

Sveučilište u Zagrebu
Prirodoslovno-matematički fakultet
Fizički odsjek

TRANSPORTNA I MAGNETSKA SVOJSTVA PANI-HCl ORGANSKOG VODIČA

PLAN IZLAGANJA:

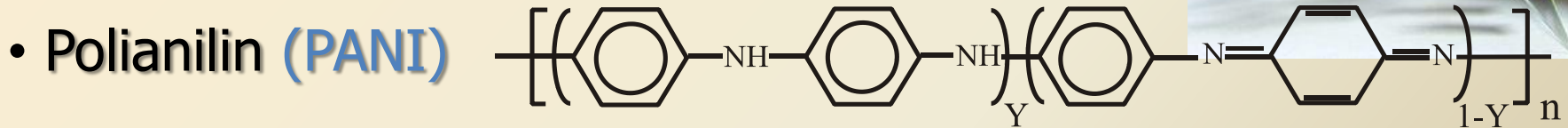
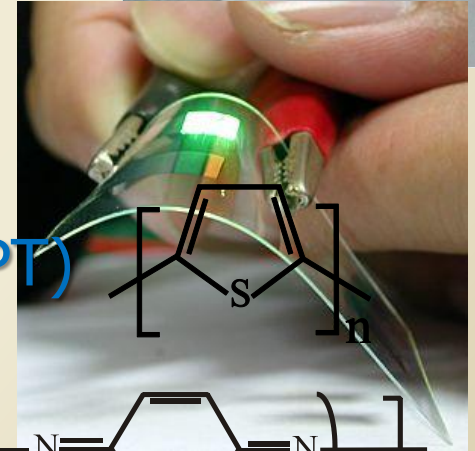
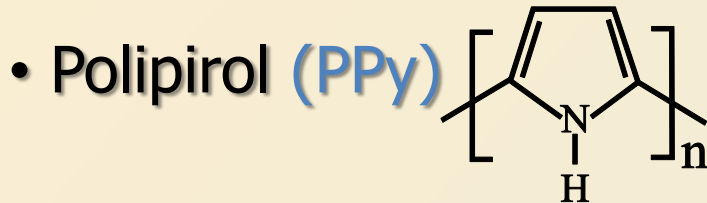
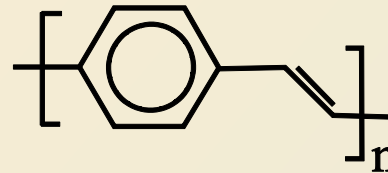
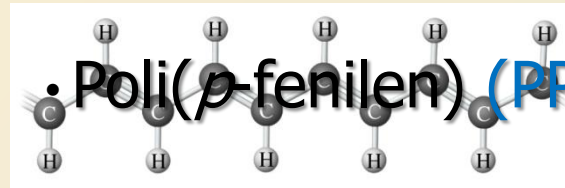
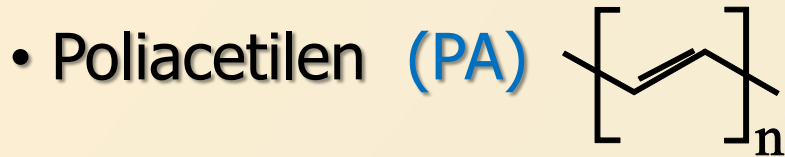
- Kratko upoznavanje s vodljivim polimerima
 - Modeli transporta naboja u jako neuređenim sustavima (Andersonova lokalizacija, VRH – modeli)
 - Sinteza polianilina, priprema uzoraka
- Eksperimentalni rezultati i njihova diskusija
- Zaključak

Motivacija za proučavanje polianilina

- Svi koraci u vlastitim rukama, od sinteze do pisanja članka
- Općeniti prioriteti su:
 - nizak stupanj nereda
 - što veća σ_{RT}
- Naš smjer: Razumjet sustav na mikroskopskoj razini
 - što jednostavniji sustav, PANI-HCl
 - snažan nered, jaka lokalizacija
 - utjecaj dopiranja na $\sigma(T)$, $\chi(T)$ i morfologiju

Kratko upoznavanje s vodljivim polimerima

- Početak, krajem 1970-ih



- i još mnogo drugih...
- Tehnološki vrlo zanimljivi materijali

“ fleksibilna elektronika ”



