

Exploring the Electronic and Optical Properties of $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$

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06-March-2015



Outline

1 Background

2 Motivation

3 Computational methods

4 Results

- Parameterization of energy bands for CIGS
- Analysis of density-of-states (DOS) and carrier concentration
- Dielectric function for $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$

5 Summary

6 Future perspectives

7 Acknowledgements

1 Background

2 Motivation

3 Computational methods

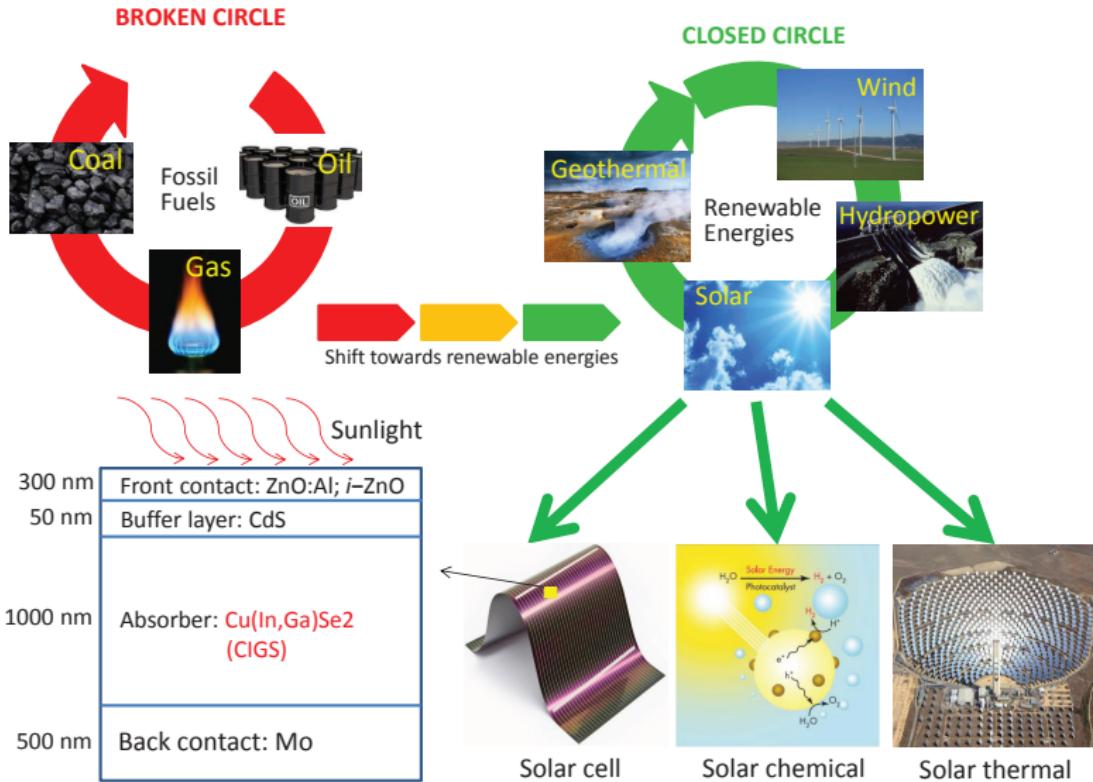
4 Results

5 Summary

6 Future perspectives

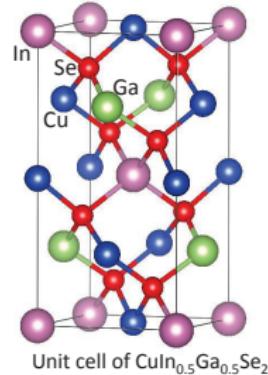
7 Acknowledgements

Which field and material am I working on?



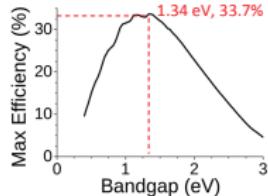
Why Cu(In,Ga)Se₂?

CIS = CuInSe₂
CGS = CuGaSe₂
CIGS = Cu(In, Ga)Se₂ = CuIn_{1-x}Ga_xSe₂



Advantages of CIGS:

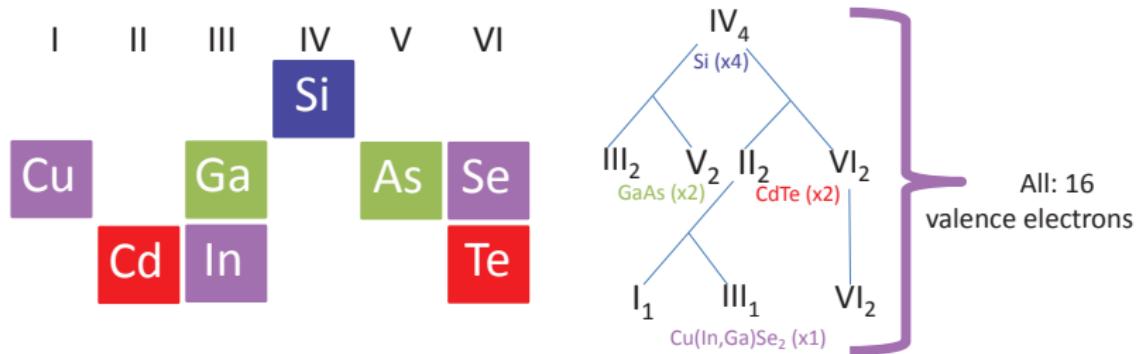
1. Tunable band-gap (1.0 to 1.7 eV)
2. Efficiency 23.3% in the lab
3. High absorption coefficient, thinner, flexible



