

Can Deep Defects Limit the Open Circuit Voltage in Cu(In,Ga)Se₂ ?

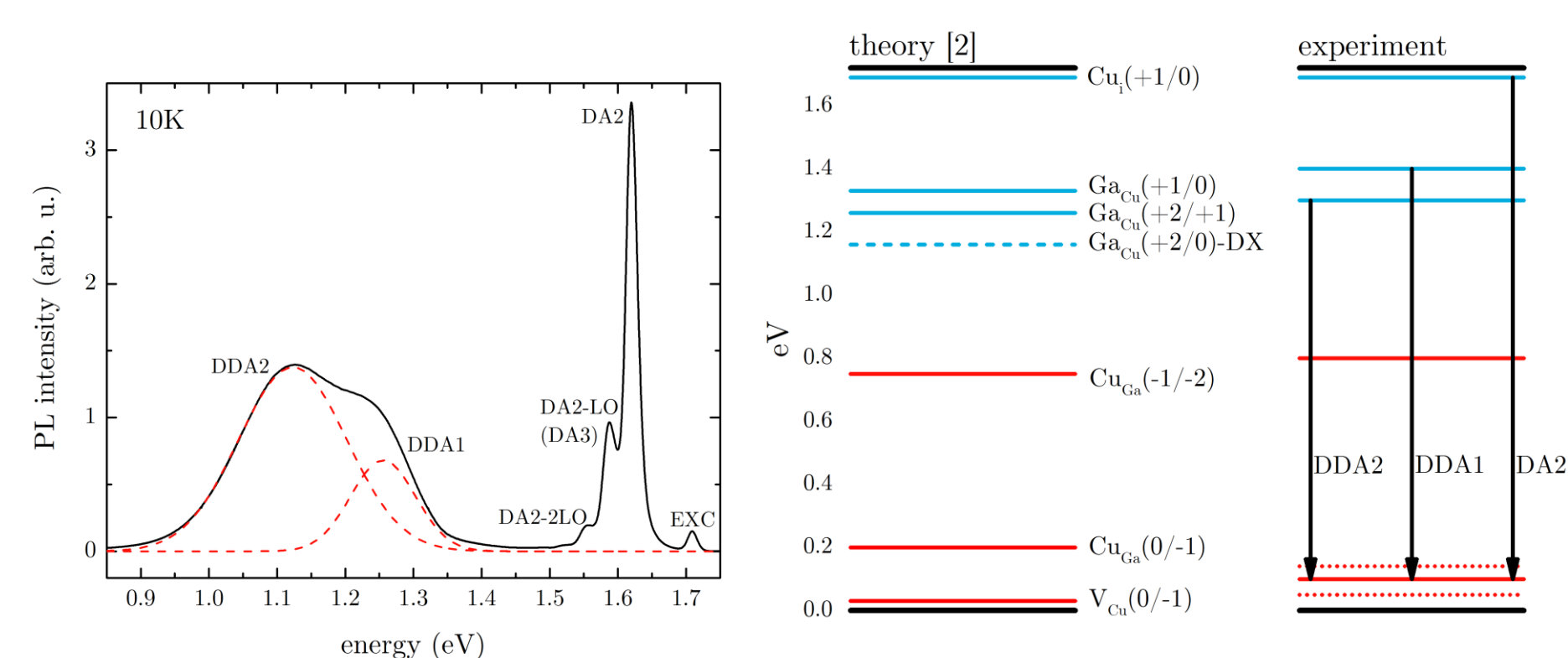
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Motivation

- recently confirmed two deep electron traps in CuGaSe₂ by photoluminescence measurements [1]
- comparison with theoretical predictions suggests Ga_{Cu} antisite to be most likely involved
- with further studies we will observe the deep defect when In is added to grow Cu(In,Ga)Se₂
- revealing its influence on solar cell parameter

