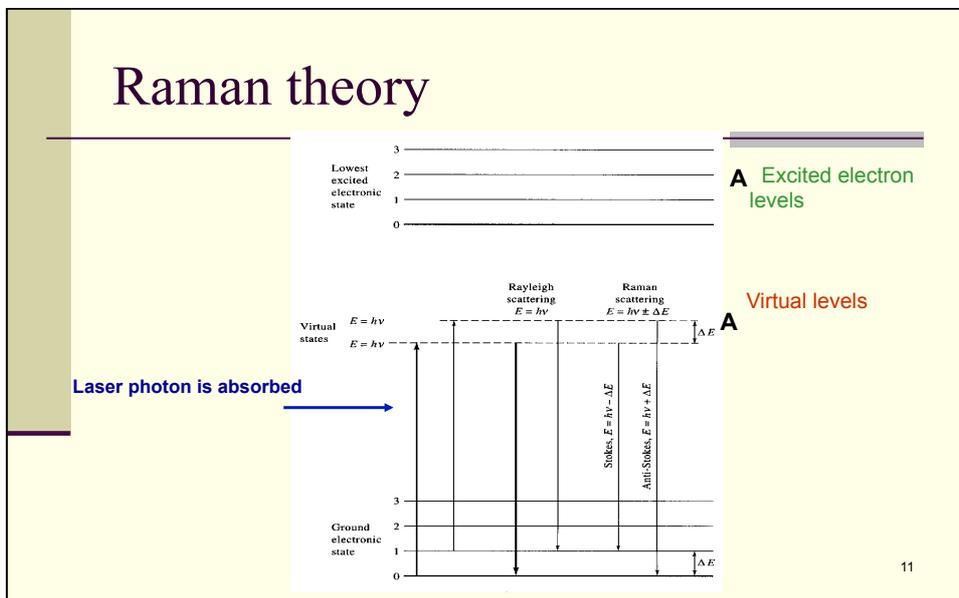
## Physics of Raman effect

- Raman spectra show very weak peaks with frequency  $\omega$  and this frequency is a combination of primary light frequency  $\omega_0$  and the frequency of vibrational states of molecules (or vibrational modes of crystals)  $\omega_i$ .

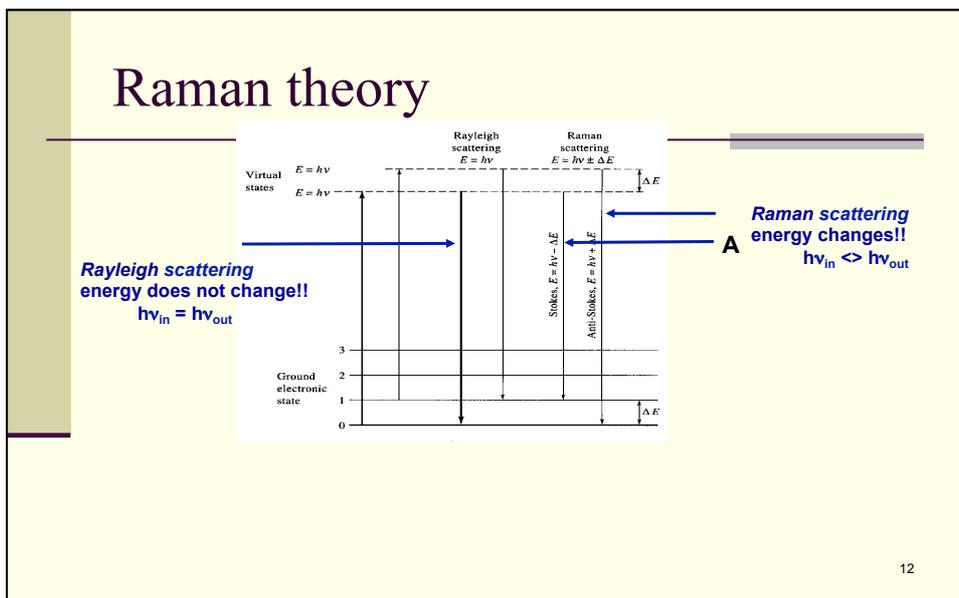
$$\omega = \omega_0 \pm \omega_i$$

10

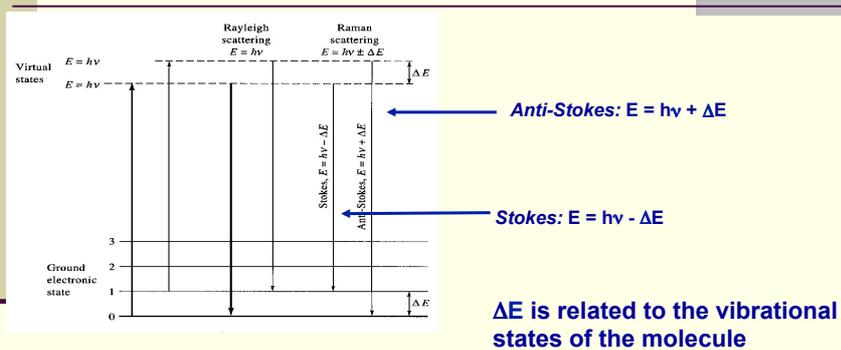
# Raman theory



# Raman theory



## Raman theory



13

## Raman spectroscopy: wavenumbers

$$\tilde{\nu} = \frac{1}{\lambda} \quad \tilde{\nu}(\text{cm}^{-1}) = \frac{10^4}{\lambda(\mu\text{m})}$$

$$1 \text{ cm}^{-1} = 0.12397 \text{ meV}$$

In spectra it means an energetic distance from laser line!!

14

## Raman spectrum

In typical Raman spektrum we have:

1. Rayleigh peak ( $\Delta E=0$ )
2. Anti-Stokes peaks, where the energy is **increased**, i.e.  $\Delta E < 0$
3. Stokesi peaks, where the energy is **decreased**, i.e.  $\Delta E > 0$

In general we record Stokesi peaks

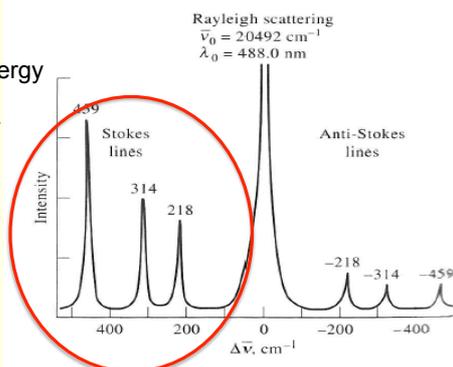
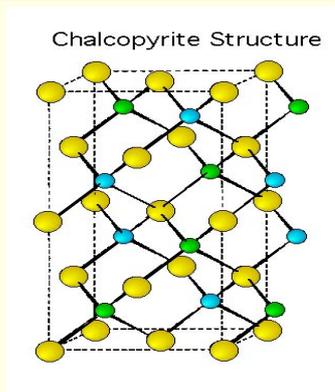


Figure 18-1. Spectrum of  $\text{CCl}_4$ , using an  $\text{Ar}^+$  laser at 488 nm. 15

## Molecules and crystals

- Molecules – vibrations of molecules
- Crystals- Lattice vibration modes (phonons)
- Lattice vibration modes depend on symmetry of the lattice, atomic masses and bond strengths between atoms

## Example- chalcopyrite



$\text{CuInSe}_2$   
 $\text{CuInS}_2$   
 $\text{CuGaSe}_2$   
 and others

17

## Vibrational modes in chalcopyrite

- In chalcopyrite  $A^I B^{III} C_2^{VI}$  crystal we have 8 atoms in unit cell. Accordingly we have 24 vibrational modes:  
 $1A_1 + 2A_2 + 3B_1 + 4B_2 + 7E,$

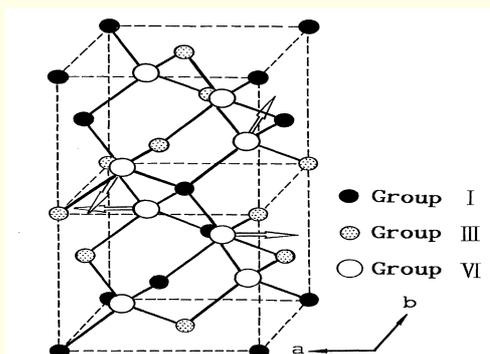
From them we have 22 Raman active modes:

$$1A_1 + 3B_1 + 3B_2(\text{LO}) + 3B_2(\text{TO}) + 6E(\text{LO}) + 6E(\text{TO}).$$

- $A_1$  always dominates spectra, because it is related to anion movement only
- $B_1$  mode is related to cation movement and  $B_2$  and  $E$  modes are related to movement of all atoms.