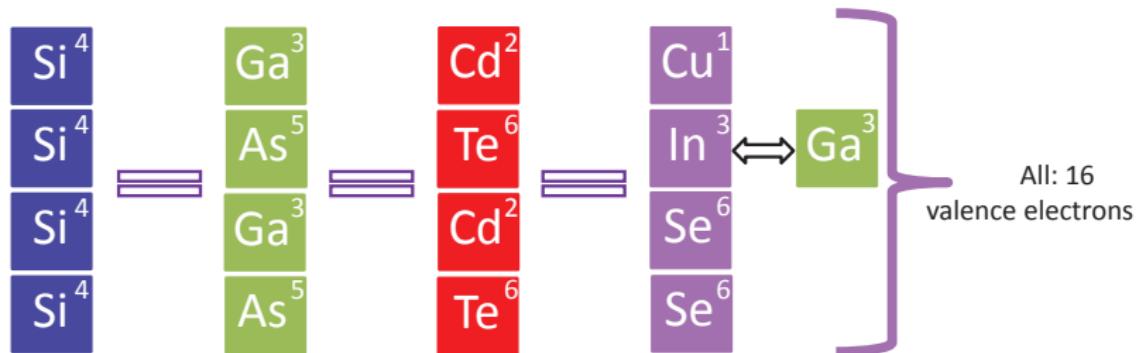
The Shockley-Queisser limit for the efficiency of a solar cell.

CIGS is doing well in the Building-integrated photovoltaics market.

Where does Cu(In,Ga)Se₂ come from?



A series of cation mutations where total number of valence electrons is the same and it keeps the charge neutral in the compound.



1 Background

2 Motivation

3 Computational methods

4 Results

5 Summary

6 Future perspectives

7 Acknowledgements

Which aspects of Cu(In,Ga)Se₂ have I been working on?

- Electronic structure

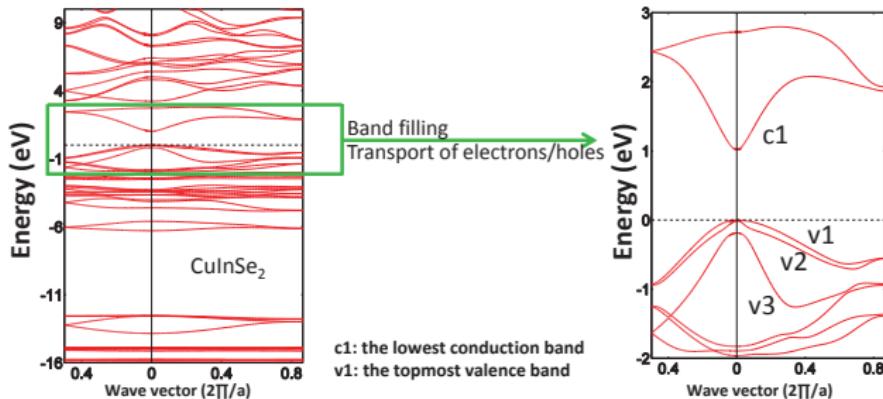
- Energy bands of CuInSe₂, CuIn_{0.5}Ga_{0.5}Se₂, and CuGaSe₂ are calculated by means of theoretical calculations. Parameterization of the lowest conduction (CB) and the three uppermost valence bands (VBs) are explored based on the calculated energy bands.
- Analysis of density-of-states (DOS) and carrier concentration based on the parameterization.

- Optical properties

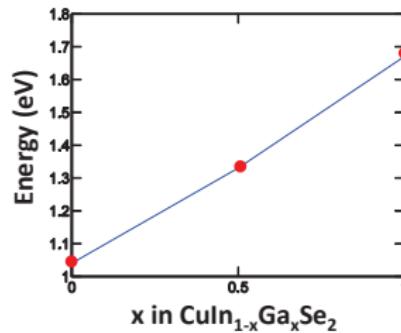
- Dielectric function of CuIn_{0.5}Ga_{0.5}Se₂ are explored by means of theoretical calculations. The band-to-band optical transitions are analyzed. The electronic origins of the observed interband critical points of the optical response are discussed.

Motivation for the parameterization

By understanding the electronic properties one can understand many of the fundamental material properties.



1. Less study on CuIn_{0.5}Ga_{0.5}Se₂.
2. Commercially interesting: CuIn_{0.7}Ga_{0.3}Se₂, CuIn_{0.5}Ga_{0.5}Se₂ indicates how CIGS behaves when alloying In and Ga.



Motivation for analysis of DOS and carrier concentration

- Better analyze the impact on DOS as well as carrier concentration taking into account the non-parabolicity of the energy bands.
- Help experimentalists to reproduce DOS from energy-dependent DOS mass.
- DOS and carrier concentration obtained by full band parameterization and parabolic band approximation are compared.