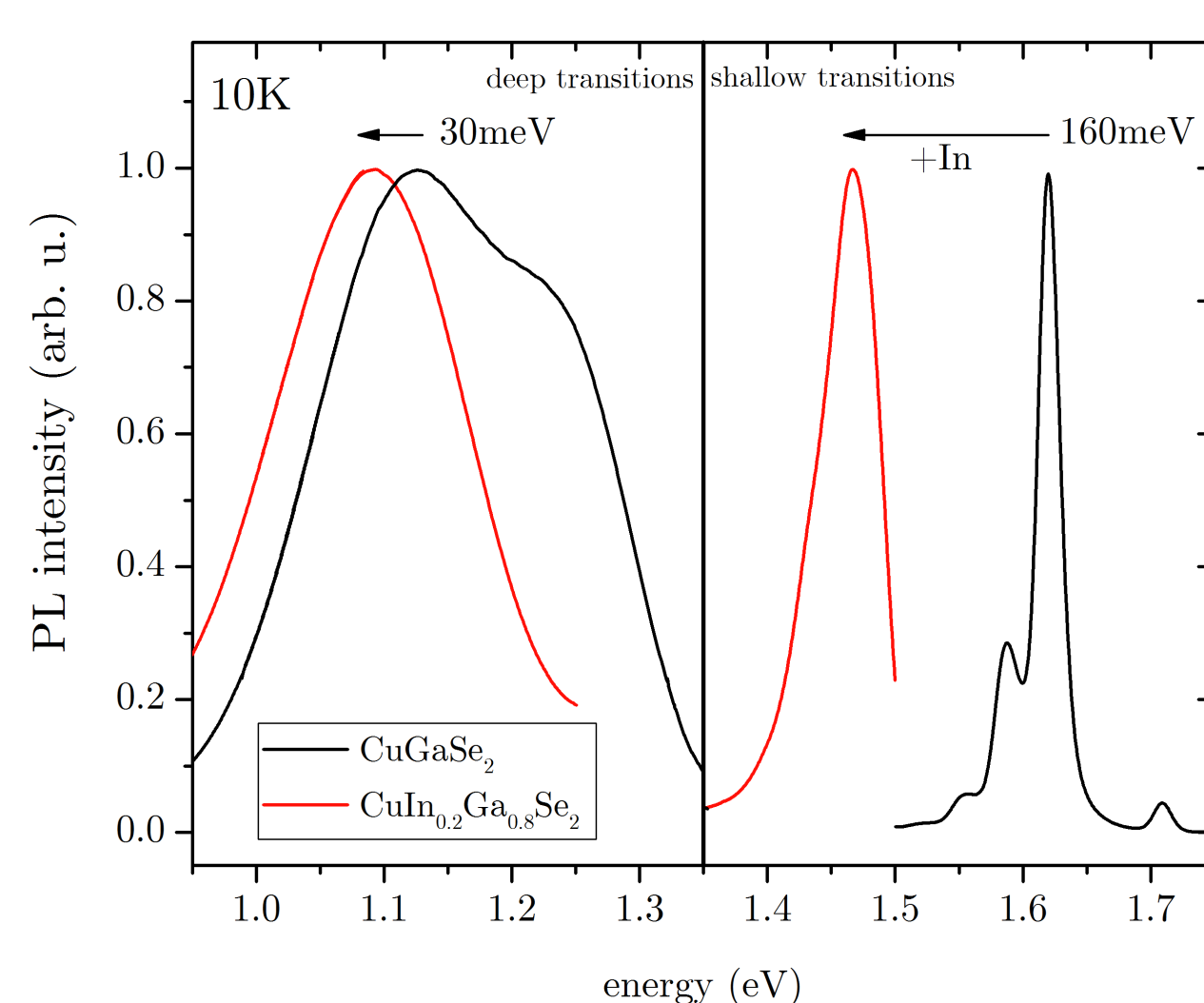
Starting-point: Cu-rich CuGaSe₂



- good agreement between experimentally determined defect levels and theoretical predictions [2]
- different charge transitions of Ga_{Cu} cannot be distinguished at the current state
- general attribution of deep PL-band DDA2 to Ga_{Cu}
- all charge transitions of Ga_{Cu} shallow in CuInSe₂ [2]

Adding 20% of Indium

- CuIn_{0.2}Ga_{0.8}Se₂ growth with MOVPE, same partial pressures and growth-temperature like for CuGaSe₂