18

## $A_1$ mode in chalcopyrite



The most intensive peak in Raman spectra

19

## $A_1$ peaks in chalcopyrites

Table I. Raman-scattering properties of I-III-VI<sub>2</sub> group compounds.

| Material            | $\bar{M}$ | $(M^{VI})^{-1/2}$ | $\left(\frac{M^I + M^{III}}{2}\right)^{-1/2}$ | Frequency of $A_1$ mode (cm <sup>-1</sup> ) |
|---------------------|-----------|-------------------|---|---|
| CuGaS <sub>2</sub>  | 49.35     | 0.1766            | 0.1225  | 312   |
| CuGaSe <sub>2</sub> | 72.80     | 0.1125            | 0.1225  | 187   |
| CuGaTe <sub>2</sub> | 97.12     | 0.0885            | 0.1225  | 136   |
| CuInS <sub>2</sub>  | 60.62     | 0.1766            | 0.1059  | 293   |
| CuInSe <sub>2</sub> | 84.07     | 0.1125            | 0.1059  | 175   |
| CuInTe <sub>2</sub> | 108.39    | 0.0885            | 0.1059  | 127   |
| AgGaS <sub>2</sub>  | 60.43     | 0.1766            | 0.1061  | 295   |
| AgGaSe <sub>2</sub> | 83.88     | 0.1125            | 0.1061  | 175   |
| AgGaTe <sub>2</sub> | 108.20    | 0.0885            | 0.1061  | 130   |
| AgInS <sub>2</sub>  | 71.70     | 0.1766            | 0.0948  | 265   |
| AgInSe <sub>2</sub> | 95.15     | 0.1125            | 0.0948  | 172   |
| AgInTe <sub>2</sub> | 119.47    | 0.0885            | 0.0948  | 127   |

20

## Raman spectra of $\text{CuInS}(\text{Se})_2$

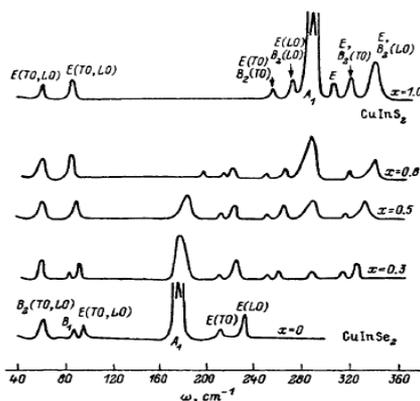
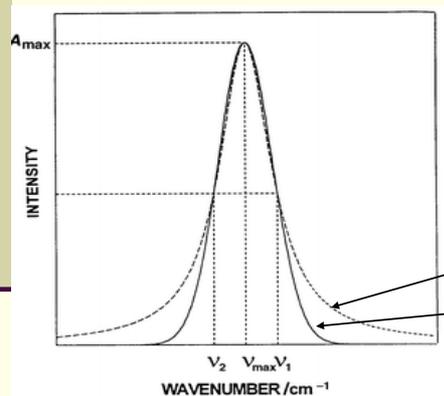


FIG. 3. Optical Raman spectra of the compounds  $\text{CuInSe}_2$  and  $\text{CuInS}_2$  and  $\text{CuInS}_{2-x}\text{Se}_{2(1-x)}$  solid solutions.

