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Frédérique Ducroquet, Louis Grenet, Raphaël Fillon, Henri Mariette. Potential fluctuations on CZTSSe solar cells admittance. 29th International Conference on Defects in Semiconductors, Jul 2017, Matsue, Japan. hal-01983597

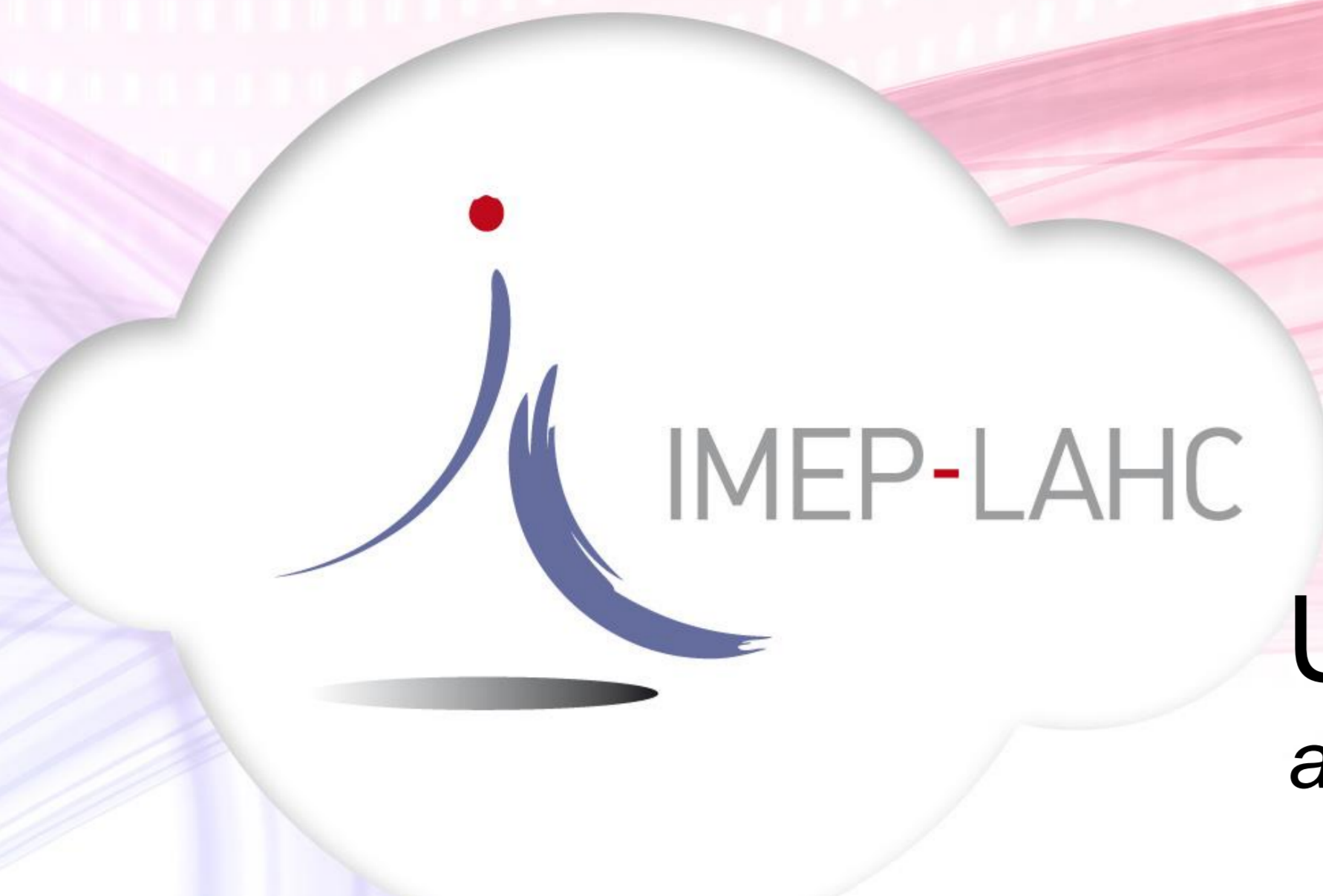
HAL Id: hal-01983597

<https://hal.science/hal-01983597>

Submitted on 5 Feb 2019

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Potential Fluctuations on CZTSSe Solar Cells Admittance