Kemijske veze, dopiranje i električna vodljivost

• sp^2p_z elektronska hibridizacija

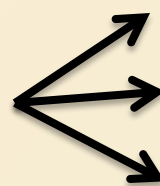


σ kovalentne veze (~ 10 eV)

π kovalentne veze (~ 1 eV)

- Niske energije ionizacije

DOPIRANJE



Oksidacija (oduzimanje elektrona) p -tip

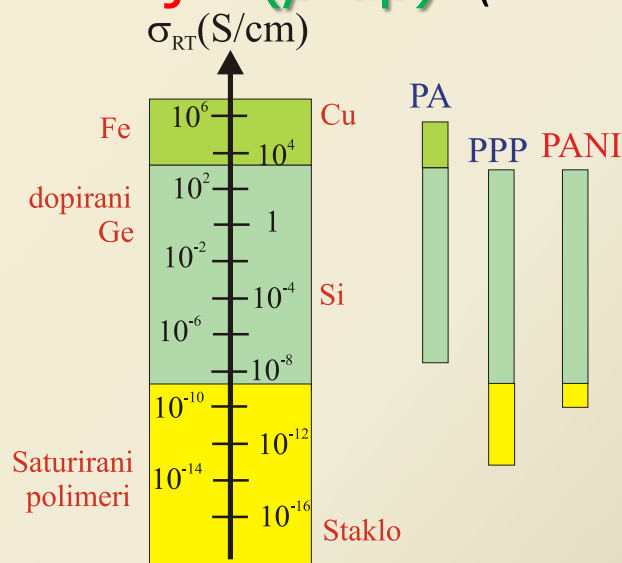
Redukcija (dodavanje elektrona) n -tip

Protonacija (p -tip) (nema promjene broja elektrona)



Nemetali ili metali

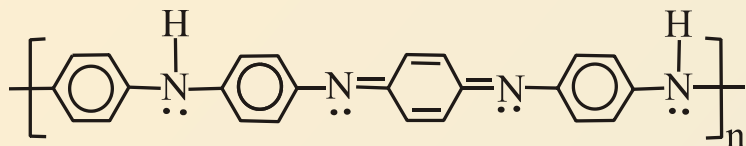
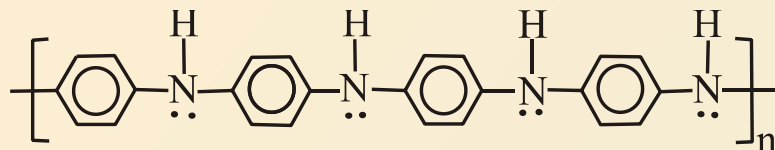
$\ll (\ll) 1\%$



Porast od 10 redova veličine

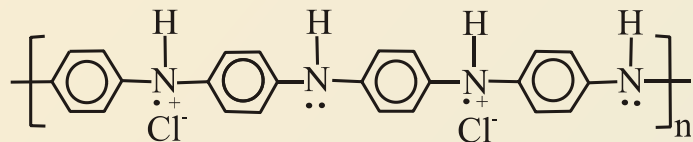
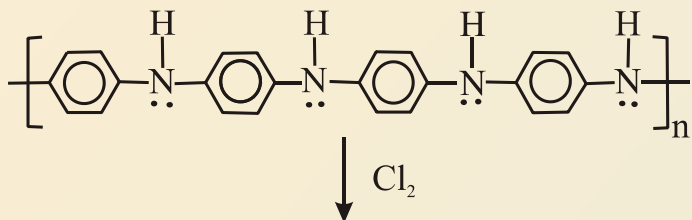
Kemijska struktura polianilina (PANI)

3 stabilna oblika



Dopiranje:

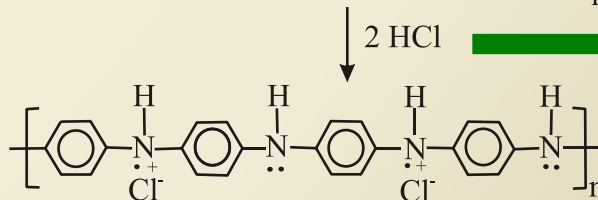
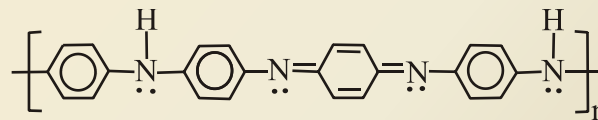
Redoks dopiranje (*p*-tip)