21

## The shape of Raman peaks



$$\text{Intensity} = \frac{a}{(\nu - \nu_0)^2 + b^2}$$

**Lorentzian Lineshape**

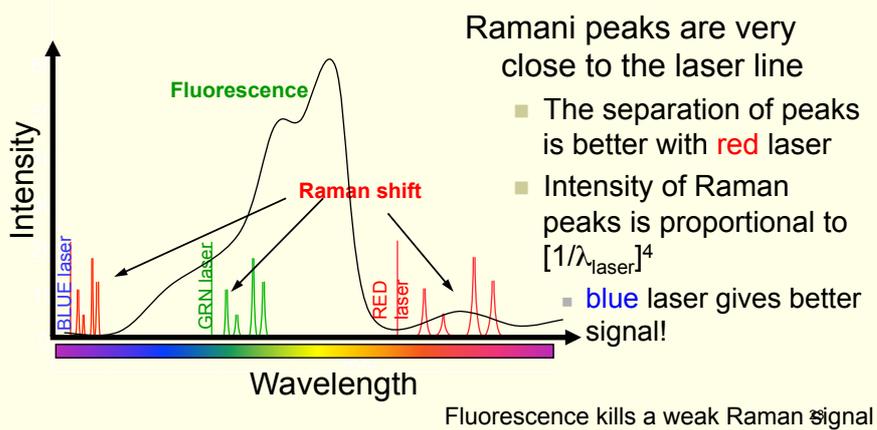
**Example: Natural Linewidth**

Lorentz shape

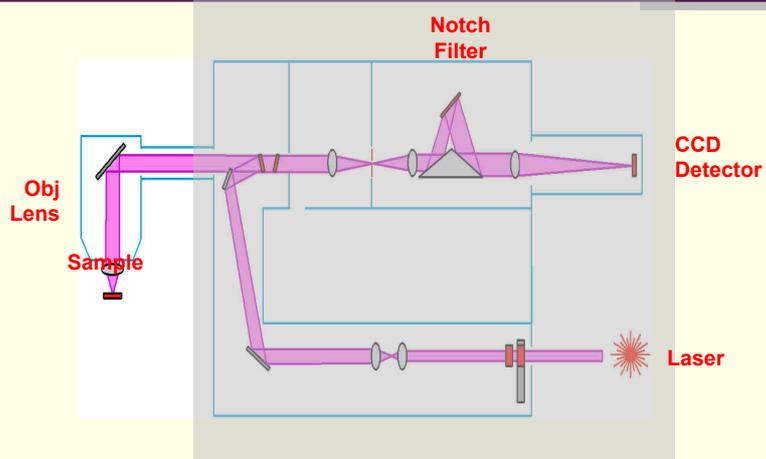
Gauss shape

22

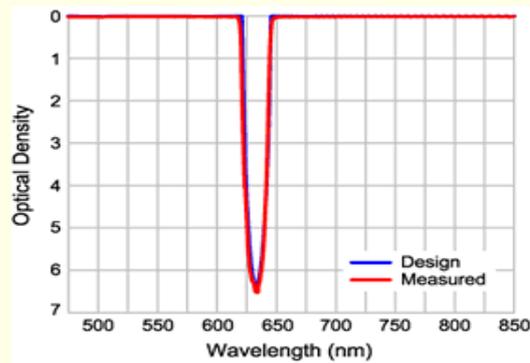
## Raman spectra



## Micro-Raman spectrometer



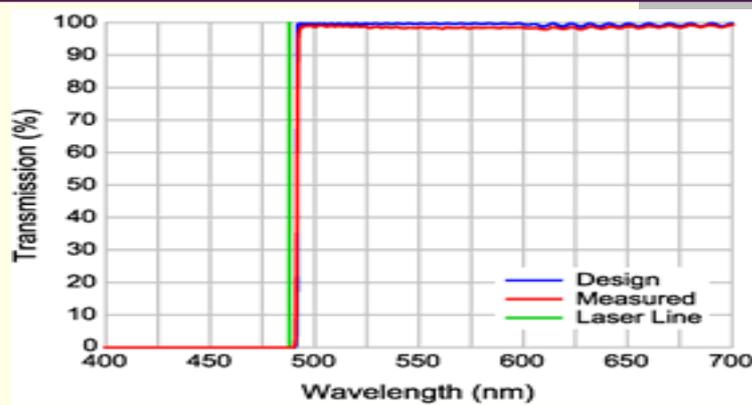
## Notch filter



It is used to remove scattered laser light

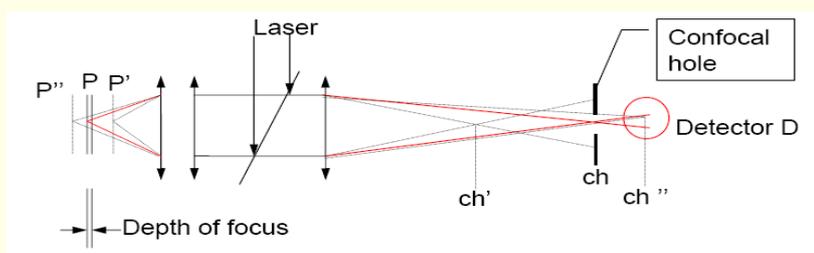
25

## Long-wave-pass filter



26

## Confocal microRaman



27

## Raman spectrometer

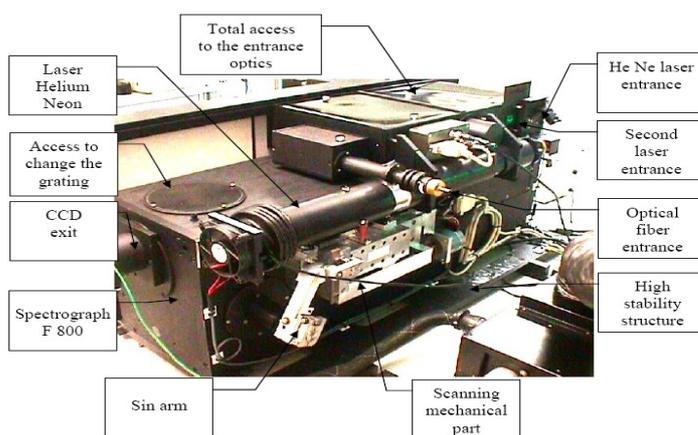


HORIBA Jobin Yvon  
LabRam HR

VI-143 room

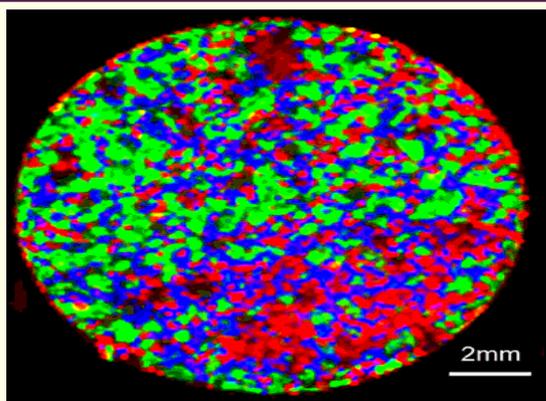
28

## Raman spectrometer (from behind)



29

## Scanning Raman

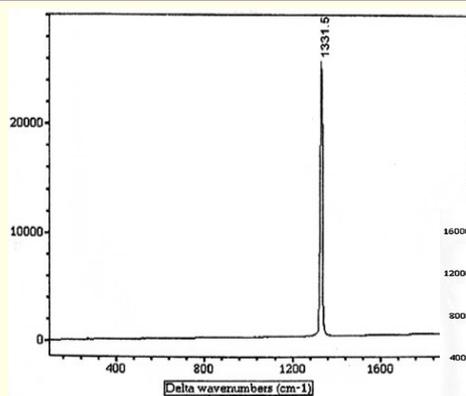


Micro scan from the surface of unknown pill

4 different peaks- 4 different colors

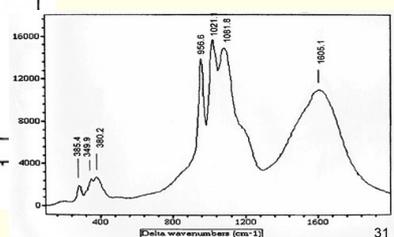
30

## Diamond Raman

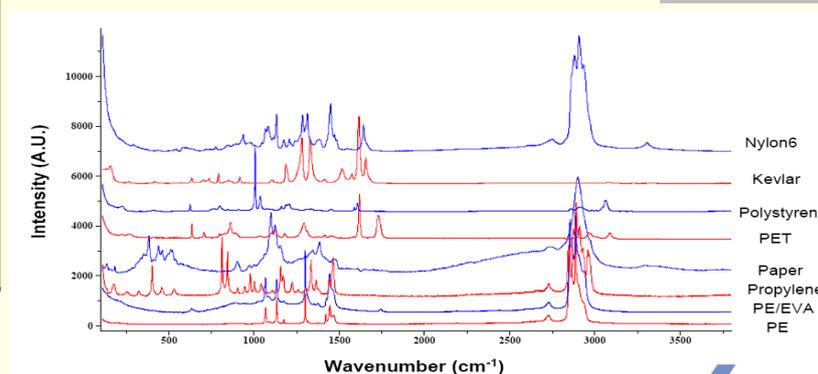


1331.5 cm<sup>-1</sup>

Zirconia (used to replace diamond) :



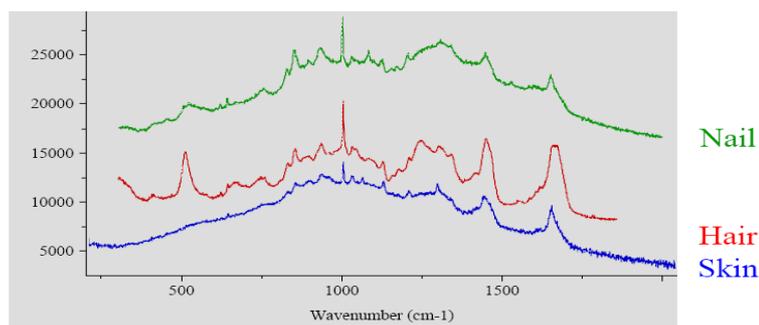
## Raman of different polymers



32

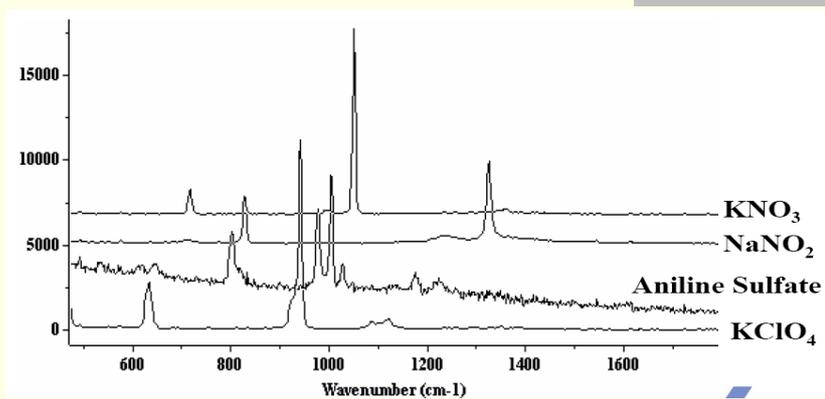
## Raman of human body

Human Nail, Hair and Skin



33

## Raman of explosives

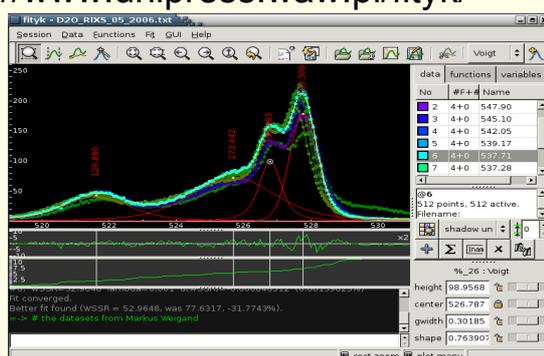


34

## Fitting of Raman (and PL) spectra

- Free **FITYK** software

<http://www.unipress.waw.pl/fityk/>



35

## Raman measurements

- Measure different samples
- Spectra fitting with Lorentzian function
- Find  $I_{max}$ ,  $E_{max}$ ,  $W$  for each peak
- Memory stick !!!!**