Motivation for calculation of dielectric function

Absorption coefficient can be calculated by dielectric function directly, and thickness of material is determined by the absorption coefficient.

- Help experimentalists to understand the dielectric function spectrum.
- Understand details in the optical transition for these types of materials.

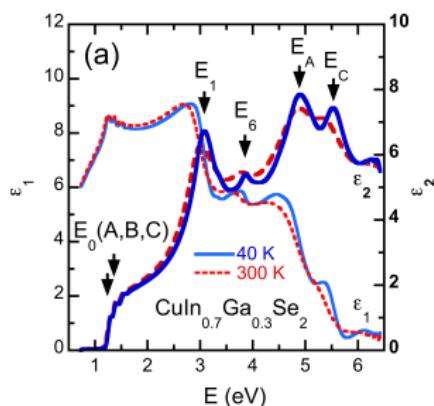


Figure : The real (ϵ_1) and imaginary (ϵ_2) part of dielectric function spectra.

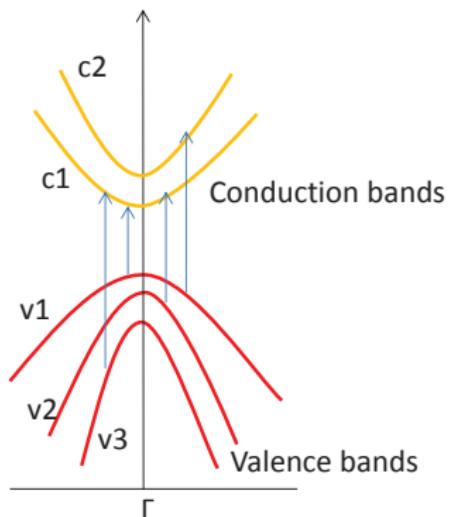


Figure : Energy bands.

- 1 Background
- 2 Motivation
- 3 Computational methods
- 4 Results
- 5 Summary
- 6 Future perspectives
- 7 Acknowledgements

Density functional theory (DFT)

DFT-based modelling is extremely successful in many-body systems.

- DFT was introduced by Hohenberg and Kohn in 1964. Kohn and Pople were awarded Chemistry Nobel Prize in 1998.
- Around 20,000 papers per year.

DFT says that ground-state total energy ($E_{total}[\rho]$) can be determined from the ground-state charge density ρ instead of many-electron wavefunction. However, we do not have explicit form for $E_{total}[\rho]$.

Kohn-Sham (KS) Equation

This problem in DFT is solved by KS equation:

$$E_{total}[\rho] = T_0[\rho] + V_H[\rho] + V_{ext}[\rho] + E_{xc}[\rho]. \quad (1)$$

The KS equation is derived as

$$\left(-\frac{\nabla^2}{2} + V^{KS}(\mathbf{r}) \right) \Psi_i^{KS}(\mathbf{r}) = \epsilon_i^{KS} \Psi_i^{KS}(\mathbf{r}). \quad (2)$$

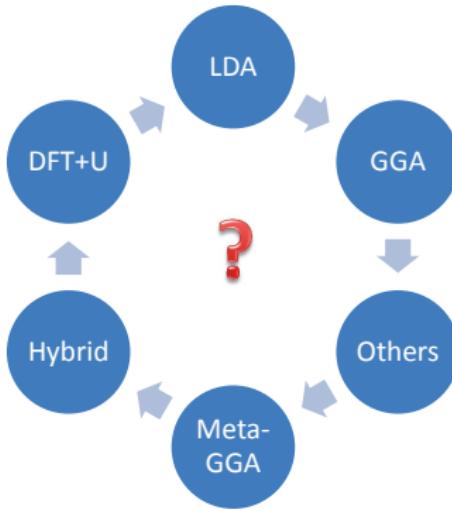
The $V^{KS}(\mathbf{r})$ is given as

$$V^{KS}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \overbrace{\frac{\delta E_{xc}}{\delta \rho(\mathbf{r})}}^{V_{xc}(\mathbf{r})}. \quad (3)$$

Here

$$\rho = \sum |\Psi_i^{KS}(\mathbf{r})|^2. \quad (4)$$

Different exchange-correlation potentials $V_{xc}(\mathbf{r})$



In our calculations, we took the GGA+U (d-states), which was proved to improve the effective mass, that is curvature of energy band.

1 Background

2 Motivation

3 Computational methods

4 Results

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5 Summary

6 Future perspectives

7 Acknowledgements

Result 1: Parabolic band approximation (pba)

The parabolic approximation of ellipsoidal energy bands is expressed

$$E_j^{pb}(\mathbf{k}) = E_j(\mathbf{0}) \pm \left[\frac{\tilde{\mathbf{k}}_x^2 + \tilde{\mathbf{k}}_y^2}{m_j^\perp} + \frac{\tilde{\mathbf{k}}_z^2}{m_j^\parallel} \right] \quad (5)$$

$$\tilde{\mathbf{k}}_\alpha^2 = \frac{\hbar^2 \mathbf{k}_\alpha^2}{2e}, \text{ where } \alpha = x, y, \text{ and } z.$$

It is valid in the very vicinity of the Γ -point. However, away from the Γ -point, the parabolic approximation fails to describe the energy dispersion for the CIGS.