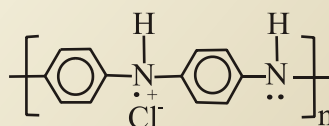
Leukoemeraldinska baza

Emeraldinska baza

Pernigranilinska baza
Protonacija (*p*-tip)



Bilo koja
kiselina



Emeraldinska
sol

Transport naboja 1/3 (u polianilinu)

3D Sustav načinjen od 1D elemenata

“Morfologija kuhanih špageta”



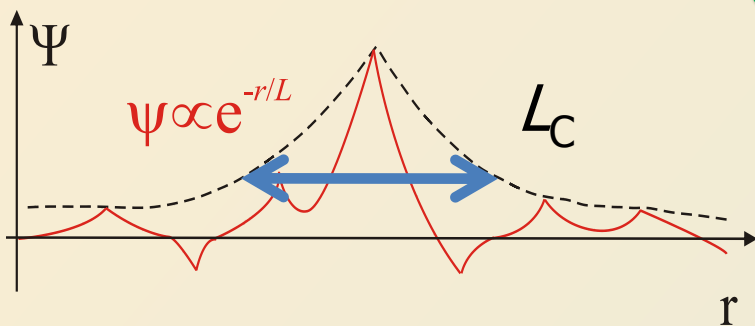
Prekrivanje valnih funkcija $t_{||} \gg t_{\perp}$

Velik stupanj nereda – defekti, distorzija lanaca.....

(jaka) Lokalizacija nosilaca naboja

Andersonova lokalizacija

Izolator $\sigma(T \rightarrow 0) \rightarrow 0$



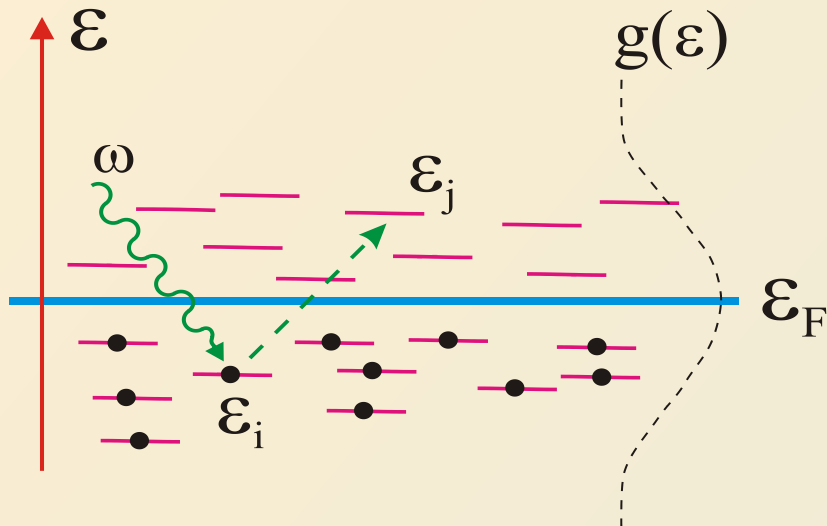
Fononi omogućuju transport naboja

Transport naboja 2/3 (VRH transport)

Transport naboja

Fononski potpomognutim preskocima između lokaliziranih stanja

N. F. Mott → Variable-range hopping (VRH)



$$I_{ij} \begin{cases} \propto e^{-r_{ij}/L} \\ \propto e^{-\epsilon_{ij}/k_B T} \end{cases}$$