36

# YFR8010

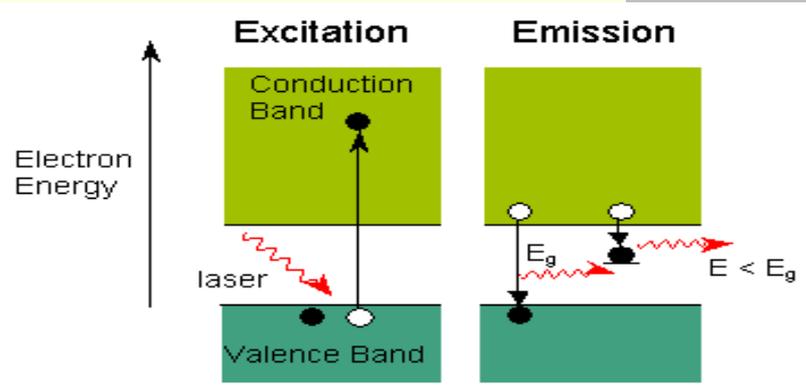
## Practical Spectroscopy

### PHOTOLUMINESCENCE

Prof. Jüri Krustok

37

## Photoluminescence in semiconductors



38

## Recombination

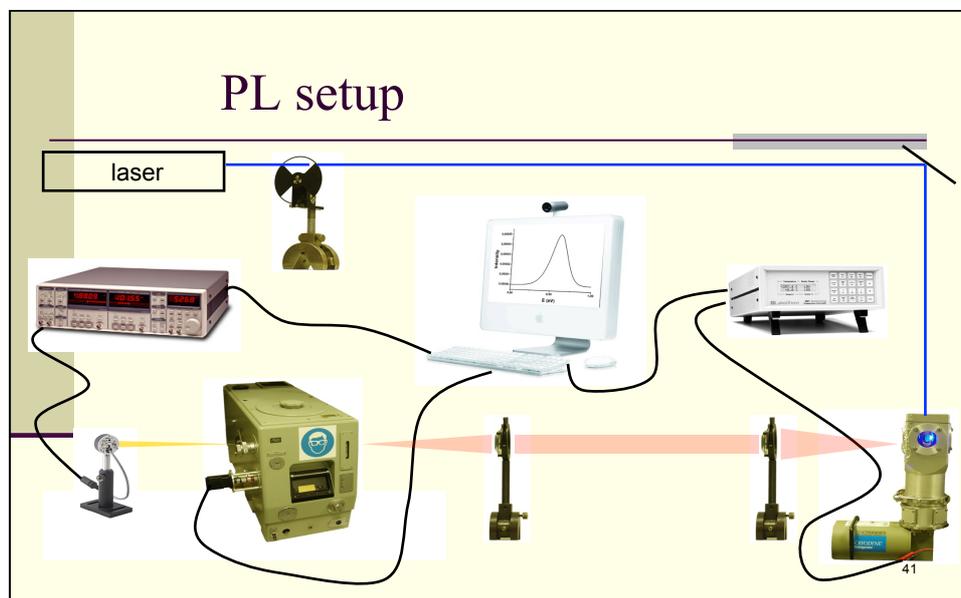
- Radiative recombination- photoluminescence
- Non radiative recombination- DARK!

39

## Equipment for photoluminescence



40



## PL measurements

---

**Detectors:**

Photomultiplier tubes (PMT) :

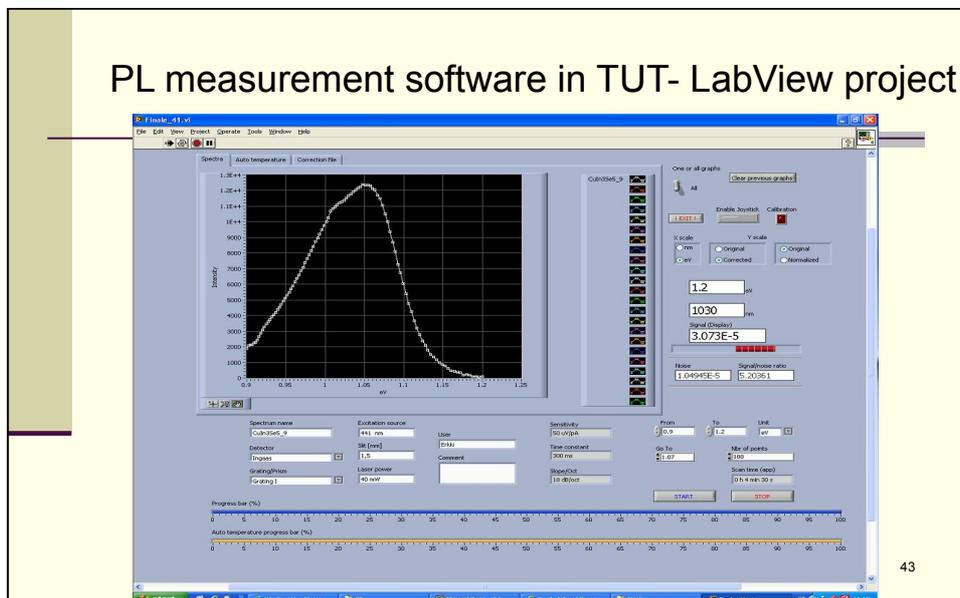
- FEU-79 (visible range)
- R632- red and near infrared range

Semiconductor detectors:

- Si- Visible and near infrared range (~1000nm)
- InGaAs- near infrared range (~1700 nm)
- PbS- infrared (~3000 nm)

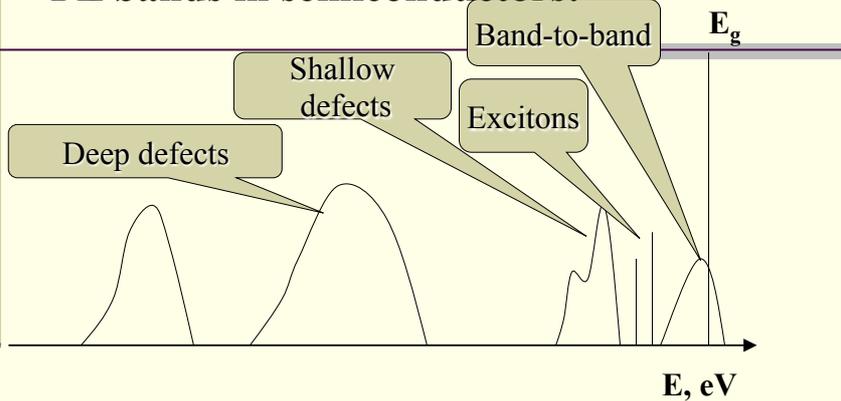
42

## PL measurement software in TUT- LabView project



43

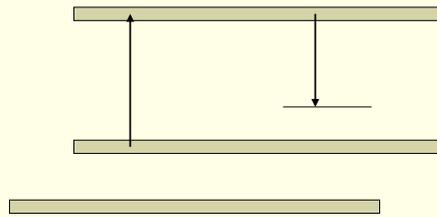
## PL bands in semiconductors:



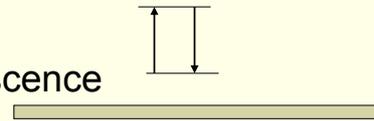
44

## Photolumuminescence in semiconductors

- Recombination luminescence



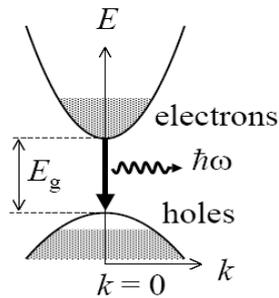
- Center luminescence



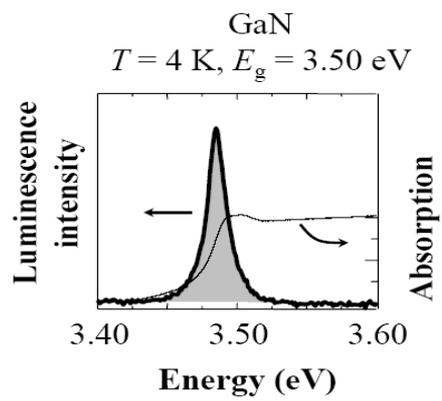
45

## Edge emission

conduction band

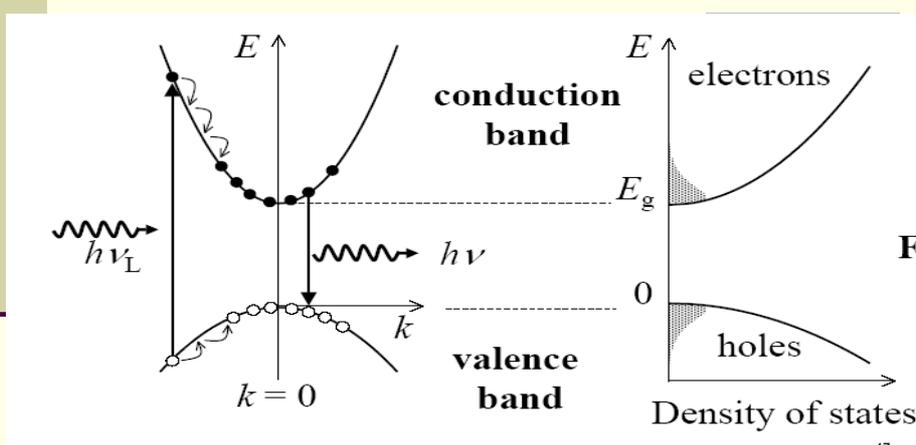


valence band

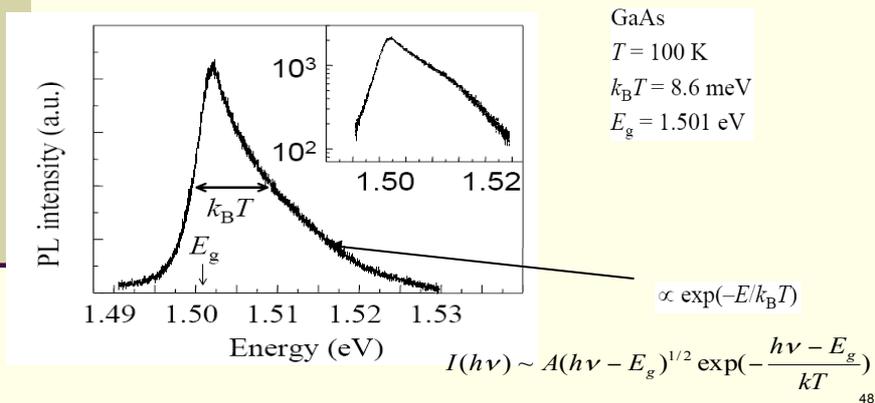


46

## Edge emission



## GaAs edge emission

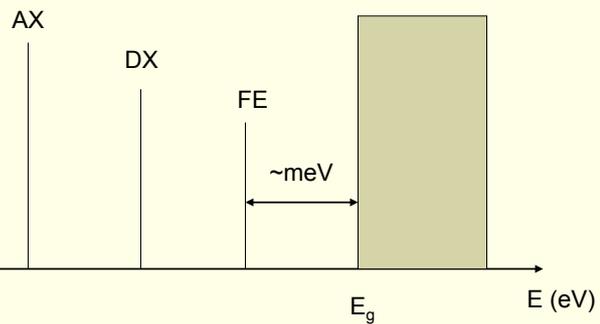


## Edge emission is used in:

- LED (Light emitting diode)
- Semiconductor lasers

49

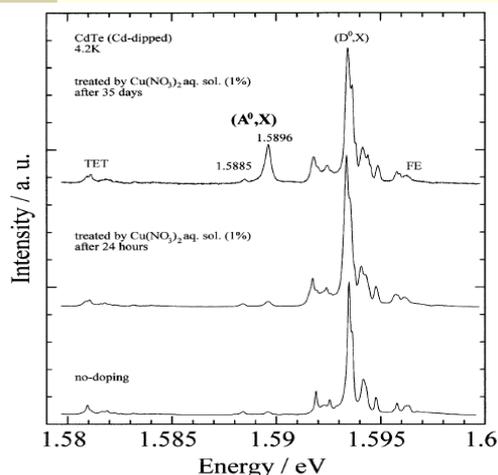
## Excitons



Exciton: electron and hole pair

50

## PL of excitons



S.H. Song et al. / Journal of Crystal Growth 257 (2003) 231–236

CdTe excitons

51

## Excitons in CuInS<sub>2</sub>

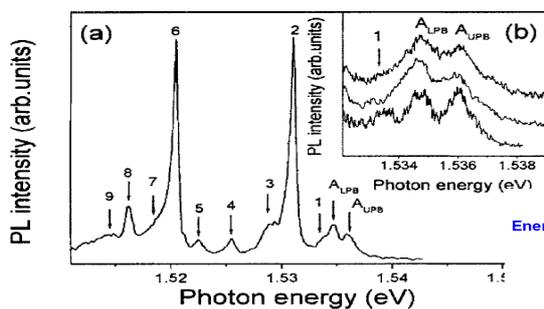


FIG. 2. (a) High-resolution band-edge emission spectra from CuInS<sub>2</sub> single crystals at 4.2 K. (b) The A excitonic region for three different samples; the spectral resolution is about 0.1 meV.

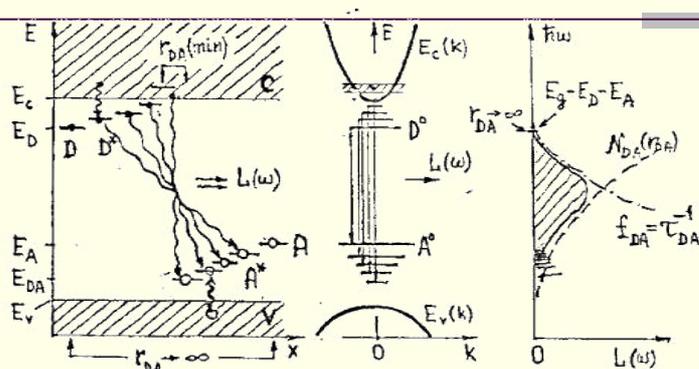
APPLIED PHYSICS LETTERS 88, 011922 (2006)

### Energy of excitons in CuInS<sub>2</sub> single crystals

M. V. Yakushev<sup>1)</sup>  
 Department of Physics, Strathclyde University, G4 0NG Glasgow, United Kingdom  
 A. V. Mudryi and I. V. Victorov  
 Institute of Solid State and Semiconductor Physics, P. Brovki 17, 220072 Minsk, Belarus  
 J. Krustok and E. Mellikov  
 Tallinn Technical University, Ehitajate tee 5, Tallinn 19086, Estonia

52

## Photoluminescence of donor-acceptor pairs



53

## Photoluminescence of donor-acceptor pairs

- Probability of electron (on the donor defect) and hole (on the acceptor defect) recombination:  $W_{DA} = W_0 \exp(-2R/a_0)$
- The PL energy of each DA pair depends on the distance between donor and acceptor  $R$ :

$$h\nu_{DA}(R) = E_g - (E_D + E_A) + \frac{e^2}{\epsilon R}$$

- In case of shallow levels we have a distribution of pairs:

$$N_{DA}(R) = N_D N_A 4\pi R^4 \exp\left(-\frac{4\pi}{3} N_D R^3\right)$$

54

## Photoluminescence of donor-acceptor pairs

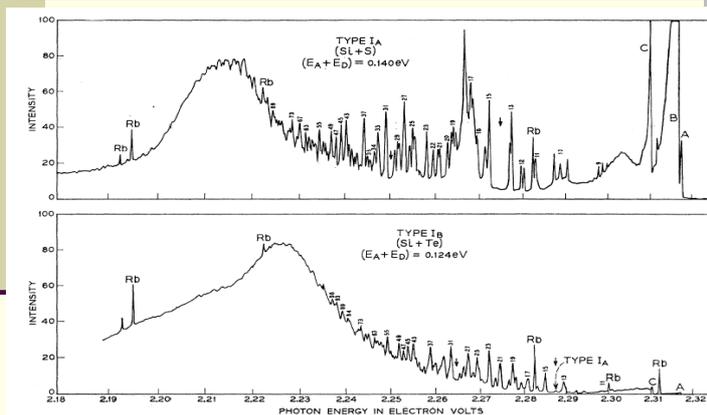


Fig. 2. The photoluminescent spectra (on arbitrary scales) of type  $I_A$  and  $I_B$  crystals taken at 1.6°K. The lines marked Rb are rubidium calibration lines. The small numbers indicate the shell numbers of the pair spectra. A, B, and C are bound exciton lines. The arrows indicate some positions for which  $N(r)=0$ , and mark a gap in the spectra. The type  $I_A$  crystals are grown without the addition of impurities; the  $I_B$  crystals are produced by adding  $I_c$ .

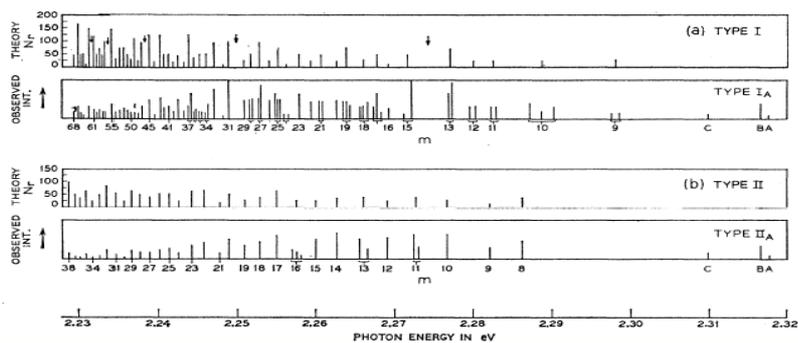
classic work!

DAP in GaP

Phys. Rev. 133,  
1964, p. A269

55

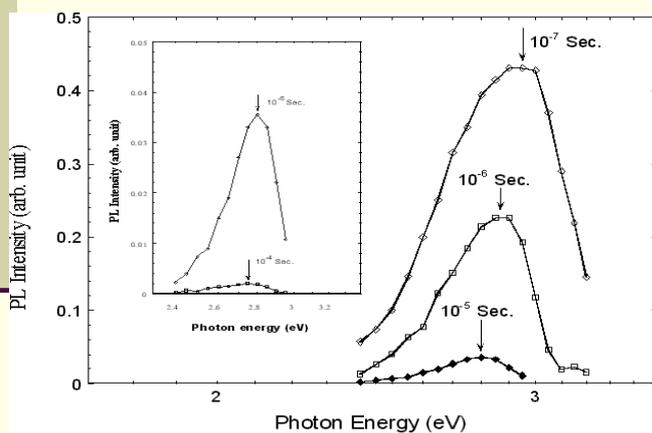
## Photoluminescence of donor-acceptor pairs



DAP in GaP

56

## Photoluminescence of donor-acceptor pairs



**t-shift**

GaN  
*MRS Internet J. Nitride Semicond. Res.* **6**, 12(2001).