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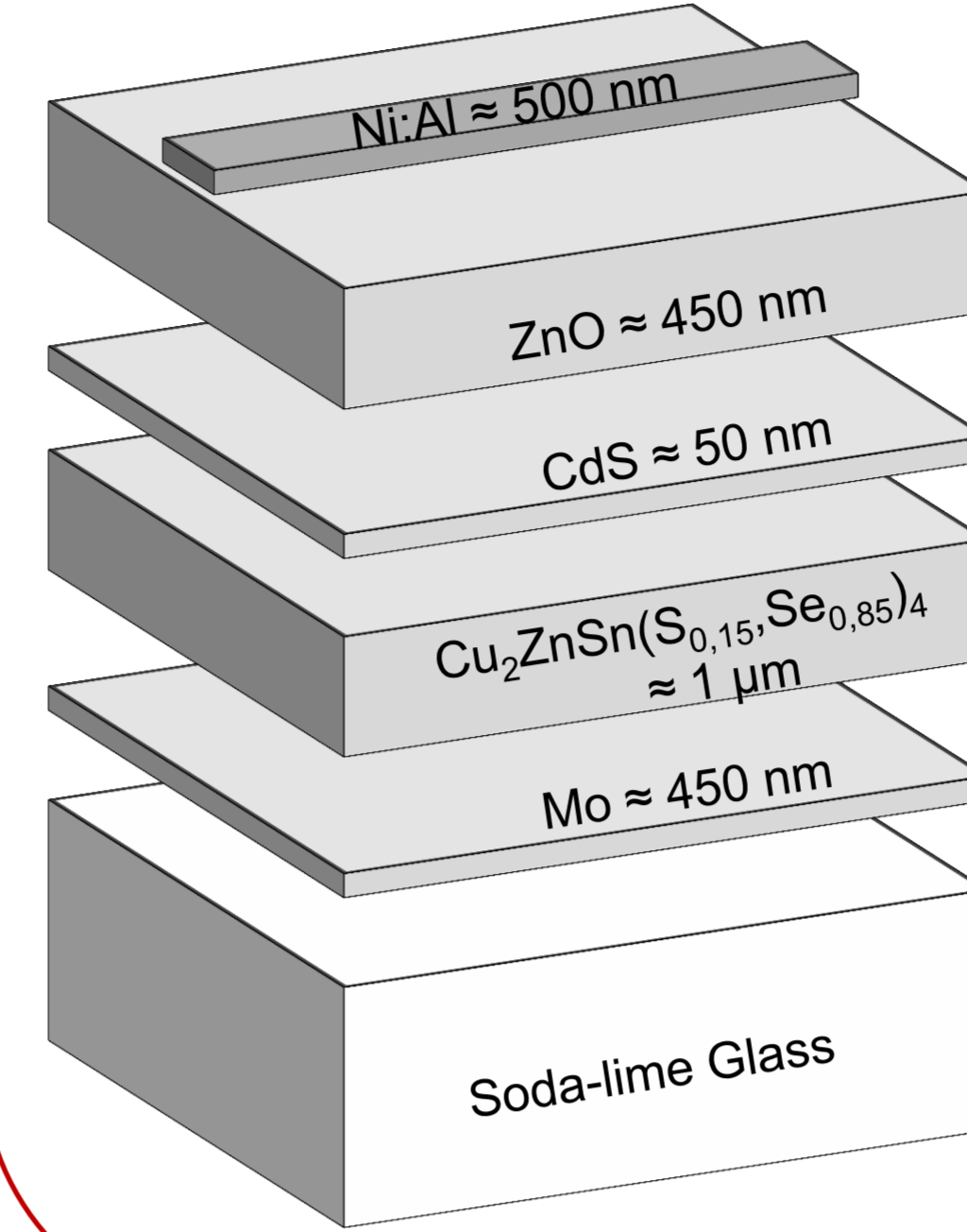
1 – Context

- Low V_{oc} on CZTSSe solar cells \Rightarrow role of point defects and potential fluctuations suggested but not clearly established
- Density Functional Theory¹ $\Rightarrow V_{Cu}$ and Cu_{Zn}
 - create acceptor levels
 - are among defects with the lowest formation energy
 - may be stabilized by the formation of neutral defect complexes: $[Cu_{Zn}+Zn_{Cu}]$, $[V_{Cu}+Zn_{Cu}]$, $[Cu_{Zn}+Sn_{Zn}]$

Objectives:

- Influence of potential fluctuations:
 - on defect analysis
 - on electrical transport