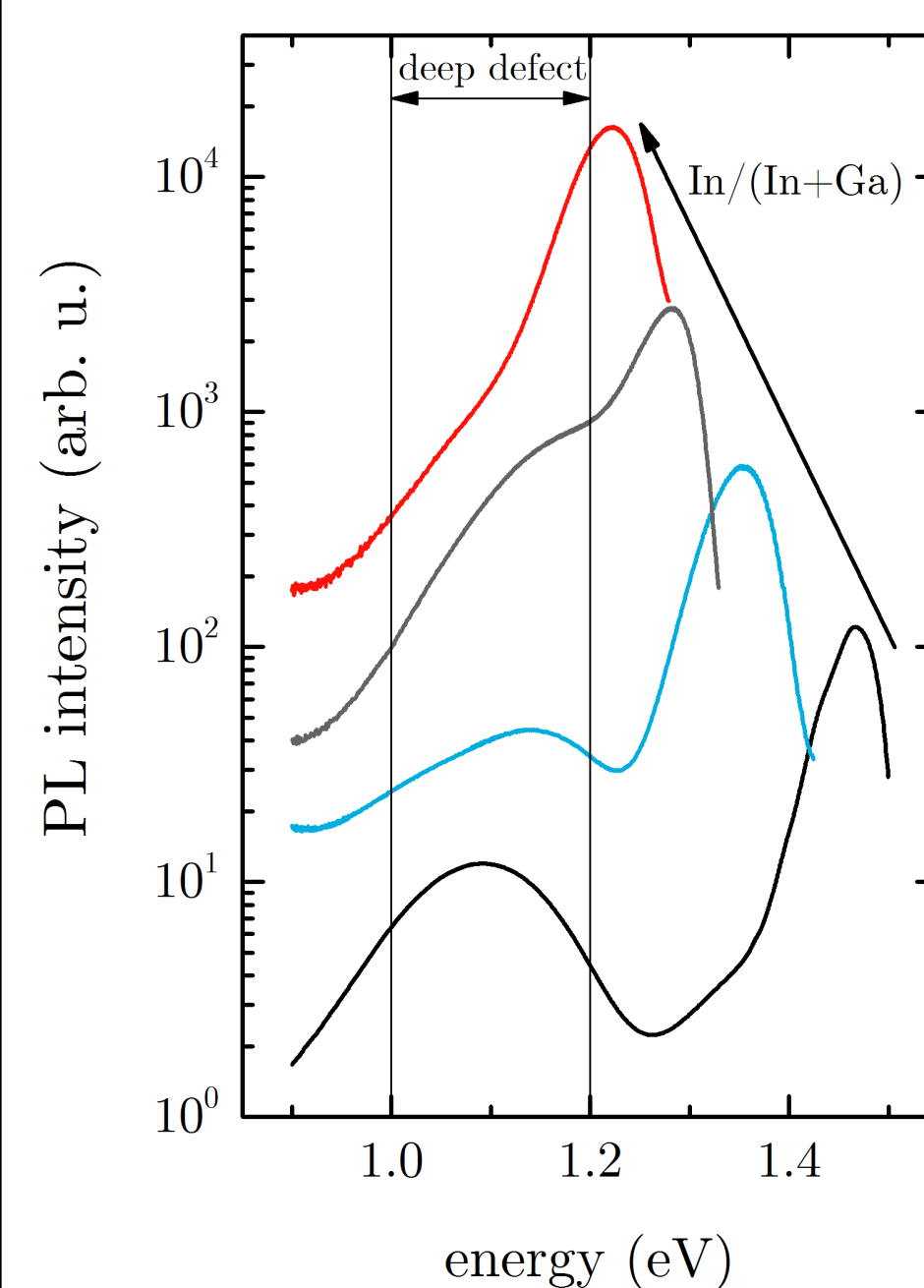
- shallow PL bands slightly broadened at low T due to compositional fluctuations of the solid solution
- band-gap, exciton and shallow donor-acceptor pair transition shifted by 160 meV (just DA shown here)
- deep PL with nearly no shift** (excitation dependent)
- absence of second deep band DDA1 not clear yet