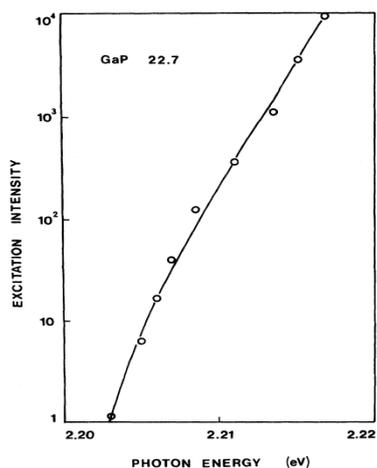
R increases  
 W decreases

t increases  
 $E_{max}$  decreases

Closest pairs will recombine  
**FASTER**

57

## Photoluminescence of donor-acceptor pairs



**j-shift**

*Phys. Rev. B*, **6**,  
 1972, 3072

R increases  
 W decreases

$I_{laser}$  increases  
 $E_{max}$  increases

The recombination of DA pairs having larger distance will start to saturate, because the recombination probability W is small

58

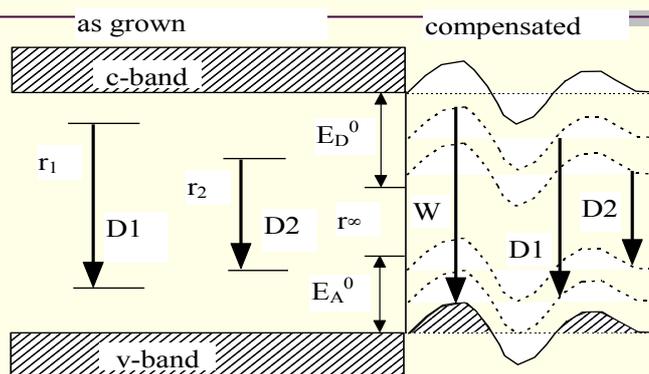
## Deep donor-deep acceptor pairs -> DD-DA pairs.

- DD-DA can be found in different materials.
- Only closest pairs can exist between these deep defects, because of overlap of wave-functions.
- It is possible to find an energy difference between closest pairs:

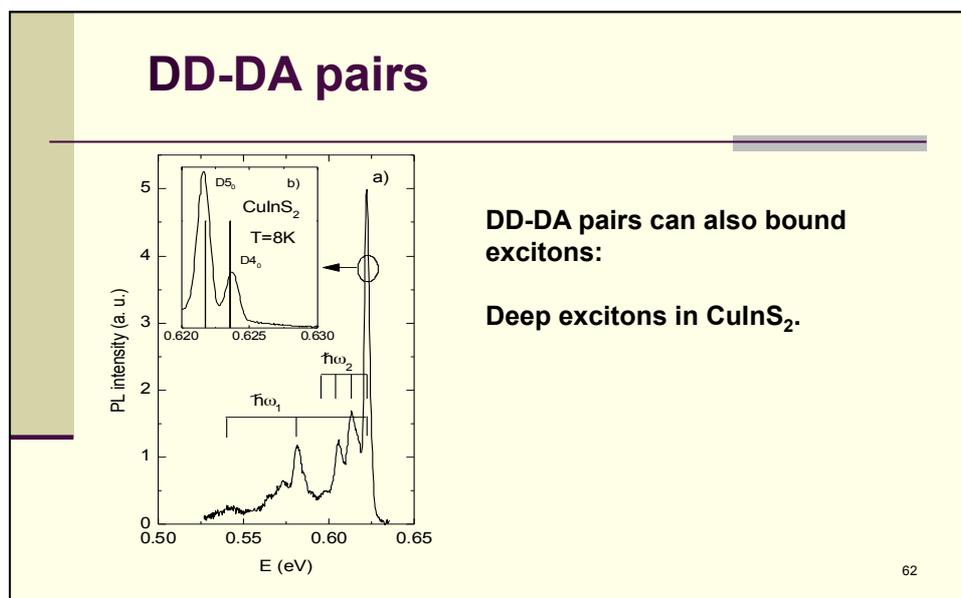
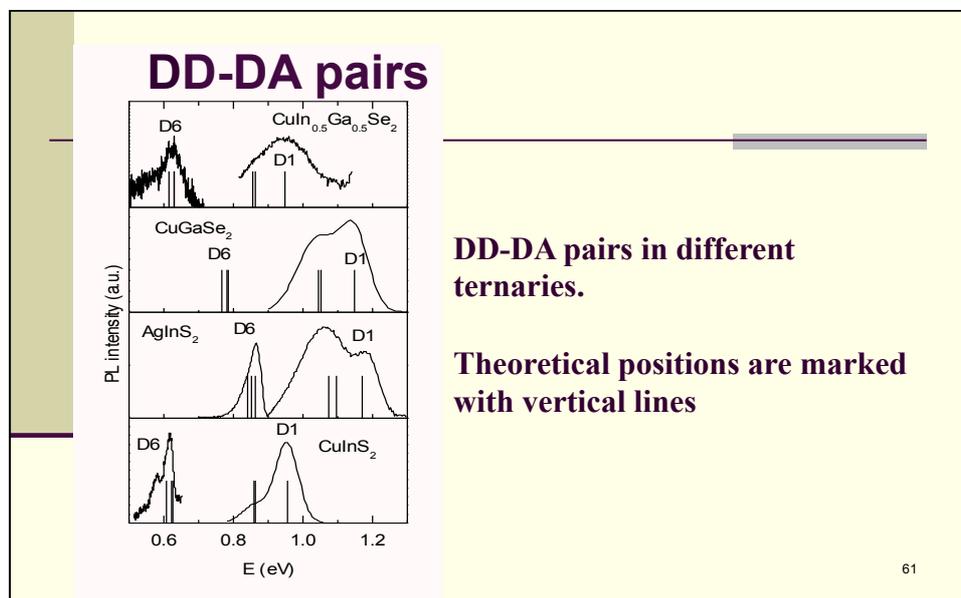
$$\Delta E_{mn} = \frac{e^2}{\epsilon} \left( \frac{1}{r_m} - \frac{1}{r_n} \right)$$

59

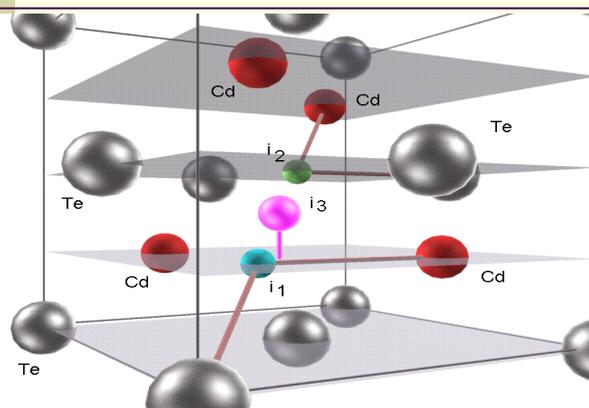
## DD-DA pairs



60



## DD-DA pairs in CdTe



### Different interstitial positions - different PL bands

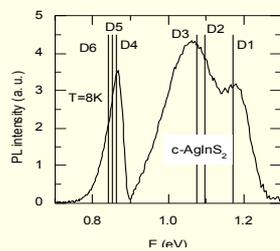
J. Krustok, H. Collan, K. Hjelt, J. Mädasson, V. Valdna.

