

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

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# Outline

1 Background

2 Motivation

3 Computational methods

4 Results

- Paper 1: parameterization of energy bands for CIGS
- Paper 2: analysis of density-of-states (DOS) and carrier concentration
- Paper 3: 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

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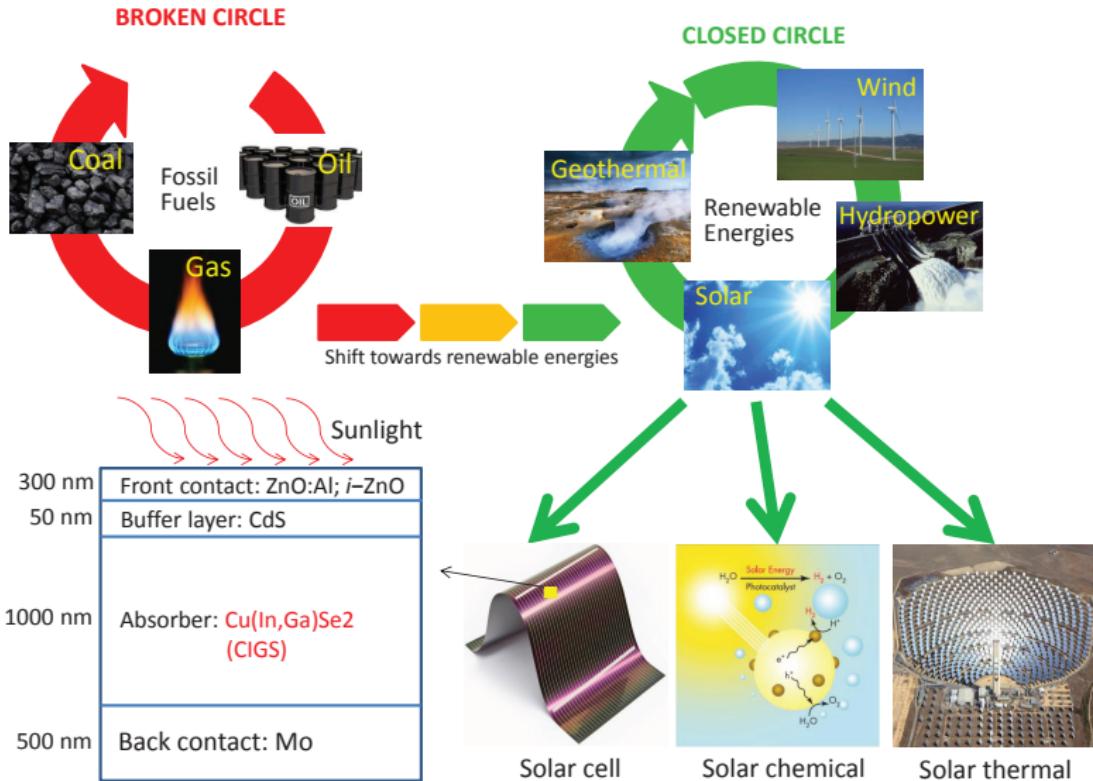
4 Results

5 Summary

6 Future perspectives

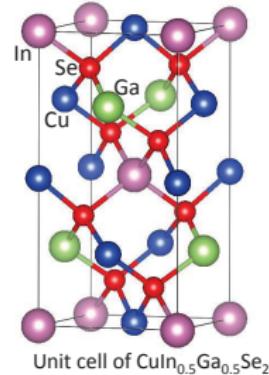
7 Acknowledgements

# Which field and material am I working on?



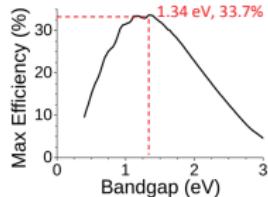
# Why Cu(In,Ga)Se<sub>2</sub>?

CIS = CuInSe<sub>2</sub>  
CGS = CuGaSe<sub>2</sub>  
CIGS = Cu(In, Ga)Se<sub>2</sub> = CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub>



Advantages of CIGS:

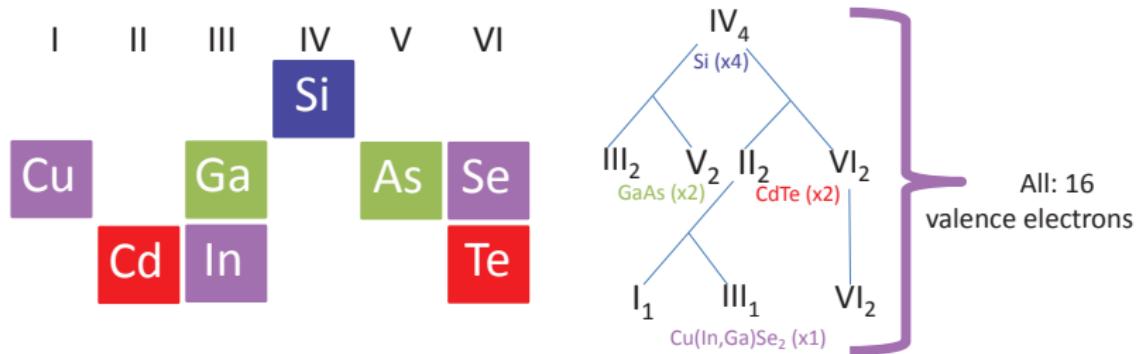
1. Tunable band-gap (1.0 to 1.7 eV)
2. Efficiency 23.3% in the lab
3. High absorption coefficient, thinner, flexible