Acknowledgements

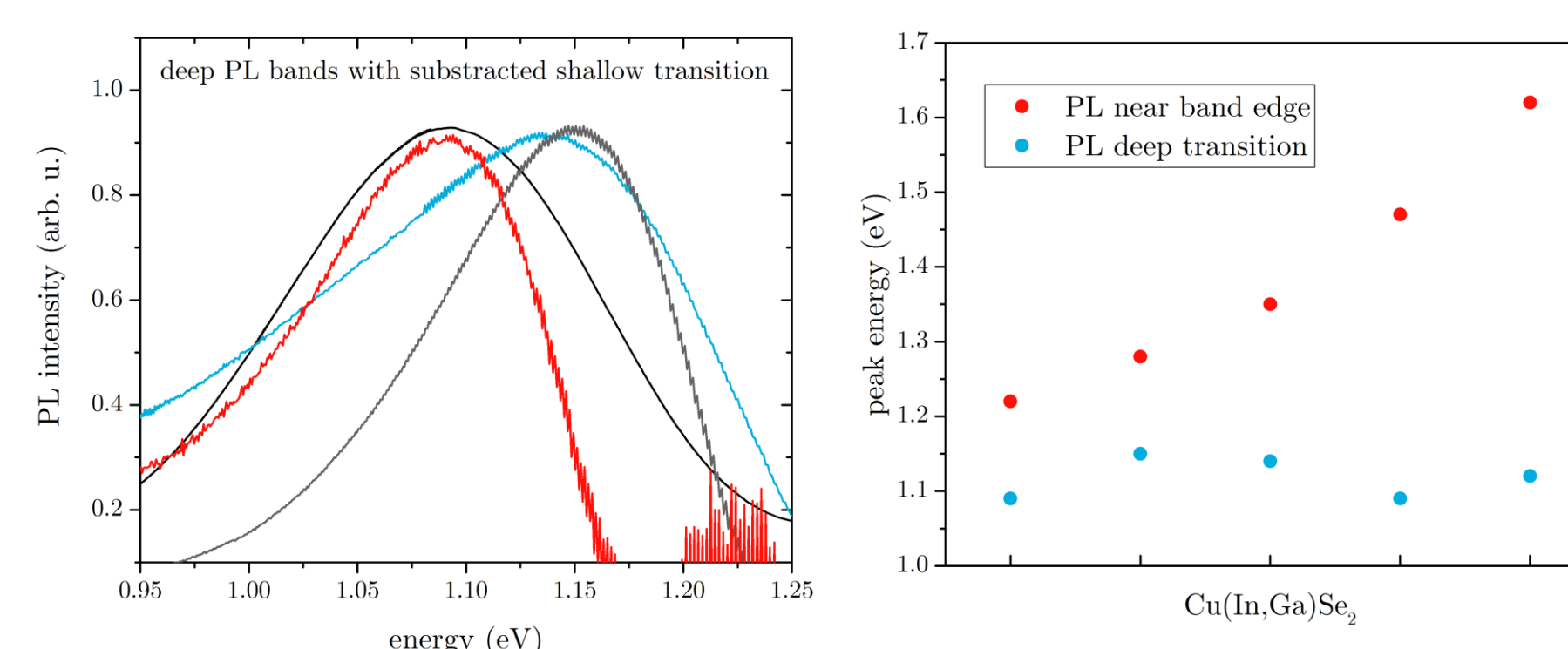


- [1] Spindler et. al., Appl. Phys. Lett. 109 (032105), 2016
[2] Pohl et. al., Phys. Rev. B 87 (245203), 2013
[3] Alkauskas et. al., J. Appl. Phys. 119 (181101), 2016

Photoluminescence Cu(In,Ga)Se₂



- epitaxial Cu-poor films
- Cu/(Ga+In) around 0.75
- except black curve with: 20% Indium, CGI 1.13
- near band edge luminescence shifts about 0.4 eV
- normalized deep bands in linear scale shown below