2 – Solar cell structure



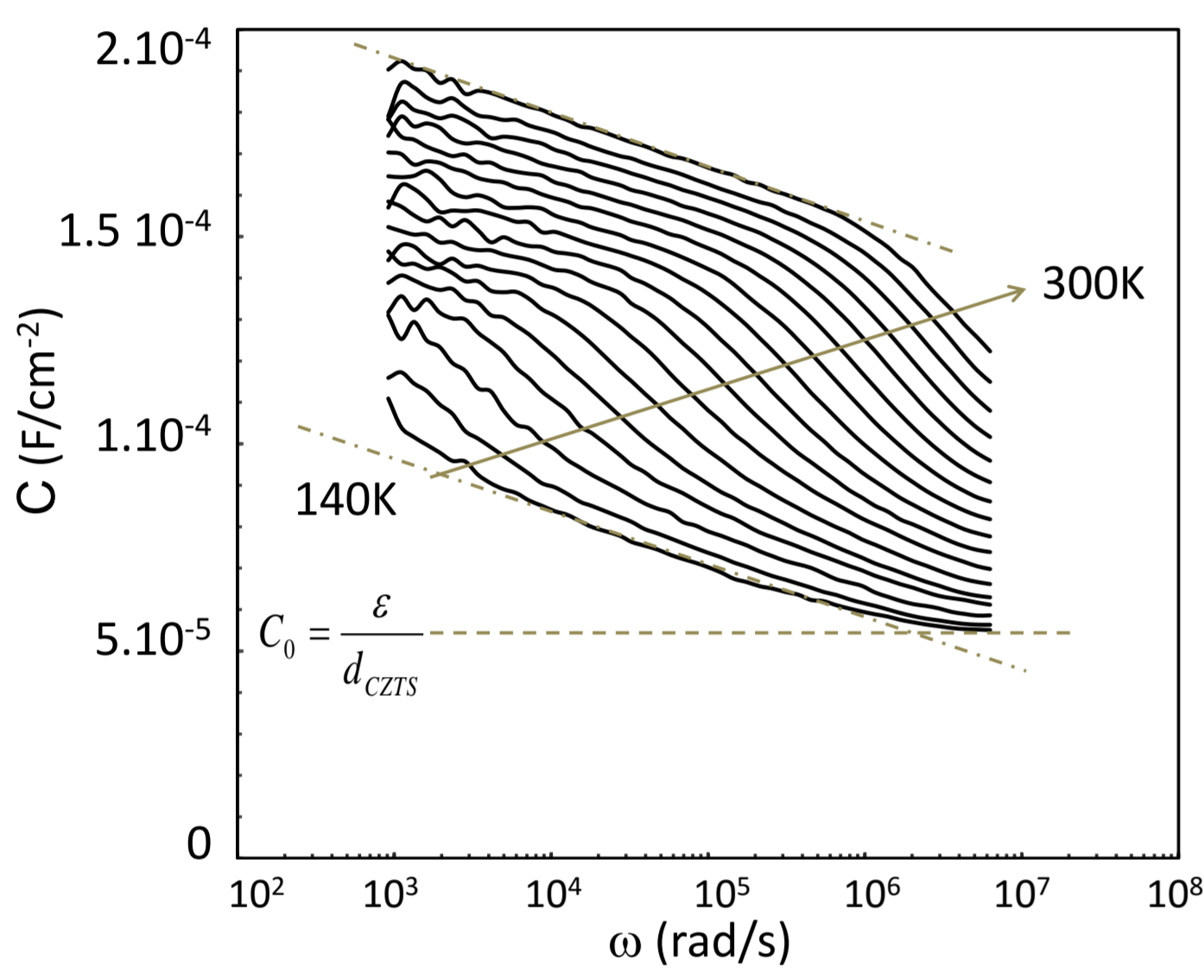
- Two steps process²:
 - Precursors deposition: ZnS by sputtering, Cu/Sn by electron beam evaporation
 - Selenization: annealing under Se vapor

V_{oc} (V)	J_{sc} (A.cm ⁻²)	FF	η (%)
~ 0.33-0.38	~ 0.03	50	~ 5.3-6.6

Experiment:

Admittance spectroscopy @ 0V from 140K to 300K, 100Hz to 1MHz

3 – Admittance measurement: $C(\omega)$



One capacitance step: response of a deep acceptor level at $E_{aexp} = E_v + (0.2 \pm 0.03)eV$ not observed on G/ω spectrum
At low temperature, geometrical capacitance value \Rightarrow CZTSSe absorber fully depleted

\Rightarrow can explain the strong increase of the series resistance at low temperature generally observed on CZTSSe solar cells.

4 – Admittance modelling

- **plane capacitor:**³ $C_{ac}(x, \omega) = \frac{\delta\sigma(x, \omega)}{\delta\psi(x, \omega)} = \frac{\varepsilon \delta\mathcal{L}(x, \omega)}{\delta\psi(x, \omega)}$
- **one deep acceptor level:** small signal Poisson equation including the deep level ac response:

$$\frac{d^2 \delta\psi}{dx^2} = -\frac{\delta\rho(x)}{\varepsilon} = -q \frac{\delta p(x) - \delta n(x) - N_{Ta}(x) \delta f(x)}{\varepsilon}$$