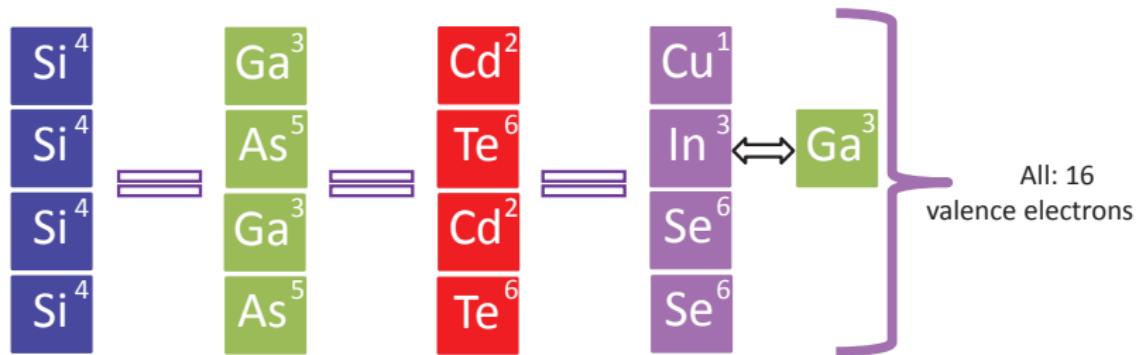
The Shockley-Queisser limit for the efficiency of a solar cell.

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

# Where does Cu(In,Ga)Se<sub>2</sub> 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

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4 Results

5 Summary

6 Future perspectives

7 Acknowledgements

# Which aspects of Cu(In,Ga)Se<sub>2</sub> have I been working on?

- Electronic structure

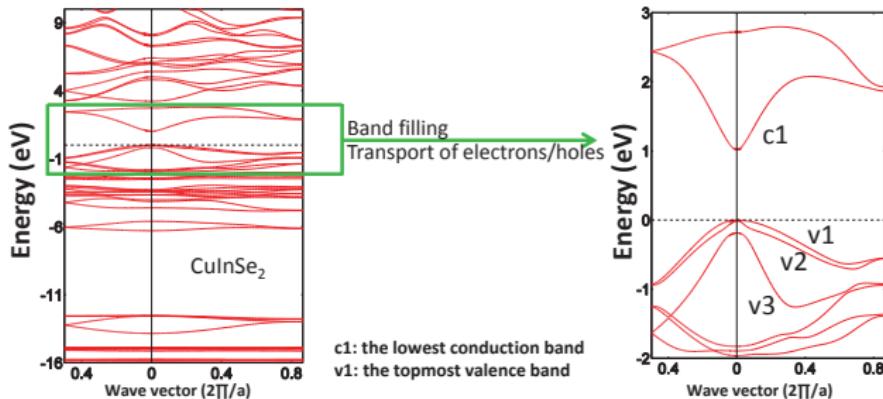
- Energy bands of CuInSe<sub>2</sub>, CuIn<sub>0.5</sub>Ga<sub>0.5</sub>Se<sub>2</sub>, and CuGaSe<sub>2</sub> are calculated by means of theoretical calculations. Parameterization of the lowest conduction (CB) and the three uppermost valence bands (VBs) are explored based on the calculated energy bands.
- Analysis of density-of-states (DOS) and carrier concentration based on the parameterization.

- Optical properties

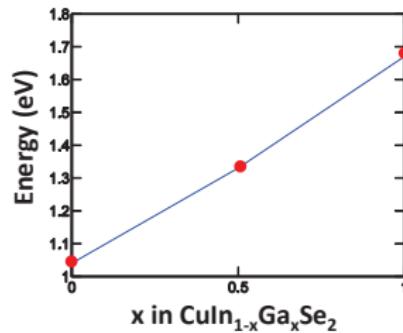
- Dielectric function of CuIn<sub>0.5</sub>Ga<sub>0.5</sub>Se<sub>2</sub> are explored by means of theoretical calculations. The band-to-band optical transitions are analyzed. The electronic origins of the observed interband critical points of the optical response are discussed.

# Motivation for the parameterization

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



1. Less study on CuIn<sub>0.5</sub>Ga<sub>0.5</sub>Se<sub>2</sub>.
2. Commercially interesting: CuIn<sub>0.7</sub>Ga<sub>0.3</sub>Se<sub>2</sub>, CuIn<sub>0.5</sub>Ga<sub>0.5</sub>Se<sub>2</sub> 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.

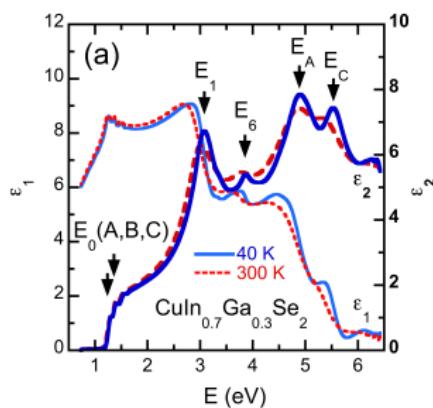


Figure : The real ( $\epsilon_1$ ) and imaginary ( $\epsilon_2$ ) part of dielectric function spectra.