**J.Luminescence**, v. 72-74, pp. 103-105 (1997).

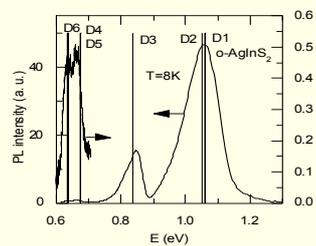
63

## DD-DA pairs in AgInS<sub>2</sub>

### Chalcopyrite

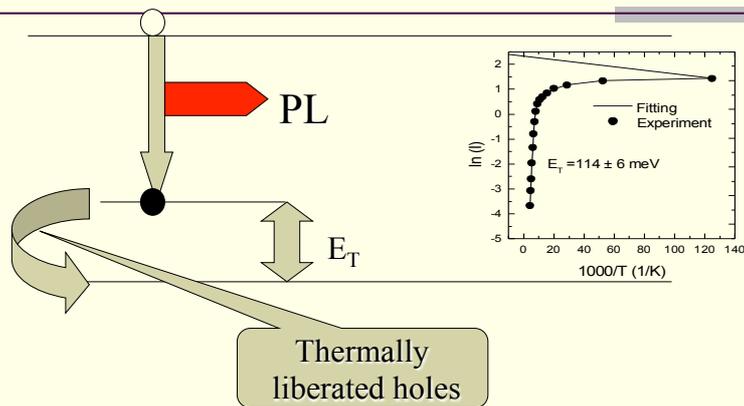


### Orthorhombic



64

## Temperature quenching of PL



65

## Temperature quenching of PL

### □ THEORY:

□ J. Krustok, H. Collan, and K. Hjelt. J. Appl. Phys. v. 81, N 3, pp. 1442-1445 (1997) .

$$I(T) = \frac{I_0}{1 + \varphi_1 T^{3/2} + \varphi_2 T^{3/2} \exp(-E_T / kT)}$$

66

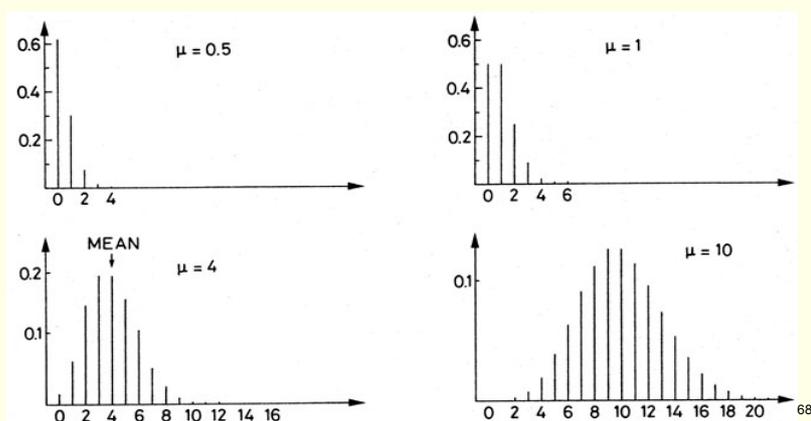
## Shape of PL band

- Theory – Pekar, Huang, Rhys, jt.
- The shape is not easy to calculate
- Simplifications:
  - T=0
  - only one phonon is present and not the phonon spectrum

Then it is possible to find transition probability from each energy level of excited state to each energy level of ground state- all these probabilities follow Poisson distribution

67

## Poisson distribution $P(r) = \frac{\mu^r \exp(-\mu)}{r!}$



## Shape of PL band

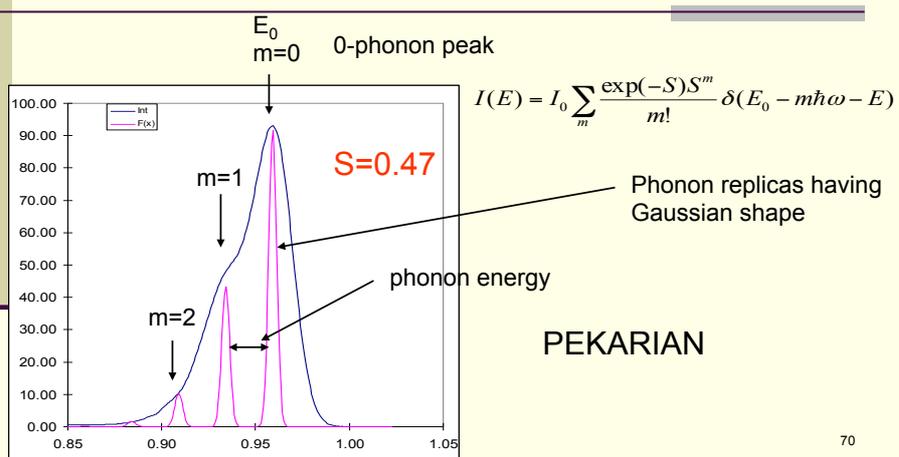
- The theoretical shape of PL band is:

$$I(E) = I_0 \sum_m \frac{\exp(-S)S^m}{m!} \delta(E_0 - m\hbar\omega - E)$$

The shape of each m-th small PL band depends mainly on interactions with acoustic phonons

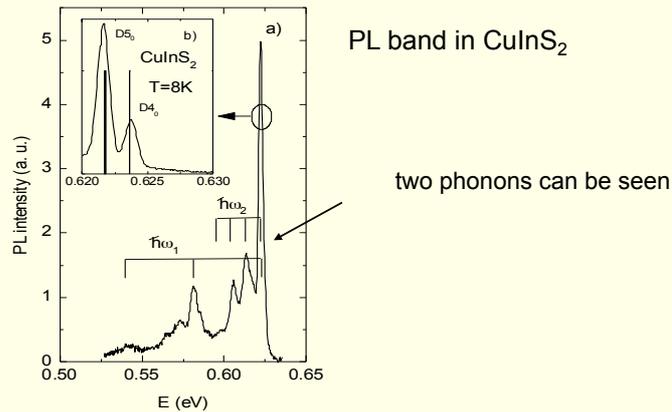
69

## Shape of PL band



70

## Shape of PL band



## Shape of PL band

Gaussian shape:

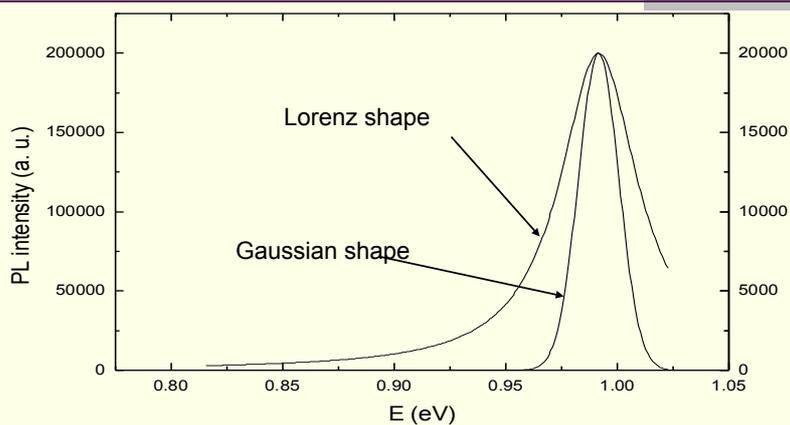
$$I(E) = I_0 \exp\left[-\frac{4 \ln 2 (E - E_{\max})^2}{W^2}\right]$$

If in Pekarian  $S \rightarrow \infty$ , then we also will have a pure Gaussian shape:

$$I(E) = I_0 \exp\left[-\frac{4 \ln 2 (E - E_0 - S\hbar\omega)^2}{8 \ln 2 S (\hbar\omega)^2}\right]$$

72

## Shape of PL band



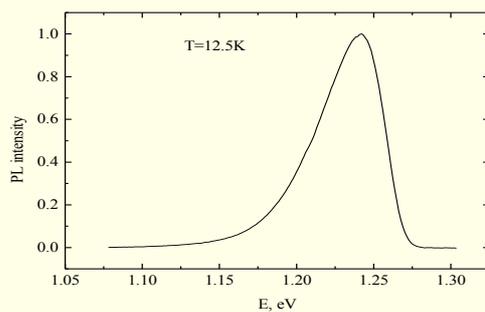
73

## PL of heavily “doped” semiconductors

- Most of ternaries and quaternary compounds are heavily doped, i.e. they have huge amount of defects.
- distance between defects is smaller than the Bohr radius of electrons and holes on defects  $\rightarrow$  heavy doping.
- Edges of conduction and valence bands are curved because of potential fluctuations.

74

## PL of heavily “doped” semiconductors

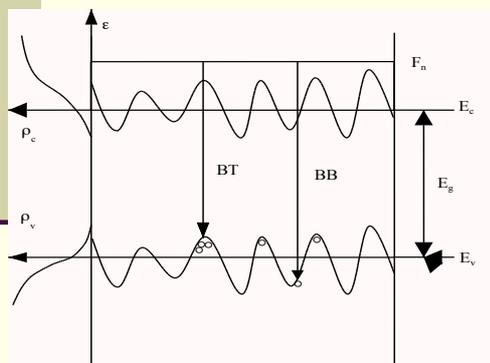


### Typical PL spectrum in $\text{CuInGaSe}_2$

- J. Krustok, H. Collan, M. Yakushev, K. Hjelt. The role of spatial potential fluctuations in the shape of the PL bands of multinary semiconductor compounds. *Physica Scripta*, T79, pp. 179-182 (1999).