- **potential fluctuations:**

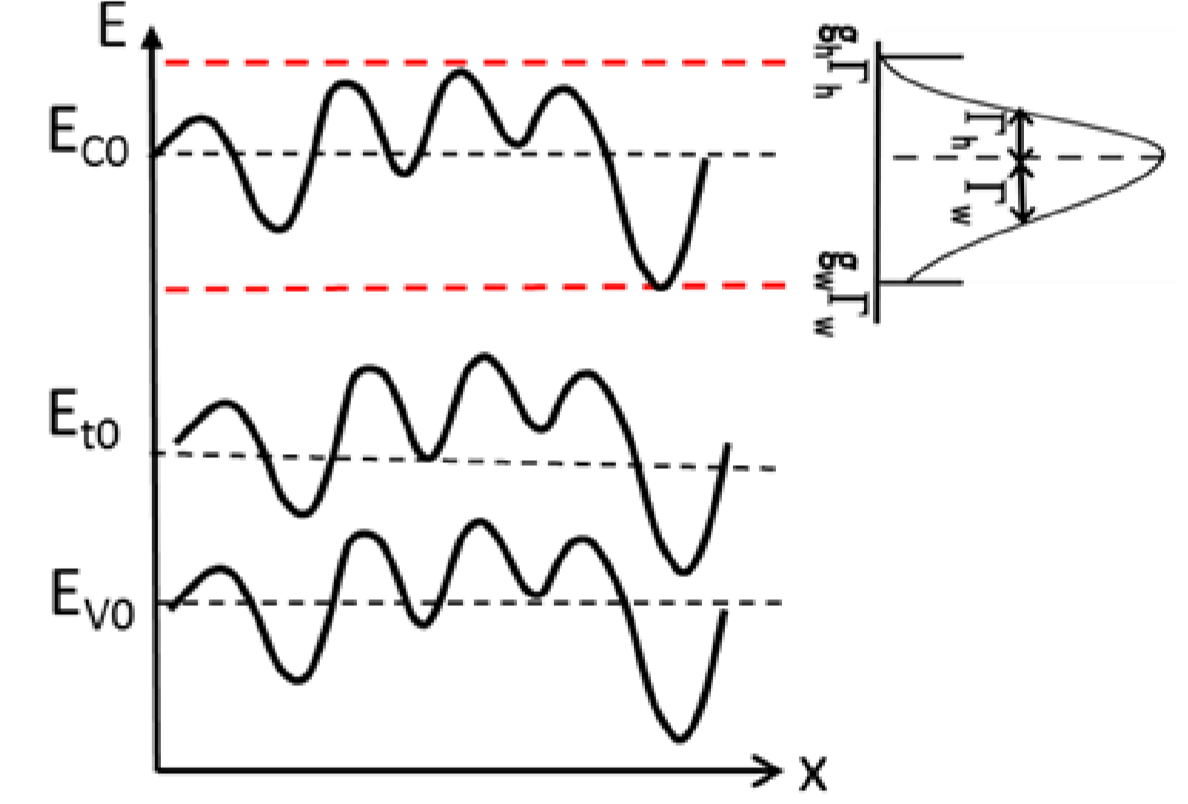
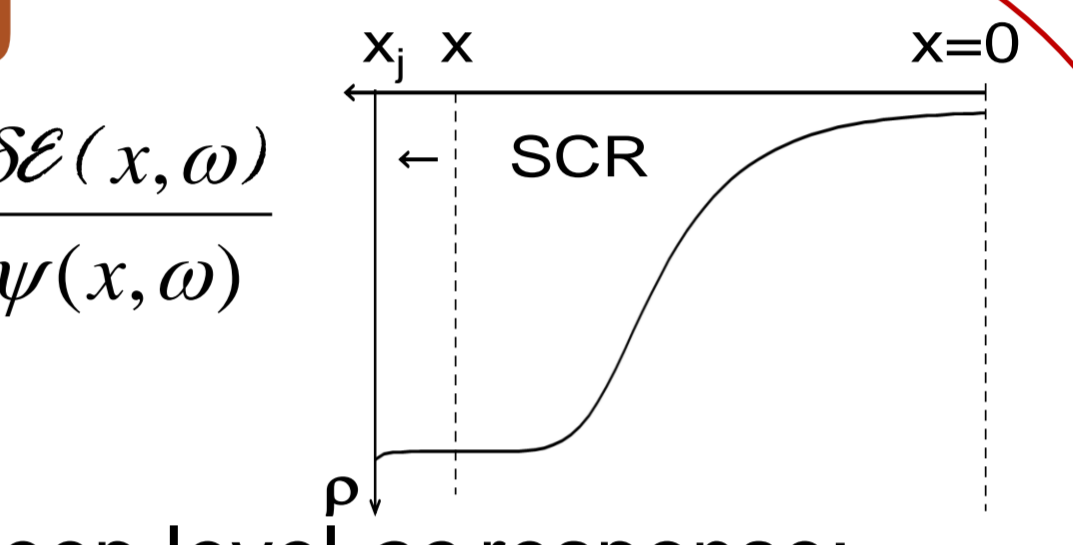
Truncated and asymmetric Gaussian distribution⁴