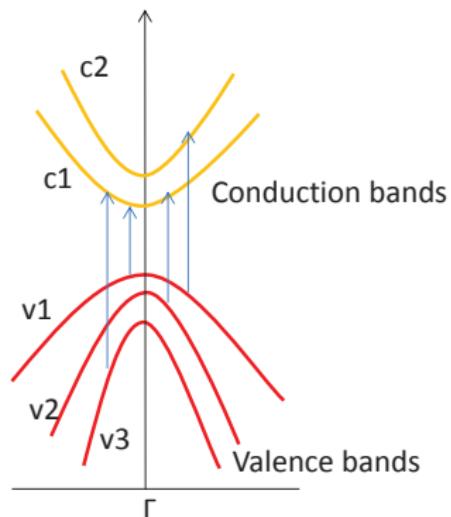


Figure : Energy bands.

- 1 Background
- 2 Motivation
- 3 Computational methods
- 4 Results
- 5 Summary
- 6 Future perspectives
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# Density functional theory (DFT)

DFT-based modeling 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  $\rho$  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

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

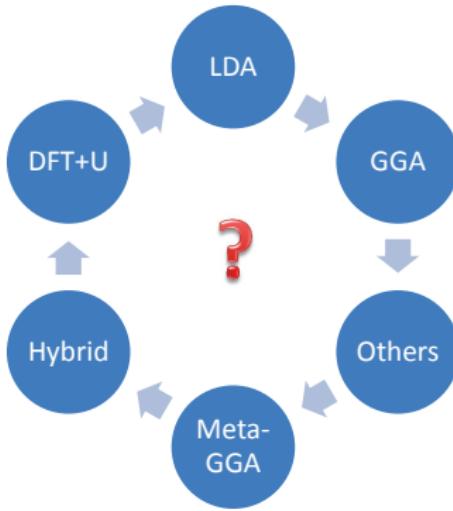
The  $V^{KS}(\mathbf{r})$  is given as

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

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. ???? explain LDA GGA ....

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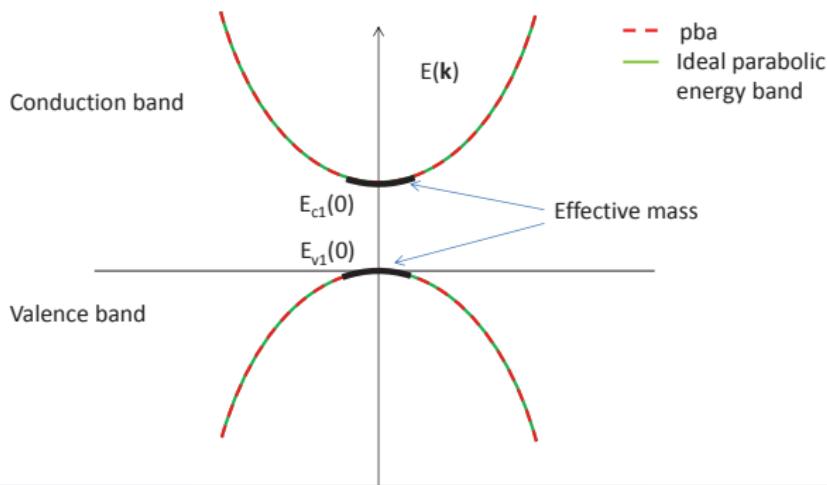
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# Paper 1: parabolic band approximation (pba)

The parabolic approximation of ellipsoidal energy bands is expressed

$$E_j^{pb}(\mathbf{k}) = E_j(\mathbf{0}) \pm \left[ \frac{\tilde{\mathbf{k}}_x^2 + \tilde{\mathbf{k}}_y^2}{m_j^{xy}} + \frac{\tilde{\mathbf{k}}_z^2}{m_j^z} \right] \quad (5)$$
$$m^{ab} = \pm \hbar^2 / (\partial E(\mathbf{k}) / \partial k_a k_b).$$

In the case of ideal parabolic energy band, the pba can describe energy band perfectly.

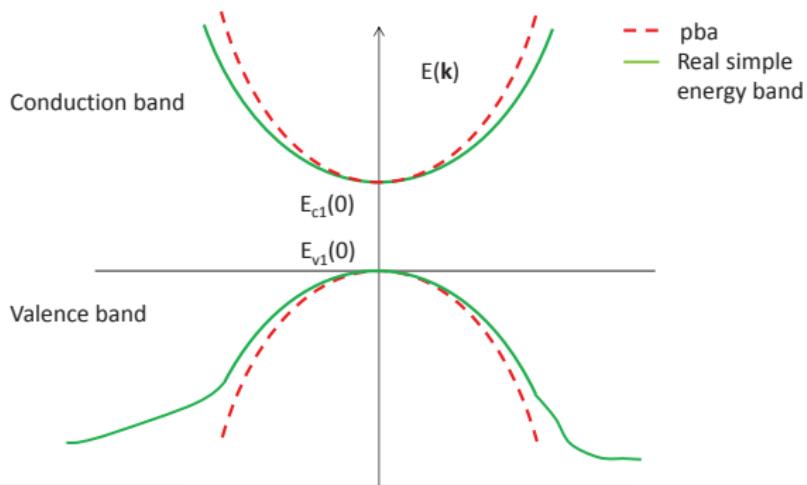


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$$m^{ab} = \pm \hbar^2 / (\partial E(\mathbf{k}) / \partial k_a k_b).$$

The parabolic approximation is valid in the vicinity of the  $\Gamma$ -point. However, away from the  $\Gamma$ -point, it fails to describe the energy dispersion.