75

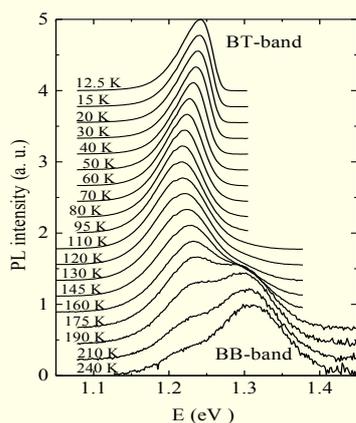
## Theory of heavily doped materials



Theory: Shklovskii, Efros  
Levaniuk, Osipov

76

## Edge emission of $\text{CuInGaSe}_2$

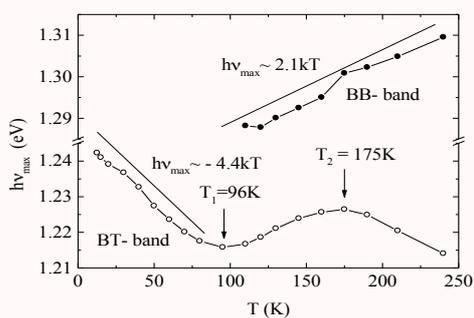


• J. Krustok, H. Collan, M. Yakushev, K. Hjelt. The role of spatial potential fluctuations in the shape of the PL bands of multinary semiconductor compounds. *Physica Scripta*, T79, pp. 179-182 (1999).

### BB and BT bands

77

## Temperature dependence of BB and BT bands

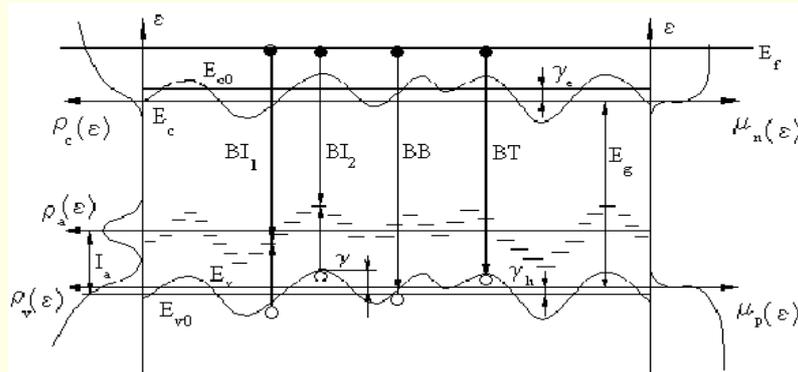


• J. Krustok, J. Raudoja, M. Yakushev, R. D. Pilkington, and H. Collan. *phys. stat. sol. (a)* v. 173, No 2, pp. 483-490 (1999).

• J. Krustok, H. Collan, M. Yakushev, K. Hjelt. *Physica Scripta*, T79, pp. 179-182 (1999).

78

## PL of heavily “doped” semiconductors



79

## PL measurements

- Measure PL spectra
- Spectra fitting with Gaussian function
- Find I<sub>max</sub>, E<sub>max</sub> and W for each PL band

80

# YFR8010

Practical Spectroscopy

## Spectral Response of Solar Cells

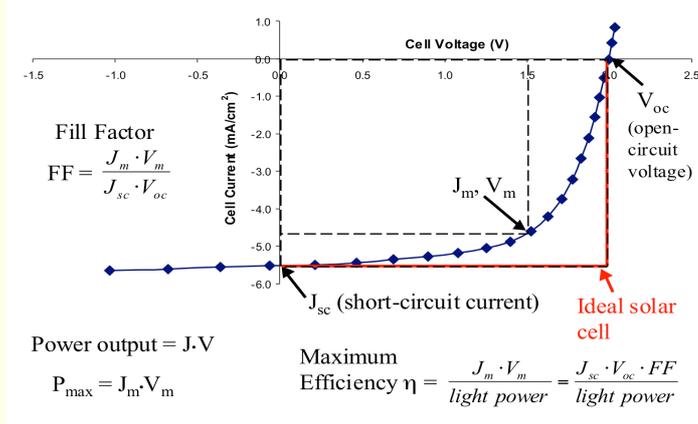
Professor Jüri Krustok

[Juri.Krustok@ttu.ee](mailto:Juri.Krustok@ttu.ee)

<http://staff.ttu.ee/~krustok>

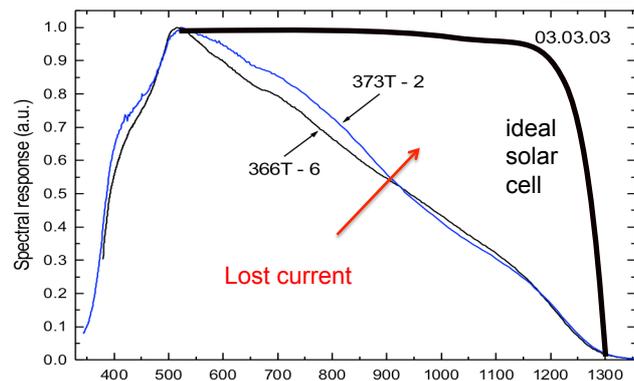
81

## I-V Curve of Solar Cell



82

## Spectral Response



83

## Spectral Response- theory

### EXTERNAL QUANTUM EFFICIENCY

$$QE(\lambda) = k [1 - \exp(-L_{eff}\alpha(\lambda))]$$

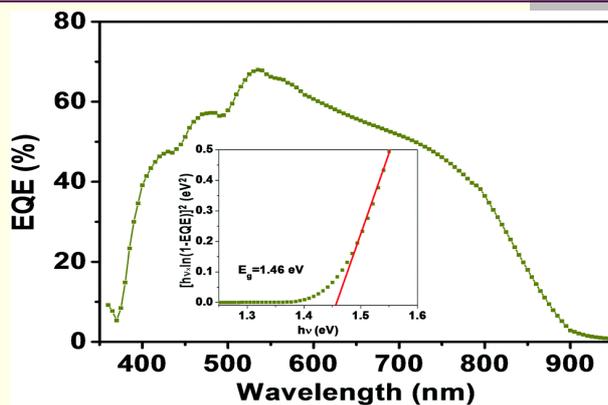
$$L_{eff} \approx L_{diff} + w_a$$

$$\alpha(E) = A(E - E_g)^{\frac{1}{2}},$$

$$EQE \approx K\alpha L_{eff} \approx A(E - E_g^*)^{1/2} / E$$

84

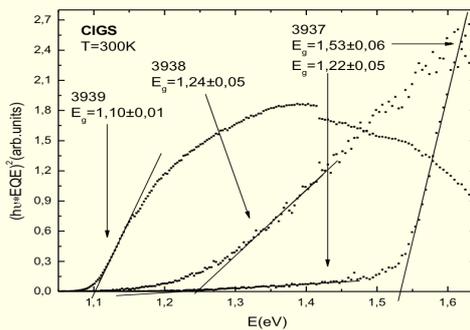
## Finding $E_g$



85

## Finding $E_g$

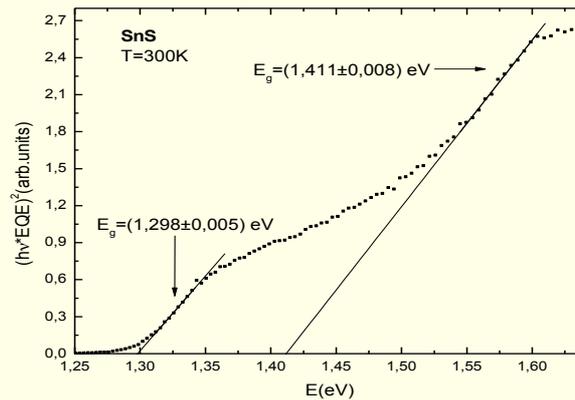
$$(QE * E)^2 \approx A^2 (E - E_g)$$



$$EQE \approx K \alpha L_{eff} \approx A (E - E_g^*)^{1/2} / E$$

86

## Finding $E_g$



87

## What to do?

- Measure EQE (E) spectrum for solar cell
- Draw  $(EQE \cdot E)^2$  vs E curves
- Calculate  $E_g$

88

## Meeting point

---

U06 first floor  
end of the building  
room 156

Phone: +372 5236945

89