Result 1: Full band parameterization (fbp)

$$E_j(\mathbf{k}) = E_j^{pb}(\mathbf{k}) + E_j^0 + \Delta_{j,1} \left(\delta_{j,1}^2 \left(\frac{\tilde{\mathbf{k}}_x^4 + \tilde{\mathbf{k}}_y^4}{m_0^2} \right) + \delta_{j,2}^2 \left(\frac{\tilde{\mathbf{k}}_x^2 \tilde{\mathbf{k}}_y^2}{m_0^2} \right) + 1 \right)^{1/2}$$
$$+ \Delta_{j,2} \left(\delta_{j,3}^3 \left(\frac{\tilde{\mathbf{k}}_x^6 + \tilde{\mathbf{k}}_y^6}{m_0^3} \right) + \delta_{j,4}^3 \left(\frac{\tilde{\mathbf{k}}_x^2 \tilde{\mathbf{k}}_y^4 + \tilde{\mathbf{k}}_x^4 \tilde{\mathbf{k}}_y^2}{m_0^3} \right) + 1 \right)^{1/3}$$
$$+ \Delta_{j,3} \left(\delta_{j,5}^2 \left(\frac{\tilde{\mathbf{k}}_z^4}{m_0^2} \right) + 1 \right)^{1/2} + \Delta_{j,4} \left(\delta_{j,6}^3 \left(\frac{\tilde{\mathbf{k}}_z^6}{m_0^3} \right) + 1 \right)^{1/3}$$
$$+ \Delta_{j,5} \left(\delta_{j,7}^2 \left(\frac{\tilde{\mathbf{k}}_x^2 \tilde{\mathbf{k}}_z^2 + \tilde{\mathbf{k}}_y^2 \tilde{\mathbf{k}}_z^2}{m_0^2} \right) + 1 \right)^{1/2}$$
$$+ \Delta_{j,6} \left(\delta_{j,8}^3 \left(\frac{\tilde{\mathbf{k}}_x^4 \tilde{\mathbf{k}}_z^2 + \tilde{\mathbf{k}}_y^4 \tilde{\mathbf{k}}_z^2}{m_0^3} \right) + \delta_{j,9}^3 \left(\frac{\tilde{\mathbf{k}}_x^2 \tilde{\mathbf{k}}_z^4 + \tilde{\mathbf{k}}_y^2 \tilde{\mathbf{k}}_z^4}{m_0^3} \right) + \delta_{j,10}^3 \left(\frac{\tilde{\mathbf{k}}_x^2 \tilde{\mathbf{k}}_y^2 \tilde{\mathbf{k}}_z^2}{m_0^3} \right) + 1 \right)^{1/3} \quad (6)$$

Result 1: Parameterization of band structure for CIGS

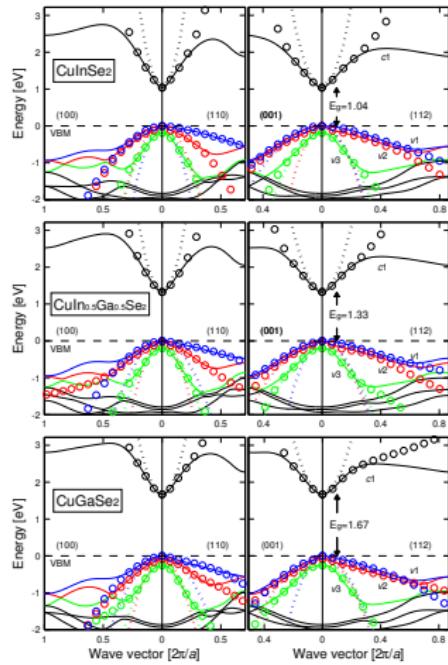


Figure : Electronic band structure along four directions. The circles are the results of the fbp, and the dotted lines represent the pba.

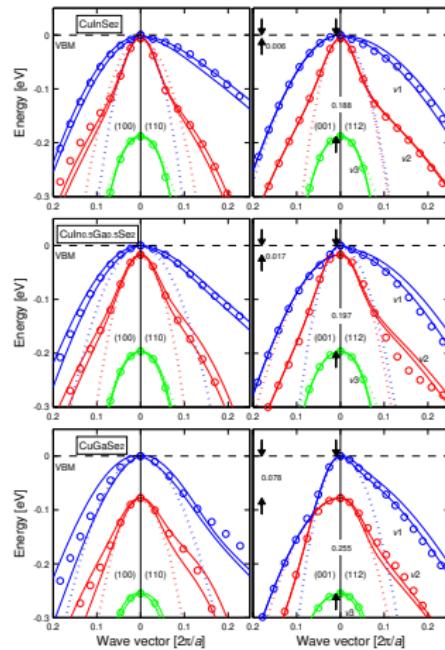


Figure : Close-up of right figure.