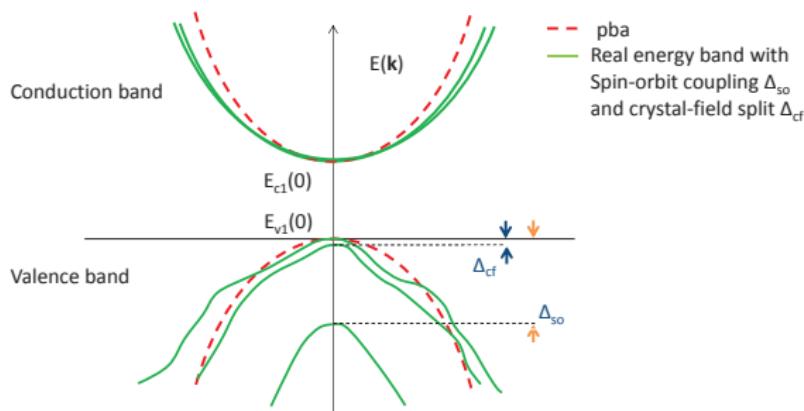


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$$m^{ab} = \pm \hbar^2 / (\partial E(\mathbf{k}) / \partial k_a k_b).$$

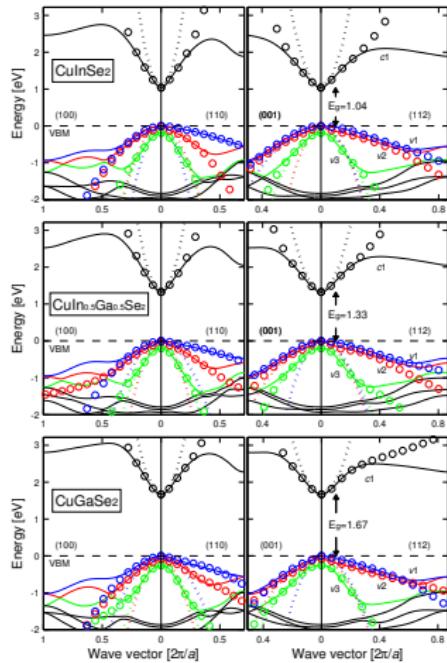
Considering spin-orbit coupling and crystal-field split, the energy band becomes very complicated. The parabolic approximation is valid in the very vicinity of the  $\Gamma$ -point.



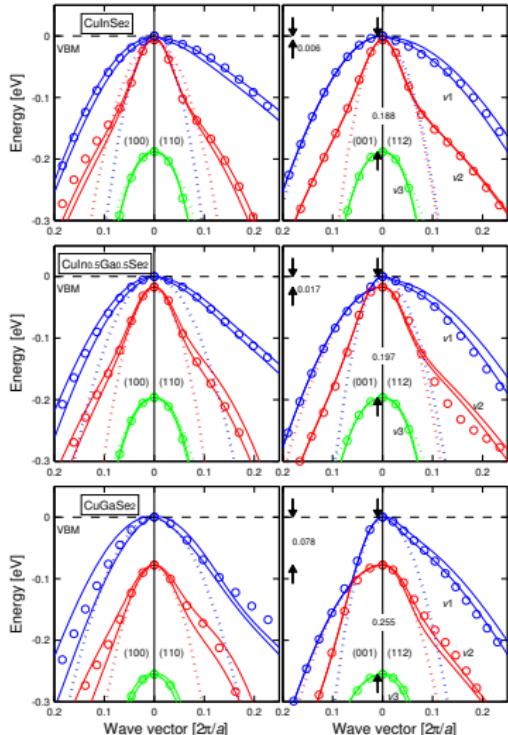
# Paper 1: Full band parameterization (fbp)

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

# Paper 1: Parameterization of band structure for CIGS

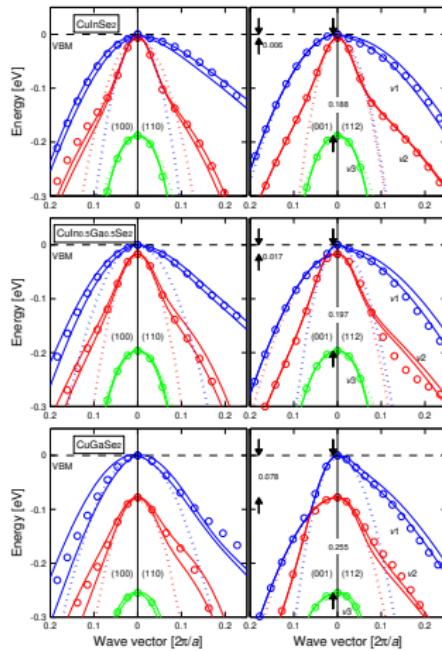


**Figure :** Electronic band structure along four directions. The circles are the results of the fbp, the dotted lines represent the pba, and