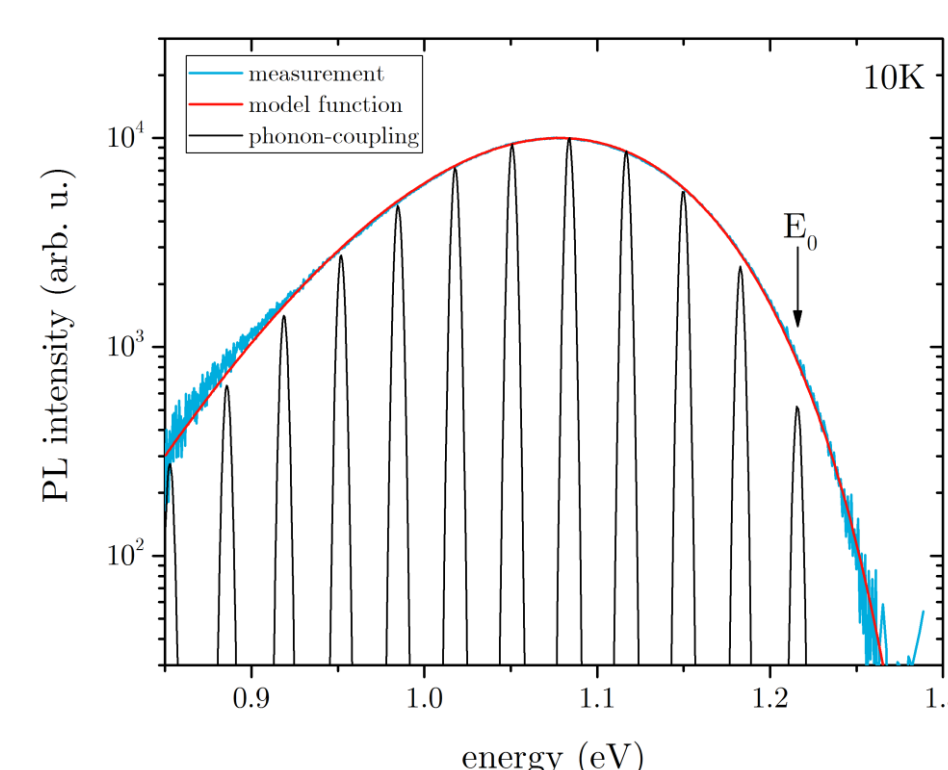


- deep defect position remains almost constant
- not detectable for «standard» Ga/(Ga+In) of 0.3
- deep level is shallow/absent in low-Ga Cu(In,Ga)Se₂

Phonon coupling of deep defect?

Luminescence line-shape within 1D-model [3]:

$$L(\epsilon) = \sum_n \exp(-S) \frac{S^n}{n!} \exp\left(\frac{\epsilon_0 - n\hbar\omega_{LO} - \epsilon}{2\sigma^2}\right)$$