$$\ln \sigma \propto -[T_0/T]^\alpha$$

$$\alpha < 1$$

- Sporije nego aktivacijsko

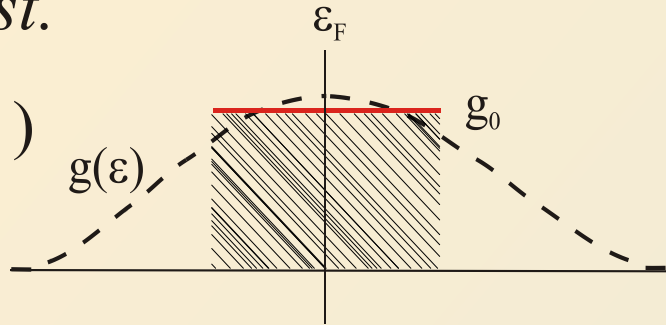
Mott-VRH

- Jednočestična gustoća stanja

$$g(\varepsilon) = \text{const.}$$

$$\alpha = 1/(1+d)$$

$$d = 2, 3$$



$$d=3 \quad \text{Ln } \sigma(T) \propto -[T_0/T]^{1/4}$$

Nema dugodesežne
Coulombove interakcije

$$V(r)$$

Kvazi-1D VRH

$$t_{||} \gg t_{\perp}$$

$$g(\varepsilon) = \text{const.}$$

$$\alpha = 1/2$$

$$\text{Ln } \sigma(T) \propto -[T_0/T]^{1/2}$$

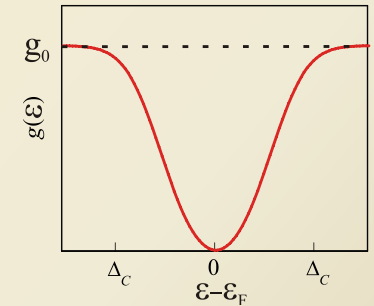
Efros-Shklovskii VRH

- Coulombova interakcija

$$g(\varepsilon) \propto (\varepsilon - \varepsilon_F)^2$$

$$\alpha = 1/2$$

$$d = 2, 3$$



$$\text{Ln } \sigma(T) \propto -[T_0/T]^{1/2}$$

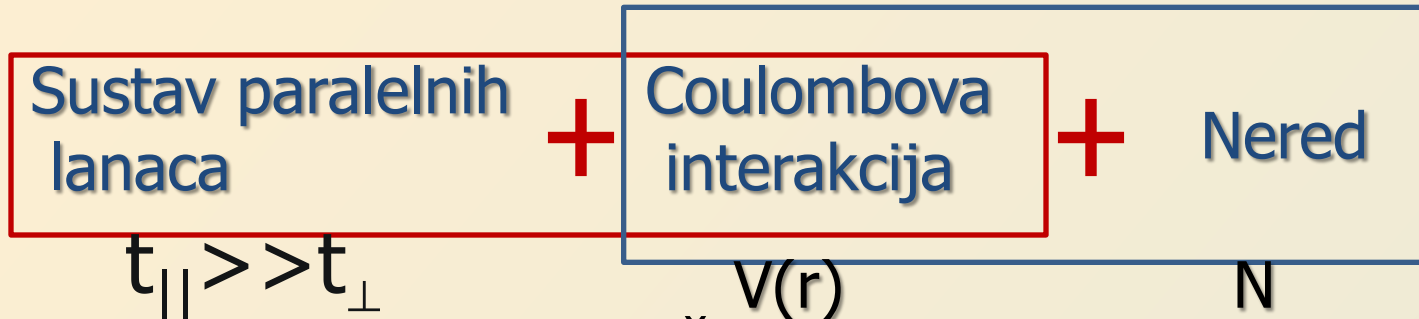
- Osiromašenje u $g(\varepsilon)$ oko E_F

Transport naboja 3/3

(FTS-VRH transport)

Fogler, Teber i Shlovskii (FTS) Proširenje kvazi-1D VRH modela

PRB **69**, 035413 (2004)