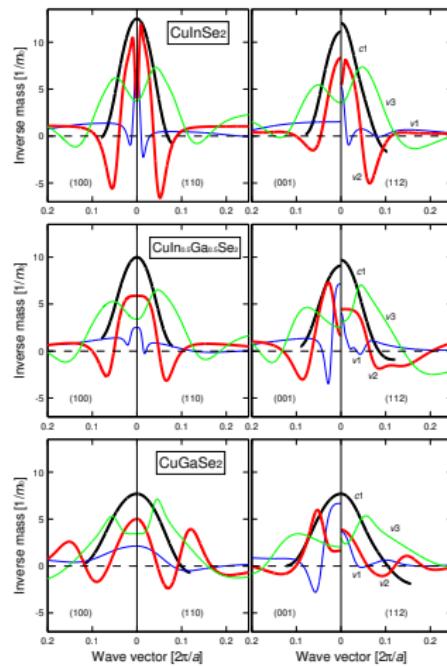


**Figure :** Close-up of the right fig-

# Paper 1: Non-parabolicity of the energy bands

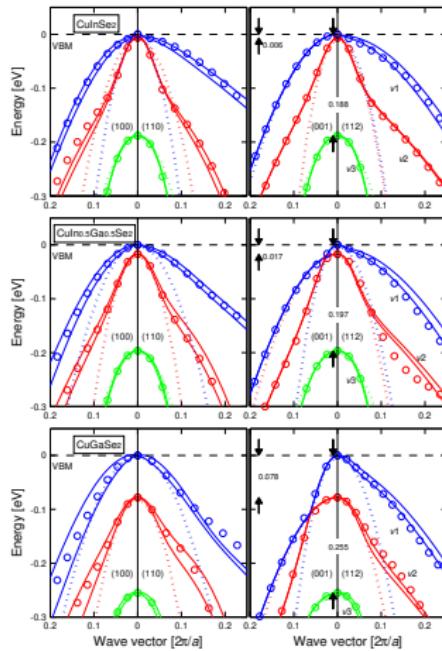


**Figure :** Close-up of electronic band structure. The circles are the results of the fbp, the dotted lines represent the pba, and the solid lines represent the theoretical cal-

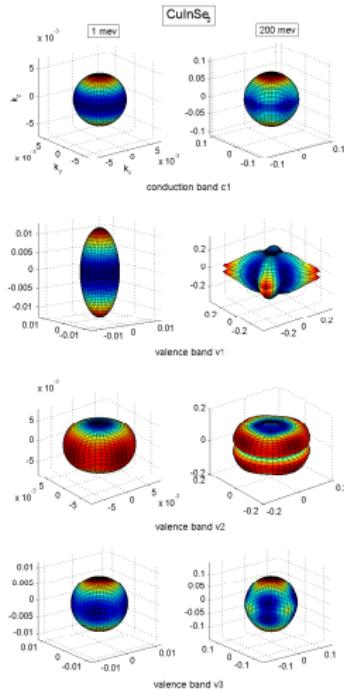


**Figure :** Inverse of the effective electron and hole masses in the four symmetry directions for the  $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$  ( $x = 0, 0.5$ , and  $1$ )

# Paper 1: Non-parabolicity of the energy bands



**Figure :** Close-up of electronic band structure. The circles are the results of the fbp, the dotted lines represent the pba, and the solid lines represent the theoretical cal-



**Figure :** Constant energy surfaces for the lowest CB and three uppermost VBs in CuInSe<sub>2</sub>

## Paper 2: Density-of-states (DOS)

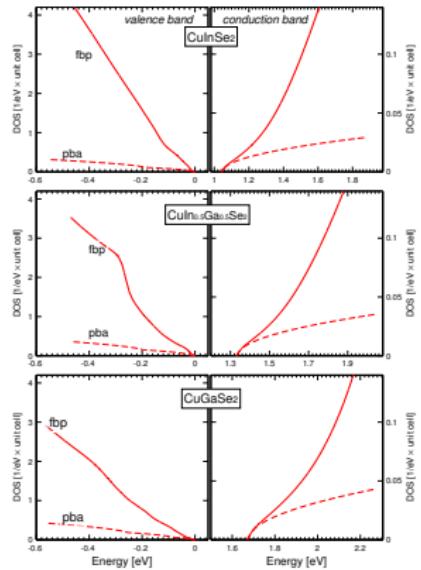
In the case of the pba, the density-of-states can be written as

$$g_j^{pba}(E) = \frac{1}{2\pi^2} \left( \frac{2m_j^{DOS}}{\hbar^2} \right)^{3/2} \sqrt{|E - E_j(\mathbf{0})|}. \quad (9)$$

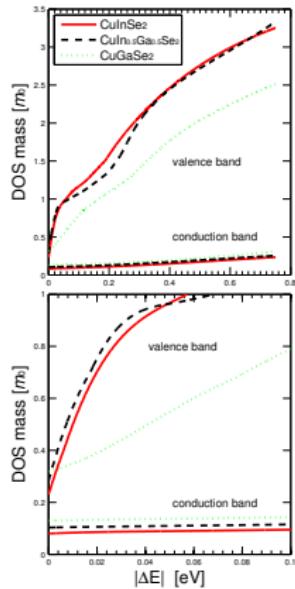
In order to take advantage of the simple **Eq. 9** for the non-parabolic energy bands, the energy-dependent DOS mass ( $m_{v/c}^{DOS}$ ) is defined as

$$g_{v/c}(E) = \sum_j g_j(E) = \frac{1}{2\pi^2} \left( \frac{2m_{v/c}^{DOS}(E)}{\hbar^2} \right)^{3/2} \sqrt{|E - E_{v1/c1}(\mathbf{0})|}. \quad (10)$$