Hole concentration in valence band:

$$p = cste \int_{E_{v0}-g_w\Gamma_w}^{E_{v0}+g_v\Gamma_h} \sqrt{E_v - E} [1 - f(E)] dE \exp\left(-\frac{(E_v - E_{v0})^2}{\Gamma^2}\right) dE_v$$

Ionized defect concentration:

$$N_{Ta}^- = cste \int_{E_{v0}-g_w\Gamma_w}^{E_{v0}+g_v\Gamma_h} \left[\frac{1}{1 + g \exp\left(\frac{E_{ta} - E_F}{kT}\right)} \right] \exp\left(-\frac{(E_{ta} - E_{ta0})^2}{\Gamma^2}\right) dE_{ta}$$



Complex occupation function defined for each elemental energy ζ :

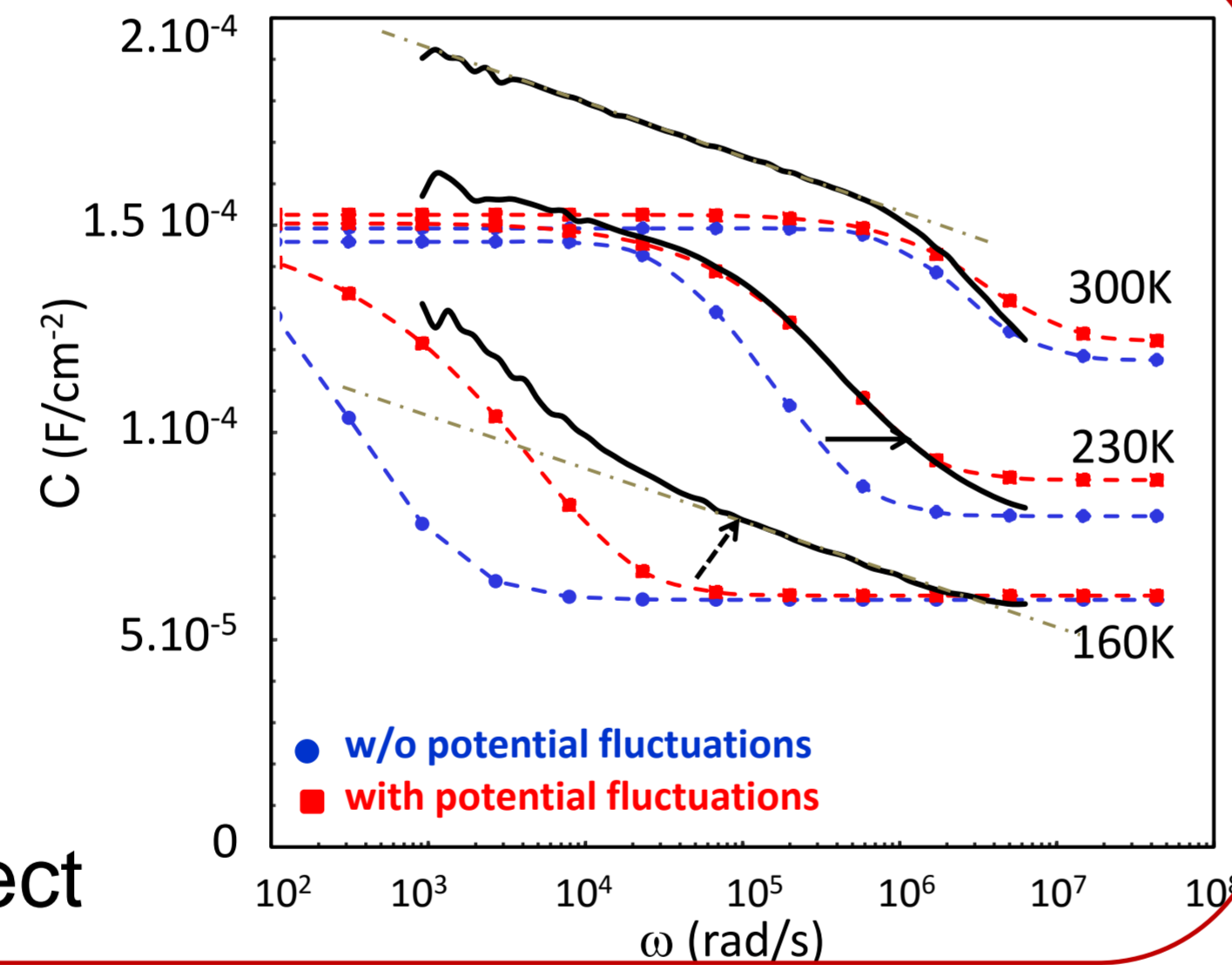
$$\delta f(x, \zeta) = \frac{\tau(x, \zeta) c_n(\zeta) [1 - f(x, \zeta)] \delta n(x) - c_p(\zeta) f(x, \zeta) \delta p(x)}{1 + j\omega\tau(x, \zeta)}$$