Result 1: Non-parabolicity of the energy bands

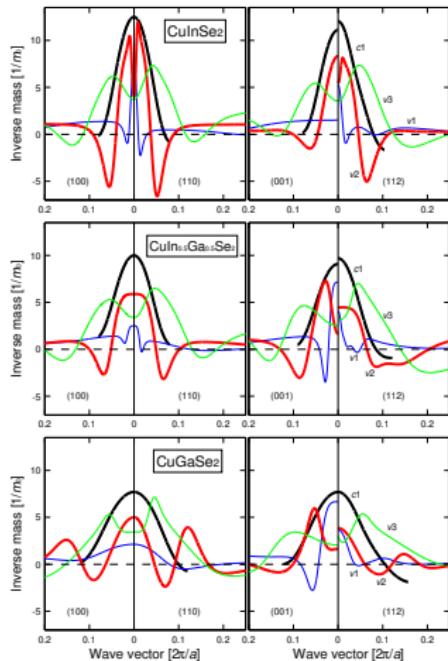


Figure : Inverse of the effective electron and hole masses in the four symmetry directions for the CuIn_{1-x}Ga_xSe₂ ($x = 0, 0.5$, and 1).

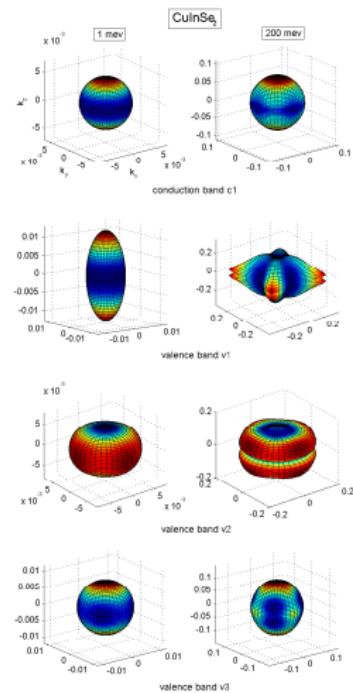


Figure : Constant energy surfaces for the lowest CB and three uppermost VBs in CuInSe₂.

Result 1: Density-of-states (DOS)

In the case of the pba, the density-of-states can be written as

$$g_j^{pba}(E) = \frac{1}{2\pi^2} \left(\frac{2m_j^{DOS}}{\hbar^2} \right)^{3/2} \sqrt{|E - E_j(\mathbf{0})|}. \quad (7)$$

Here, the DOS mass m_j^{DOS} is equal to $(m_j^\perp m_j^\perp m_j^{\parallel})^{1/3}$, which represents the extent of filling the specific band with free carriers to certain energy. In order to take advantage of the simple **Eq. 7** for the non-parabolic energy bands, the energy-dependent DOS mass ($m_{v/c}^{DOS}$), which contains the non-parabolicity and anisotropy of the band dispersion, is defined as

$$g_{v/c}(E) = \sum_j g_j(E) = \frac{1}{2\pi^2} \left(\frac{2m_{v/c}^{DOS}(E)}{\hbar^2} \right)^{3/2} \sqrt{|E - E_{v1/c1}(\mathbf{0})|}. \quad (8)$$

Result 1: Density-of-states (DOS) and DOS mass

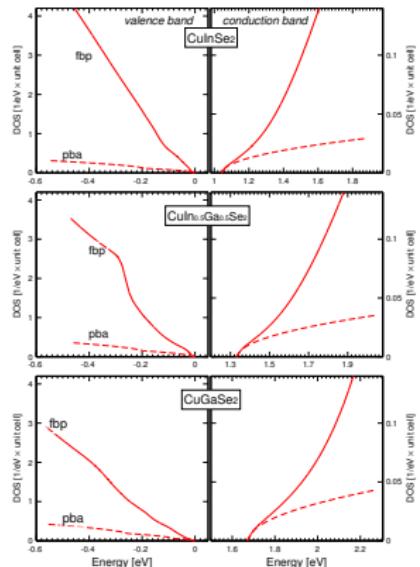


Figure : Total density-of-states of the VBs and CB. The solid lines show the results based on the fbp, and the dashed lines represent the results based on the pba.

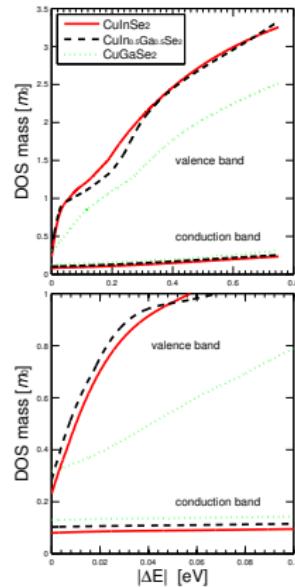


Figure : The DOS mass $m_{v/c}^{DOS}$ is calculated from Eq. 8.