# Paper 2: Density-of-states (DOS) and DOS mass

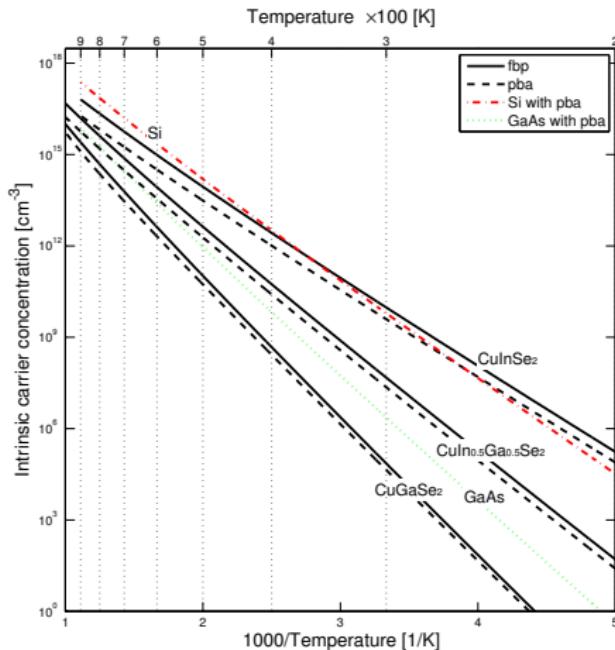


**Figure :** Total DOS of the VBS and CB. The solid lines show the results based on the fbp, and the dashed lines represent the results based on the pba.



**Figure :** The DOS mass  $m_{v/c}^{DOS}$

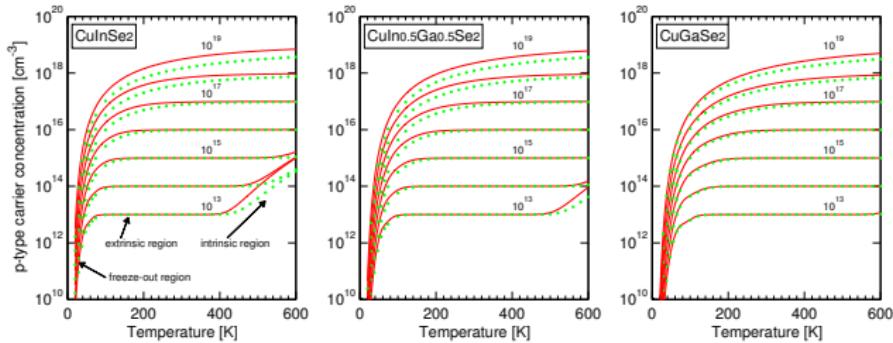
## Paper 2: intrinsic carrier concentration



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

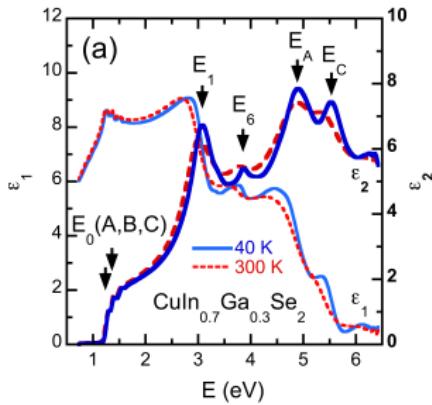
# Paper 2: Carrier concentration in different temperatures

# Paper 2: Carrier concentration in *p*-type for CIGS

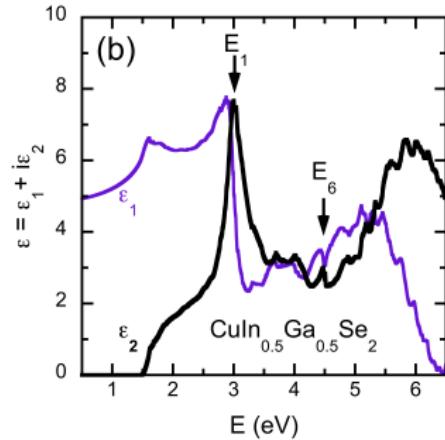


**Figure :** Free carrier concentration as function of the temperature in *p*-type for  $\text{CuInSe}_2$ ,  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ , and  $\text{CuGaSe}_2$ . The effective doping concentration  $N_A = 10^{13}, 10^{14}, 10^{15}, \dots$ , and  $10^{19} \text{ acceptors cm}^{-3}$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

# Paper 3: Dielectric function for $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$



**Figure :** The real ( $\epsilon_1$ ) and imaginary ( $\epsilon_2$ ) 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.