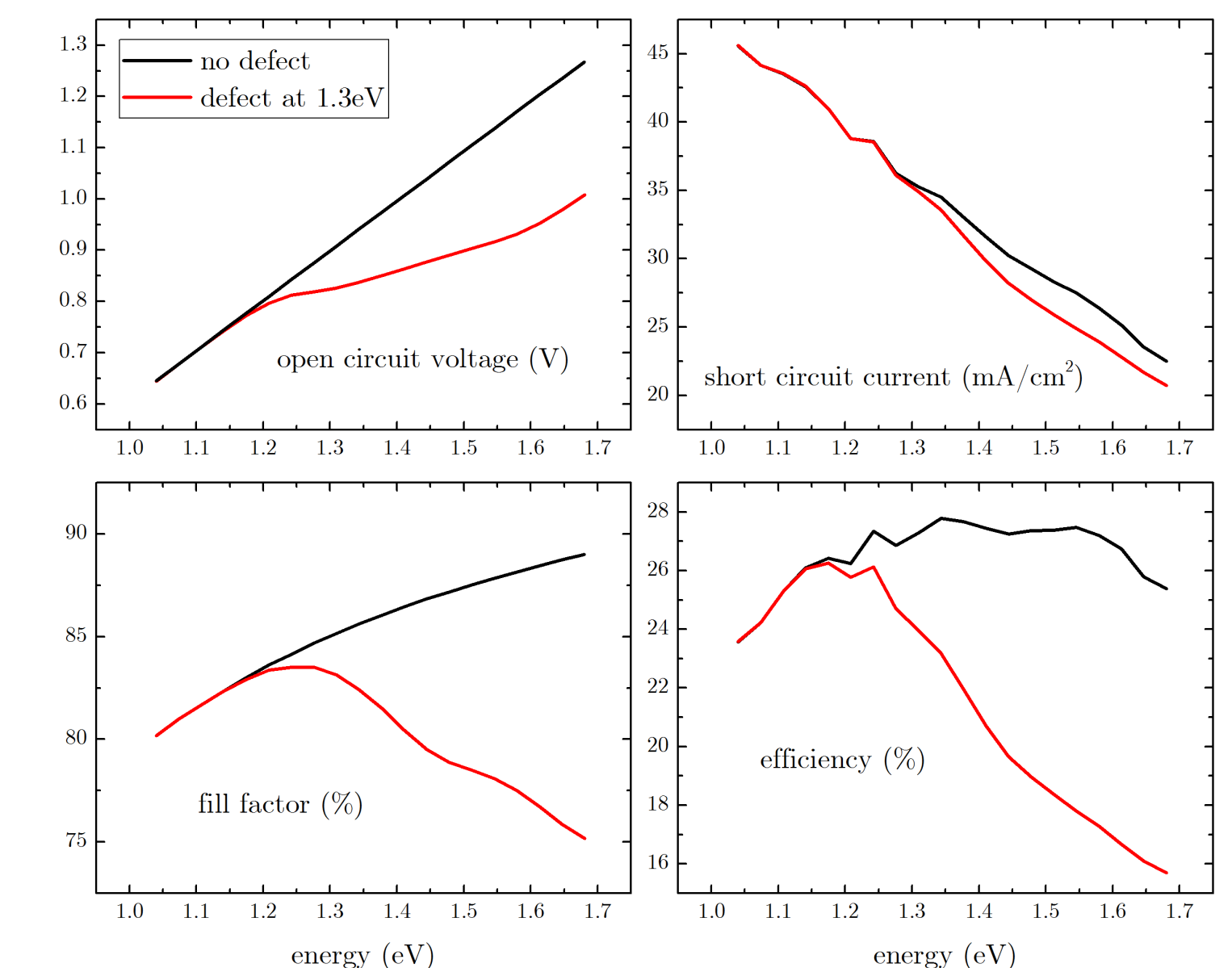


Cu-rich CuIn_{0.2}Ga_{0.8}Se₂

- fit-constants:
- phonon energy: $\hbar\omega = 32$ meV
- fit-parameter:
- zero phonon line: $\epsilon_0 = 1.22$ eV
 - Huang-Rhys factor: $S = 4.6$
 - phonon smearing $\sigma = 50$ meV