Result 1: Band-gap, Fermi energy and intrinsic carrier concentration

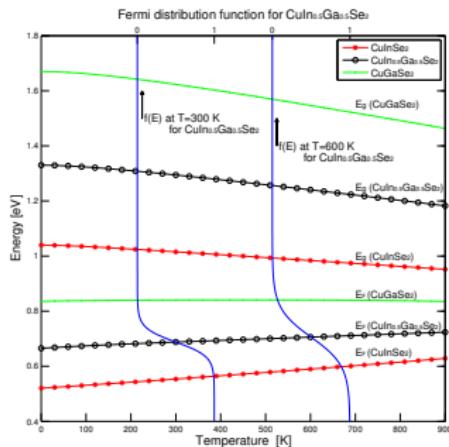


Figure : Band-gap energy and Fermi energy for $1 \leq T \leq 900$ K of intrinsic CuInSe_2 , $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$, and CuGaSe_2 , determined from the fbp. The Fermi distribution $f(E)$ of $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ is presented for $T = 300$ K and 600 K.

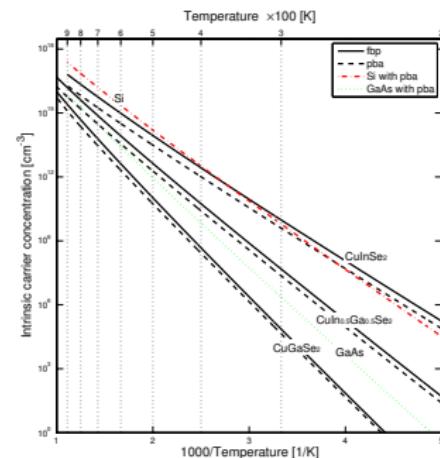


Figure : Intrinsic carrier concentration as function of temperature. For comparison, the theoretical results for GaAs and Si using the pba are given.

Result 1: Carrier concentration in *p*-type for CIGS

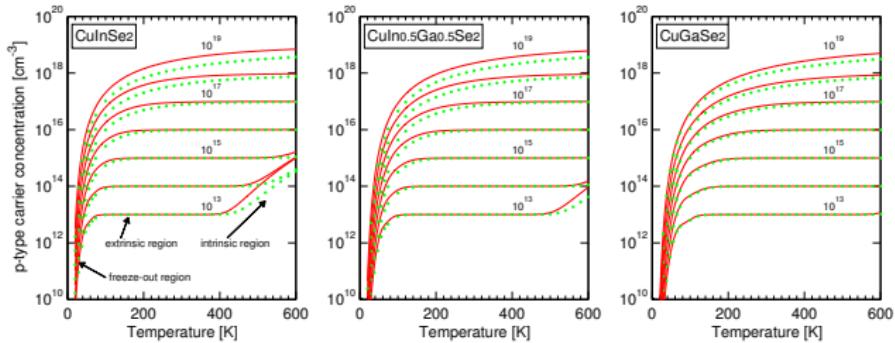


Figure : Free carrier concentration as function of the temperature in *p*-type for CuInSe_2 , $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$, and CuGaSe_2 . The effective doping concentration $N_A = 10^{13}, 10^{14}, 10^{15}, \dots$, and 10^{19} acceptors cm^{-3} are considered. Solid and dotted lines represents the fbp and the pba, respectively.

Result 2: Dielectric function for $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$

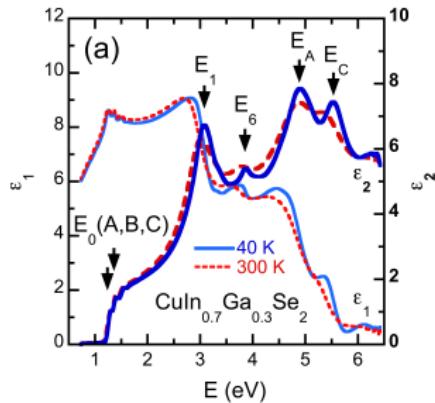


Figure : The real (ϵ_1) and imaginary (ϵ_2) part of dielectric function spectra for $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ at 40 K (solid blue line) and 300 K (dashed red lines). Four prominent CP features are shown.

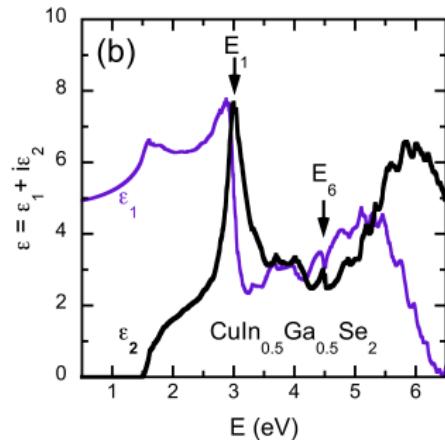


Figure : The dielectric function spectra for $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ calculated by FPLAPW method at 0 K. The major CP features are identified.