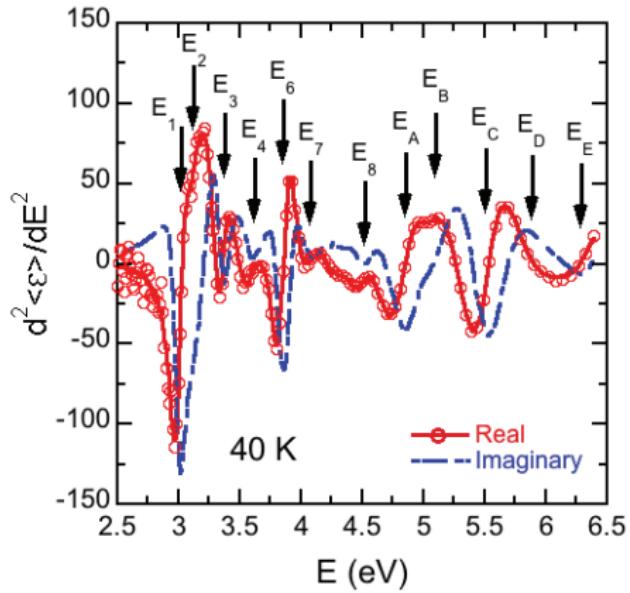
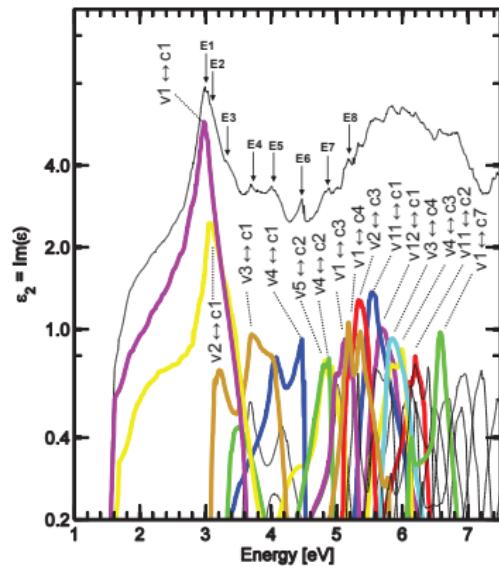
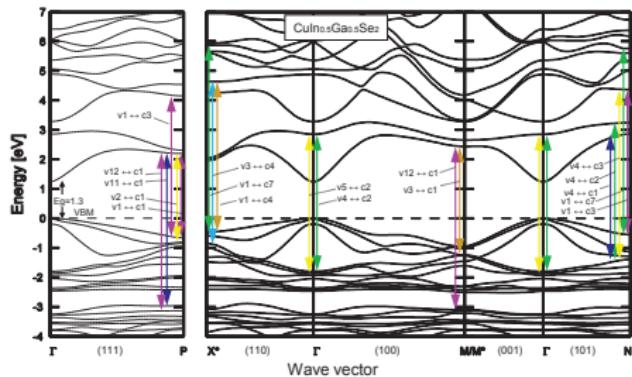


Figure : Energies of each interband critical point (CP) are indicated by arrows and labeled in a numeric and alphabetic order.

# Paper 3: Analysis of the imaginary part of dielectric function



**Figure :** Band-to-band analysis of the contribution to the total  $\epsilon_2$  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
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# 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.

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- 2 Motivation
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# 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.

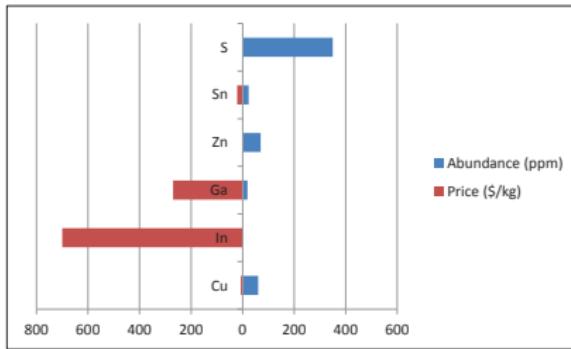


Figure : Abundance and price of Cu, In, Ga, S, Sn, and Zn in Earth's crust (parts per million (ppm) in mass; 10,000 ppm = 1%).

- 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
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# Acknowledgements

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*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.

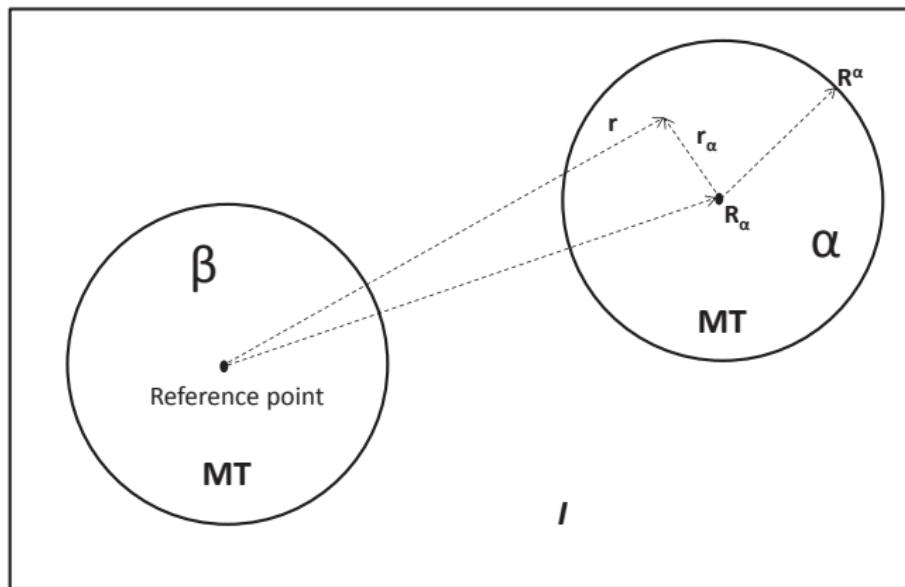


Figure : Partition of the unit cell.