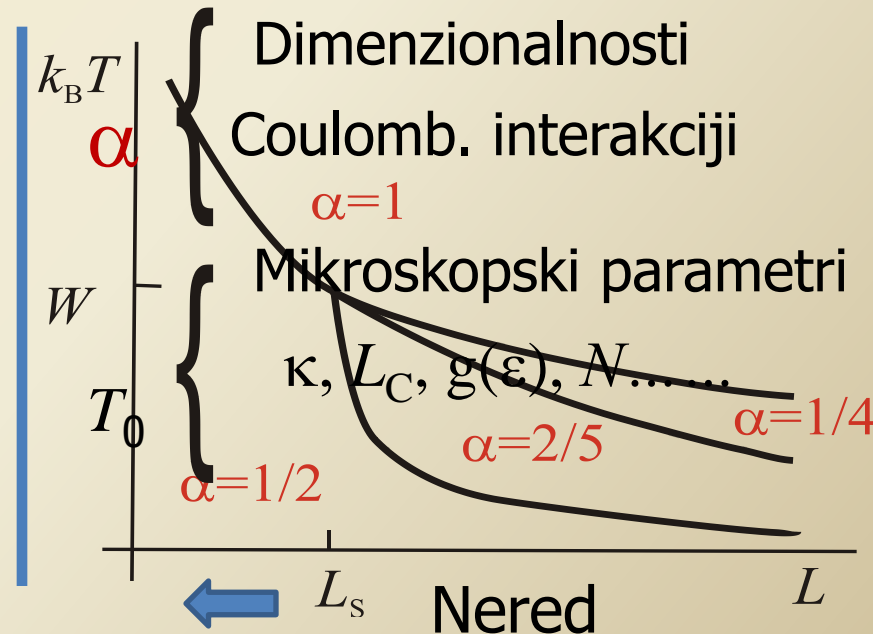
Mott – Anderson izolator

Dovoljno jako međulančano vezanje: **efektivno 3D**

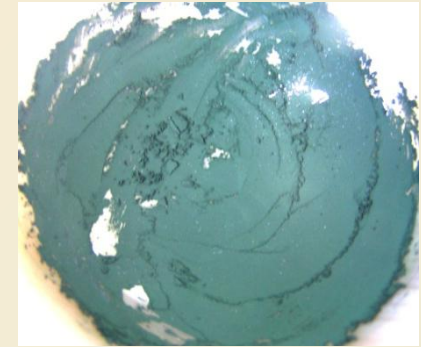
$$g(\varepsilon) \propto |\varepsilon - \varepsilon_F|^\mu \quad \leftarrow V(r) + \text{Nered}$$

$$\ln \sigma \propto -[T_0/T]^\alpha$$

$$\alpha = \frac{1 + \mu}{1 + \mu + d} = 1, 1/4, 1/2 \text{ i } \boxed{2/5}$$



Priprema uzoraka



Uzorci – pripremljeni prešanjem PANI praha

Strukturna mjerenja



8 mm x 5mm x 1mm

Transportna mjerenja

Magnetska mjerenja

5mm x 4mm

Mjerne metode

Elementna analiza, raspršenje protona

Rentgenska difrakcija

Transportna mjerenja $\sigma(T)$ i $\sigma(T, B)$ CCR, ^4He kriostat, 8 T magnet

Magnetska mjerenja $M(B, T)$ i $\chi(T)$

Rezultati mjerenja

Uzorci PANI-HCl:

Dobiveno direktno iz sinteze

- Potpuno dopiran
 - Najviša σ_{RT}
- ~ 300 S/m

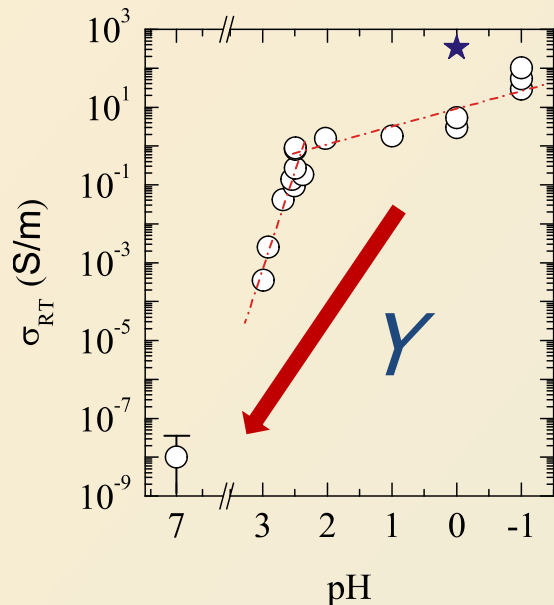
Kontrolirano dopiranje

- Potpuno dopiran \rightarrow Nedopiran

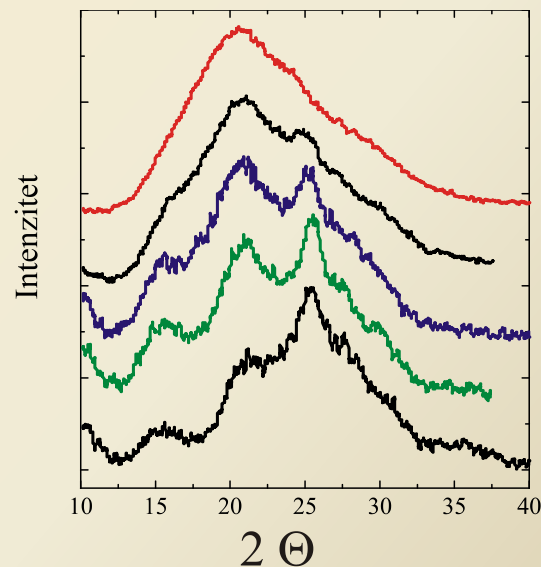
σ_{RT}
<100 S/m

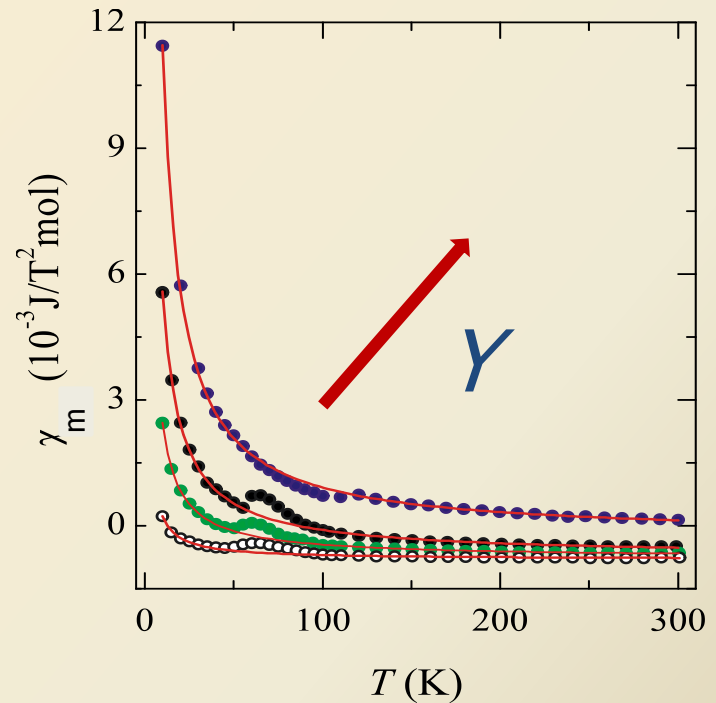
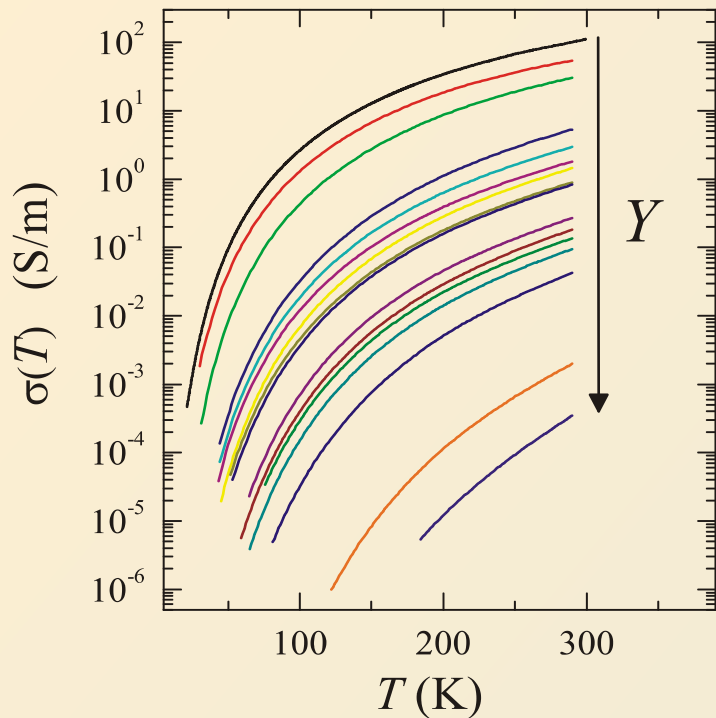
10 redova veličine
razlike u σ_{RT}