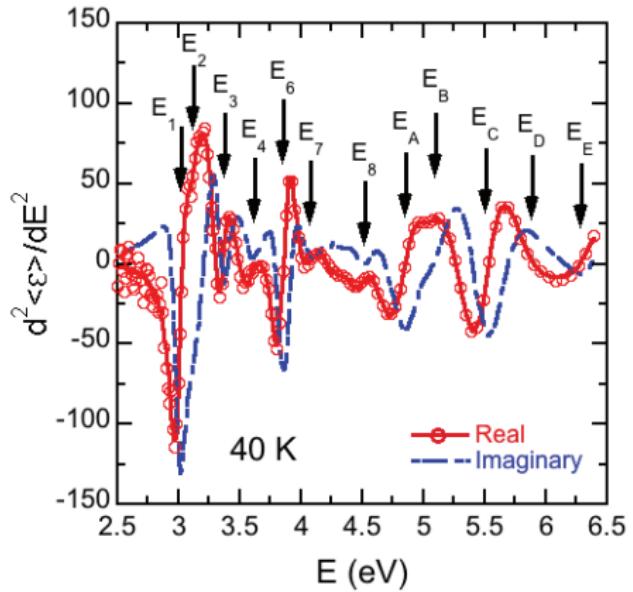


Figure : Energies of each interband critical point (CP) are indicated by arrows and labeled in a numeric and alphabetic order.

Result 2: Analysis of the imaginary part of dielectric function

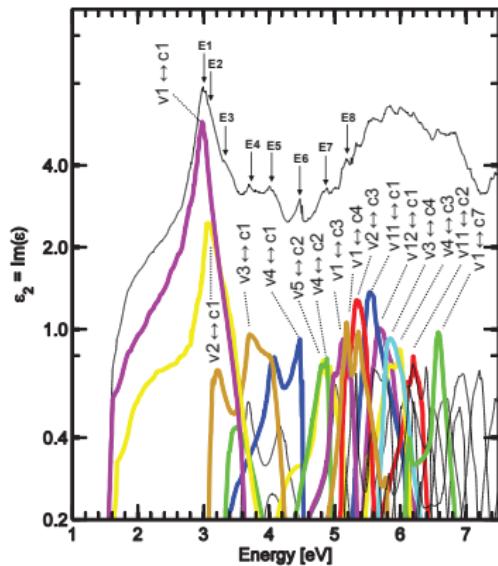


Figure : Band-to-band analysis of the contribution to the total ϵ_2 spectrum. The vertical axis is in the log scale.

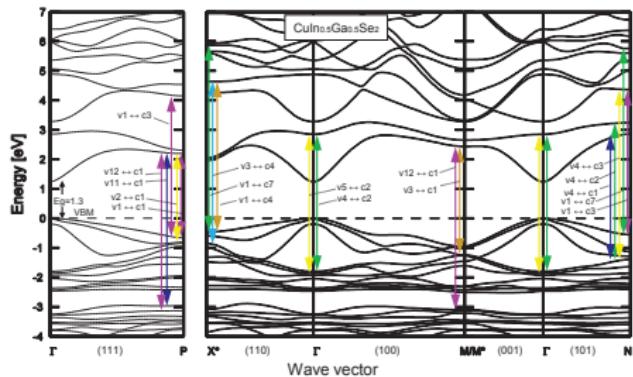


Figure : The calculated electronic band structure of $\text{Culn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ where the CPs are identified along the main symmetry directions.

- 1 Background
- 2 Motivation
- 3 Computational methods
- 4 Results
- 5 Summary
- 6 Future perspectives
- 7 Acknowledgements

Summary

In this licentiate thesis, two major researches are presented:

- Analysis of the electronic structure of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ with $x = 0, 0.5$, and 1 . Here, we parameterize the energy bands in order to better describe energy dispersions and better analyze the electron and hole dynamics in the materials. We consider intrinsic and p -type materials, and we model the temperature dependence.
- Analysis of the optical properties of $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$. Here, the dielectric function spectra is calculated and compared with experimental result. The probable electronic origins of the critical point features are discussed as well.

- 1 Background
- 2 Motivation
- 3 Computational methods
- 4 Results
- 5 Summary
- 6 Future perspectives
- 7 Acknowledgements

Future perspectives

- The cost and scarcity of indium in the CIGS device is a problem, and copper zinc tin selenide/sulfide (CZT(S,Se)) can therefore be alternative to CIGS due to the low cost and non-toxicity elements.

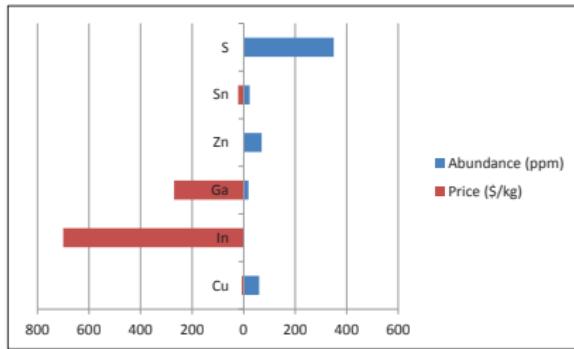


Figure : Abundance and price of Cu, In, Ga, S, Sn, and Zn in Earth's crust (parts per million (ppm) in mass; 10,000 ppm = 1%).

- If there are other similar materials that are of interest. CIGS and CZT(S,Se) can be considered to be in a class denoted as Cu-XY-chalcogenide, where X and Y are two cation elements that replace the group-III In or Ga in CIGS.