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

$$\Psi_{i,\mathbf{k}}^{KS}(\mathbf{r}) = \sum_{\mathbf{G}}^{N_G} C_{i,\mathbf{k}+\mathbf{G}} \phi_{\mathbf{k}+\mathbf{G}}^{LAPW}(\mathbf{r}). \quad (11)$$

Here

$$\phi_{\mathbf{k}+\mathbf{G}}^{LAPW}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} & \text{if } \mathbf{r} \in I \\ \sum_{\alpha} \sum_{\ell m} f_{\ell m}(r_{\alpha}, \mathbf{k} + \mathbf{G}, \epsilon_{\ell, \alpha}) Y_{\ell m}(\hat{\mathbf{r}}_{\alpha}) & \text{if } r_{\alpha} \in MT. \end{cases} \quad (12)$$

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

$$V(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{Gr}} & \text{if } \mathbf{r} \in I \\ \sum_{\ell m} V_{\ell m}^{\alpha}(r_{\alpha}) Y_{\ell m}(\hat{\mathbf{r}}_{\alpha}) & \text{if } r_{\alpha} \in MT. \end{cases} \quad (13)$$

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

# The process for solving KS equation

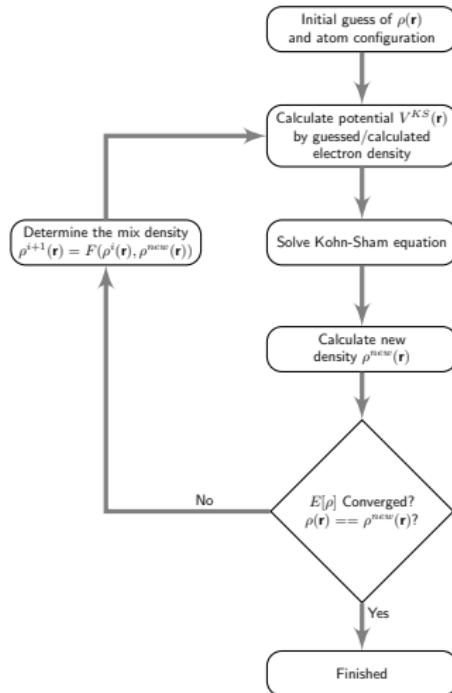
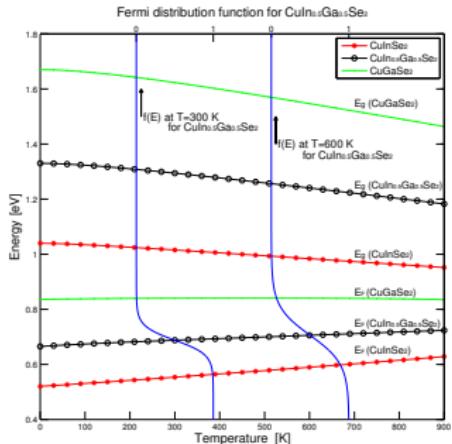
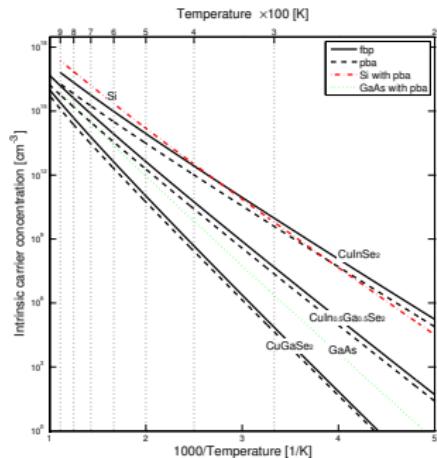


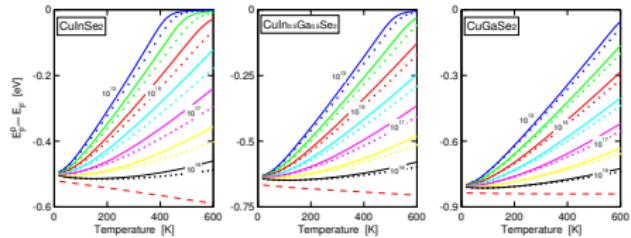
Figure : Flow chart of the  $(i + 1)$ :th iteration for solving KS equation.



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



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



**Figure :** Fermi level as function of the temperature  $20 \leq T \leq 600$  of *p*-type  $\text{CuInSe}_2$ ,  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ , and  $\text{CuGaSe}_2$  for the effective doping concentration  $N_A = 10^{13}$ ,  $10^{14}$ ,  $10^{15}$ , ., and  $10^{19}$  acceptors  $\text{cm}^{-3}$ . Dashed lines represent the VBM with respect to the intrinsic Fermi level. Solid and dotted lines represents the fbp and the pba, respectively.