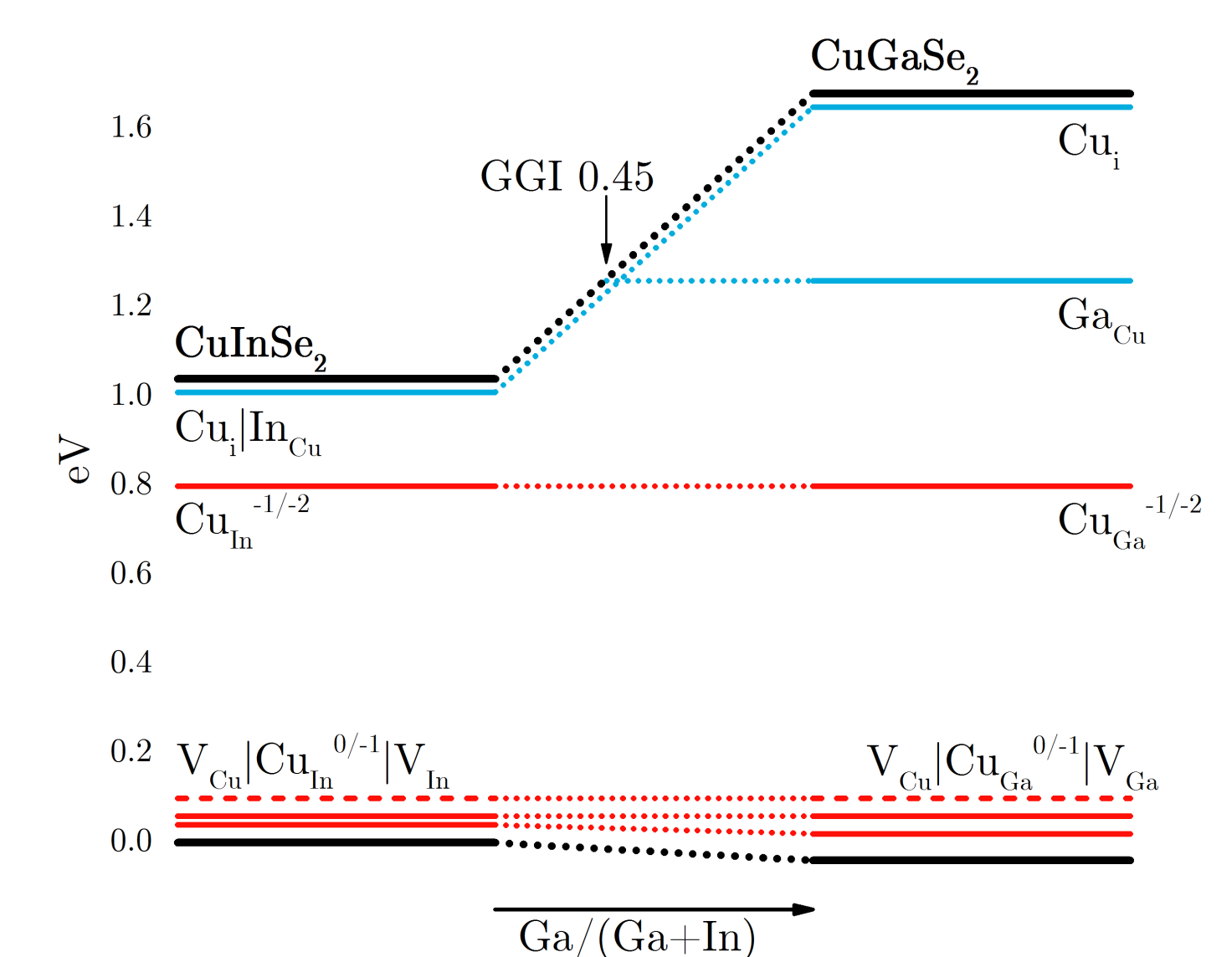
- in Cu-rich CuIn_{0.2}Ga_{0.8}Se₂ single peak well resolved
- deep DAP-transition with broad asymmetric peak
- no potential fluctuations in Cu-rich material
- \Rightarrow strong electron-phonon coupling involved
- DA zero phonon line at 1.22 eV, acceptor at 0.1 eV
- \Rightarrow deep donor level at 1.32 eV above valence band

SCAPS simulation



- absorber: $N_A = 10^{16} \text{ cm}^{-3}$, $B_{\text{rad}} = 10^{-3} \text{ s}^{-1}$, $\sigma_n = 10^{-13} \text{ cm}^2$
- defect level: $E_T = 1.3$ eV, $N_T = 5 \cdot 10^{15} \text{ cm}^{-3}$
- band gap dependent open circuit voltage deficit agrees well with common observations in literature
- linear increase of $V_{\text{OC}}(E_g)$ just for low Ga-content

Defect model



- constant level for Ga_{Cu} antisites assumed at 1.3 eV
- for GGI 0.45 deep defect
- Cu_{III}^{-1/2} suggested to limit Cu-rich devices (Poster2)
- Ga_{Cu} suggested to limit high-Ga devices

Summary

- PL transition at approx. 1.1 eV, constant with E_g
- \Rightarrow donor-acceptor pair characteristic and strong phonon coupling yields defect level around 1.3 eV
- attributed Ga_{Cu} defect shallow in low-Ga CIGSe
- defect can cause large V_{OC} deficit in high-Ga device