- Niža razina nereda



- Snažniji nered, ovisi o dopiranju





- Izolatorsko ponašanje $\sigma(T)$
- Vodič – izolator prijelaz
- Termalno (fononski) induciran transport naboja

$T < 100\text{K}$

- Curiev doprinos, dominantan

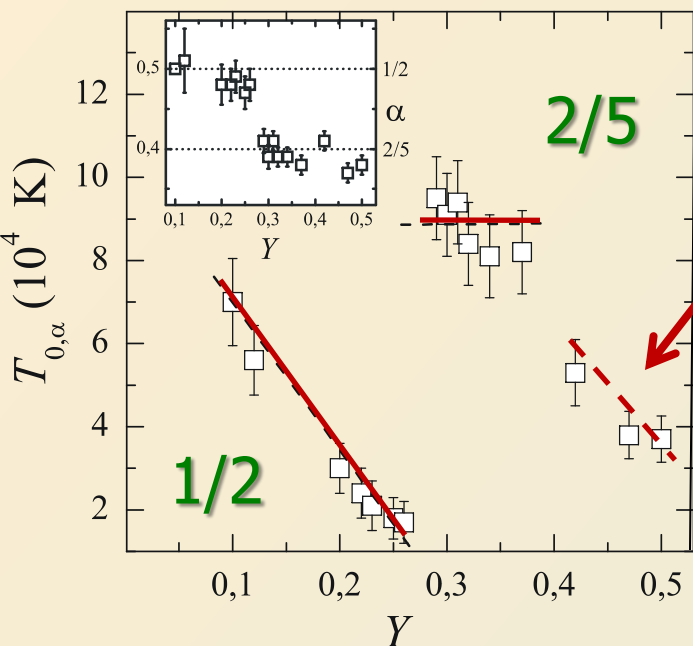
$$\chi_m = \chi_{\text{dija}} + \chi_{\text{para}} + C/T$$

Transport naboja 3/3

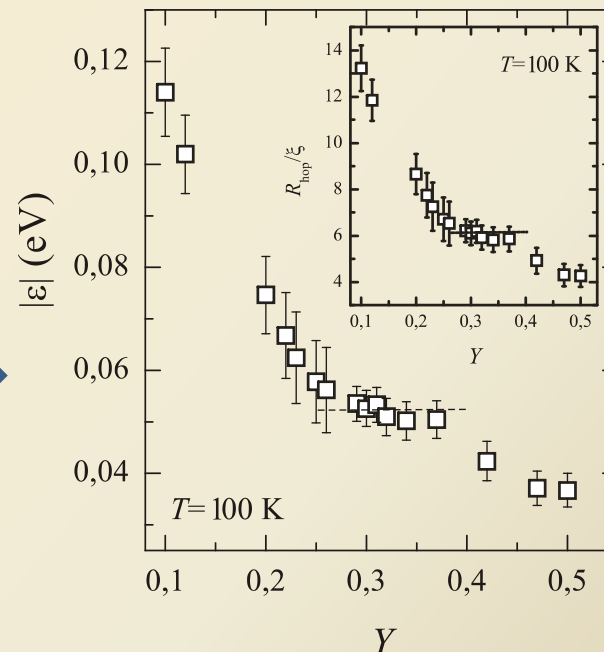
Parametri

- Parametar $T_0 \rightarrow \text{Ln} \sigma \propto -[T_0/T]^\alpha$

Niskotemperaturne
vrijednosti



$$T_0 \propto 1/\kappa$$



Srednja duljina preskoka $R_{\text{hop}} > L_C$

Energijski interval $|\epsilon| < 2\Delta_C$

Magnetootpor $L_C \sim 1$ nm

Zaključak

- Pronađeno je $\alpha=2/5$, preko velikog broja uzoraka
- Parametar α poprima vrijednosti $1/2$, $1/4$, 1 i $2/5$
(ovisno o T i Y)
- Vrlo dobro slagane transportnih rezultata s **3D FTS-VRH** modelom
- Dopiranje Y utječe na broj nosioca naboja, ali i nered
 - Podudaranje promjena $\chi(T)$ i $\sigma(T)$

Sugerira povezanost
nosioca naboja i spina