1 Background

2 Motivation

3 Computational methods

4 Results

5 Summary

6 Future perspectives

7 Acknowledgements

Acknowledgements

- I would like to express my sincere appreciation to my supervisor Prof. Clas Persson for his academic encouragement and professional guidance.
- I would like to thank all the group colleagues in Stockholm and Oslo for helpful research discussions and chatting. I would like to thank all other people at the Department of Material Sciences and Engineering at KTH for creating a nice working atmosphere.
- The China Scholarship Council, the Swedish Energy Agency, the Swedish Research Council, Stiftelsen Axel Hultgrens fond, Olle Erikssons stiftelse for materialteknik, and KTH Computational Science and Engineering Centre (KCSE) are acknowledged for financial support.

Thank you for your attention!

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Full-potential linearised augmented-plane wave (FPLAPW)

Unit cell is divided into two regions: one is sphere region called muffin tin (MT) region, which is defined by the center of atom, but non-overlap each sphere; the remaining region is called interstitial (I) region.

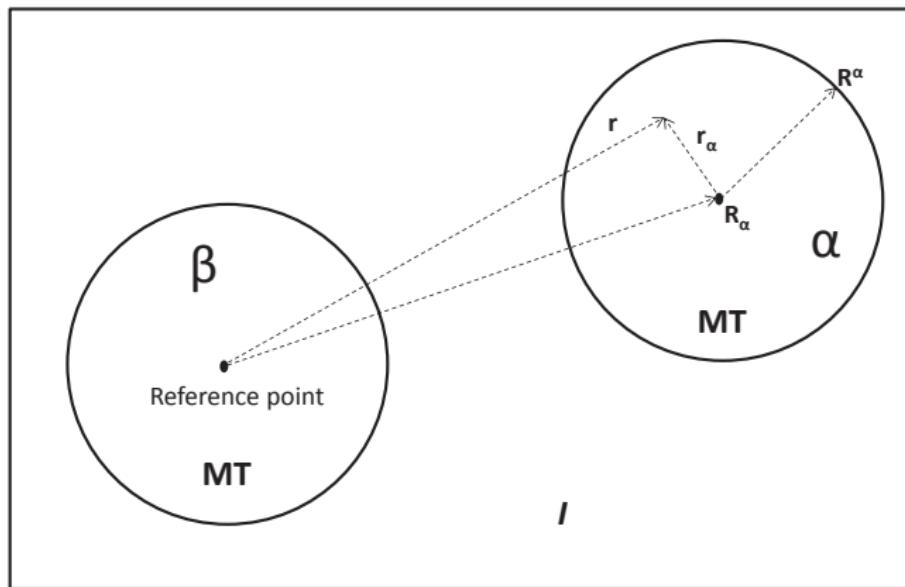


Figure : Partition of the unit cell.

The KS wavefunction can be expanded by a set of basis functions

$$\Psi_{i,\mathbf{k}}^{KS}(\mathbf{r}) = \sum_{\mathbf{G}}^{N_G} C_{i,\mathbf{k}+\mathbf{G}} \phi_{\mathbf{k}+\mathbf{G}}^{LAPW}(\mathbf{r}). \quad (9)$$

Here

$$\phi_{\mathbf{k}+\mathbf{G}}^{LAPW}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} & \text{if } \mathbf{r} \in I \\ \sum_{\alpha} \sum_{\ell m} f_{\ell m}(r_{\alpha}, \mathbf{k} + \mathbf{G}, \epsilon_{\ell, \alpha}) Y_{\ell m}(\hat{\mathbf{r}}_{\alpha}) & \text{if } r_{\alpha} \in MT. \end{cases} \quad (10)$$

The potential in the FPLAPW method is also divided into two regions, the MT region and the I region.

$$V(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{Gr}} & \text{if } \mathbf{r} \in I \\ \sum_{\ell m} V_{\ell m}^{\alpha}(r_{\alpha}) Y_{\ell m}(\hat{\mathbf{r}}_{\alpha}) & \text{if } r_{\alpha} \in MT. \end{cases} \quad (11)$$

Here, $V_{\mathbf{G}}$ and $V_{\ell m}^{\alpha}(r_{\alpha})$ can be decided by electron density.

The process for solving KS equation

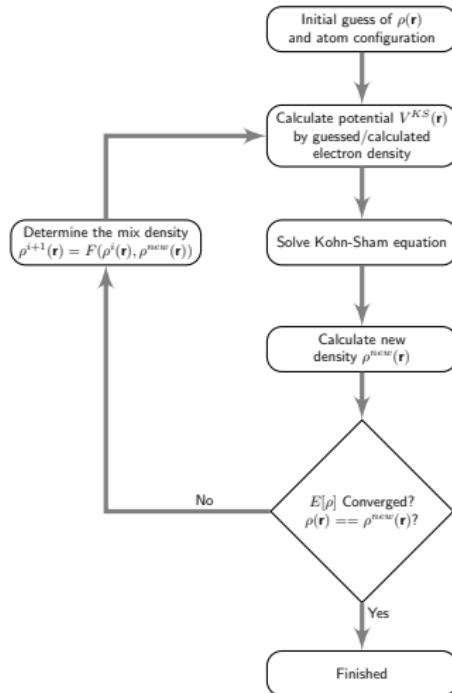


Figure : Flow chart of the $(i + 1)$:th iteration for solving KS equation.