Admittance expression:

$$\tilde{Y} = G + j\omega C \equiv j\omega \tilde{C}_{\psi_0}(x, \omega) = j\omega \frac{\delta \tilde{Q}_T(x, \omega) + \varepsilon \delta \tilde{E}(x_{bulk}, \omega)}{\delta \tilde{\psi}(x, \omega) - \delta \tilde{\psi}(x_{bulk}, \omega)}$$

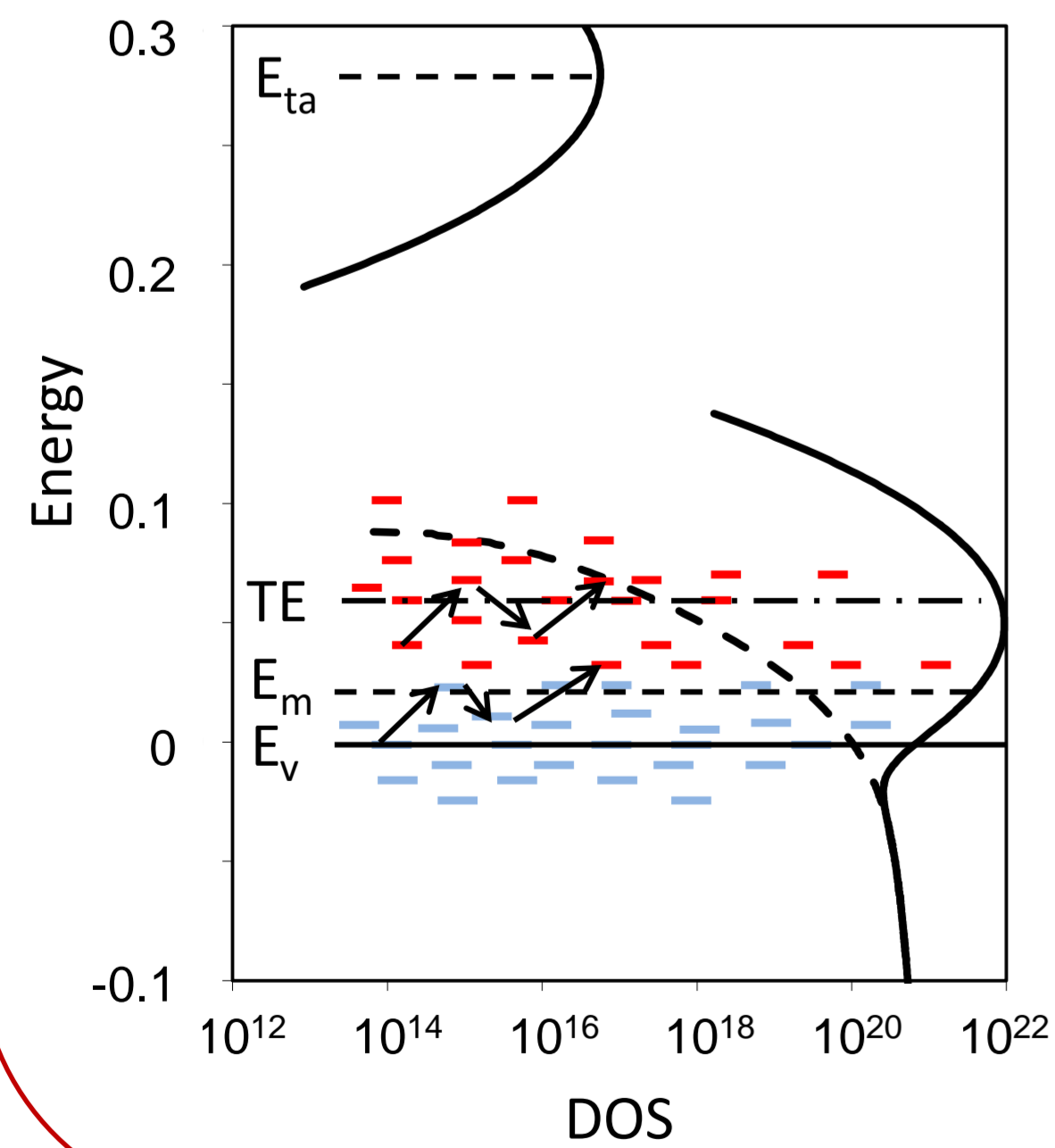
5 – $C(\omega)$ fit

- Potential fluctuations explain the stretching of the capacitance step
- E_{afit} (0.28eV) $>$ E_{aexp} due to PF
- Continuous capacitance variation superimposed to the defect related step not reproduced by the model \Rightarrow associated with ω^s conductance increase \Rightarrow dielectric relaxation effect



6 – localized states transport

Conduction in disordered materials:⁵

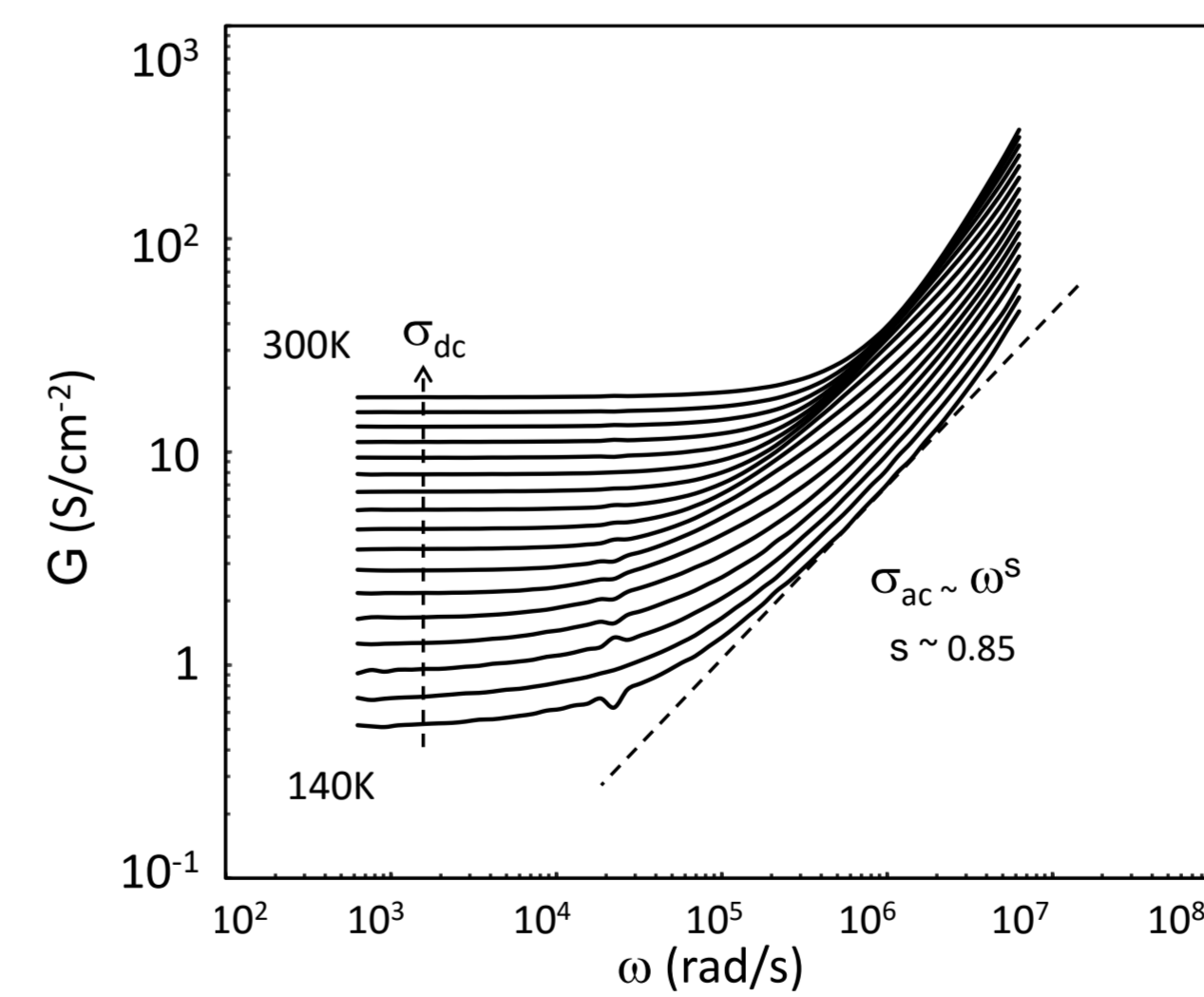


\Rightarrow At moderate temperatures, multi-trapping relaxation process dominates: hole transition between extended states below the mobility edge E_m and localized states in band tail

\Rightarrow neutral complex defects can introduce a high density of states in the band tail: hopping transport near TE, the Transport Energy, can occur at low temperature:

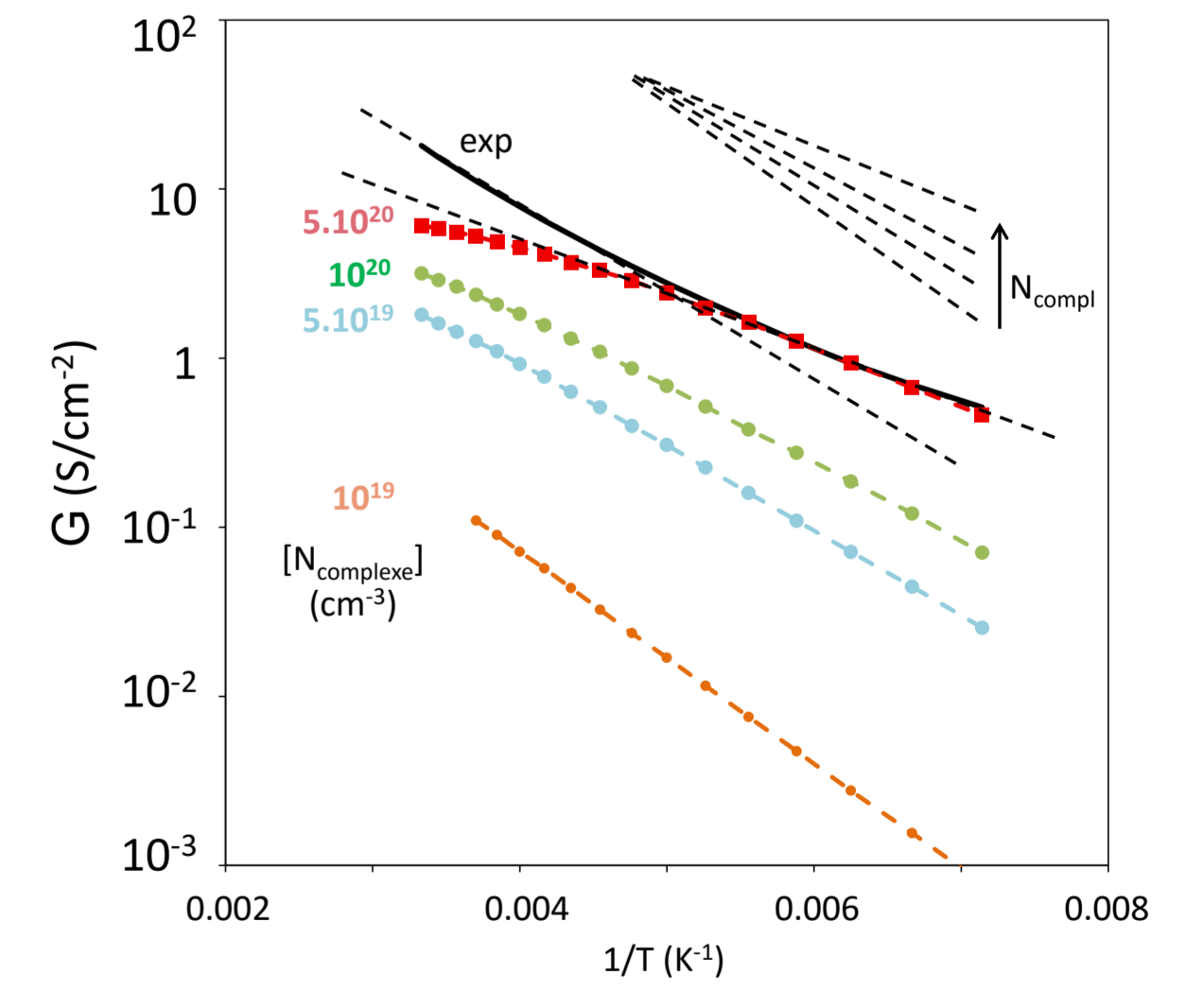
$$\sigma_{dc} \approx \sigma_0 \exp\left(-\frac{2r(TE)}{B^{-1/3}\alpha} - \frac{E_F - TE}{kT}\right)$$

7 – $G(\omega)$



- \Rightarrow low frequency: dc conductivity
- \Rightarrow high frequency/low temperature: universal power-law frequency response

8 – dc conductivity



- \Rightarrow hopping through localized states in band tail due to high concentration of neutral complexes

9 – Conclusions

- At low temperature, potential fluctuations effects are enhanced in CZTSSe bulk due to free carrier compensation mechanism.
- High density of neutral complexes can favor the dc charge carrier transport due to hopping process in the band tails

10 – Perspectives

- Hopping process in the band tails has to be taken into account to model the ac transport properties
- Effect of the potential fluctuations on V_{oc}
- Benefit of an additional shallow doping level